

Equilibrium and crystallographic measurements of the binary tetrahydrofuran and helium clathrate hydrates

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Abstract—Clathrate compounds are crystalline materials formed by a physical interaction between host and relatively light guest molecules. Various types of nano-sized cages surrounded by host frameworks exist in the highly unique crystalline structures and free guest molecules are entrapped in an open host-guest network. Recently, we reported two peculiar phenomena, swapping and tuning, naturally occurring in the hydrate cages. Helium, one of the smallest light guest molecules, must be the challengeable material in the sense of physics and moreover possesses versatile applications in the field of superconductivity technology and thermonuclear industry. In this regard, we attempted for the first time to synthesize helium hydrates at moderate temperature and pressure conditions. According to inclusion phenomena, helium itself normally cannot form clathrate hydrates due to being too small molecularly without the help of hydrate former molecules (sI, sII, and sH formers). In this study, the hydrate equilibria of the binary clathrate hydrate containing tetrahydrofuran, helium, and water were determined at 2, 3, 5.56 THF mol%. Direct volumetric measurements were also carried out to confirm the exact amount of helium captured in the hydrate cages. Finally, the crystalline structure of the formed mixed hydrates was identified by powder X-ray diffraction, resulting in structure II.

Key words: Helium, Clathrate Hydrate, Tetrahydrofuran, Phase Equilibria, Crystalline Structure

INTRODUCTION

Clathrate hydrates are crystalline compounds formed by a physically stable interaction between water and relatively small guest molecules [1]. On a molecular scale, single or multiple occupancy of small guest molecules in a nano-sized cage of non-stoichiometric hydrate is formed by hydrogen-bonded water molecules. The guest molecule repulsions induce clathrate hydrates to open a variety of cages, making three different unit crystals: cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH). While the light and small hydrocarbons, such as methane and ethane, can readily form gas hydrates, the quantum gases of He, H₂, and Ne [2] fail to form the well-defined crystalline hydrates because their molecular sizes are too small to contribute to the hydrate lattice stability, except under specific conditions at an extremely high pressure. Particularly, for synthesizing the mixed hydrogen hydrate, tetrahydrofuran (THF), an effective organic hydrate former that forms an sII cubic (*Fd-3m*) structure composed of THF·17H₂O [3], has been commonly chosen to significantly reduce the forming pressure of the binary H₂ clathrate hydrates compared with pure H₂ clathrate hydrates requiring either an extremely high pressure (~2 kbar) or low temperature [4]. It might be expected that helium requires an extreme pressure to form pure hydrate. However, unfortunately, any experimental data related to helium hydrates have not yet been reported in the literature. Accordingly, in this study the phase behavior of the binary helium hydrates was examined at three different THF concentrations together with direct volumetric measurements of helium amount entrapped in the cages. The resulting hydrate struc-

ture was also identified by using Powder X-ray diffraction (PXRD).

MATERIALS

The He gas used for the present study was supplied by World Gas (Korea) and had a stated purity of 99.9 mol%. Water with an ultrahigh purity was supplied from Merck (Germany) and tetrahydrofuran (THF, anhydrous, 99.9%) was purchased from Aldrich (USA). All materials were used without further treatment.

APPARATUS AND PROCEDURE

1. Hydrate Phase Equilibria

A detailed schematic diagram and description of the experimen-

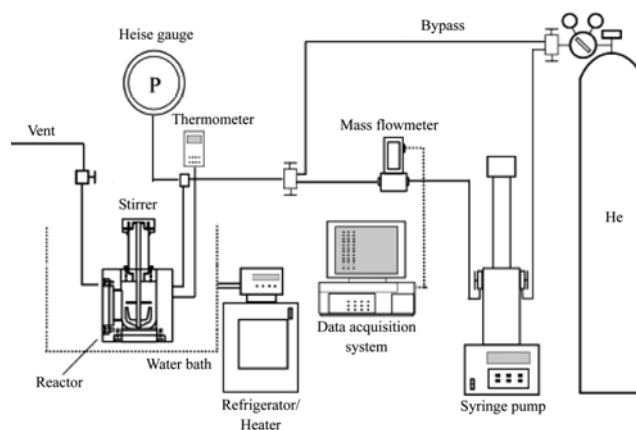


Fig. 1. Experimental apparatus for hydrate formation.

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tal apparatus for the hydrate phase equilibrium have been given in previous papers [5-7]. The apparatus in Fig. 1 was constructed to measure both the hydrate formation and the dissociation conditions, particularly focusing on accurate hydrate dissociation pressures and temperatures. The equilibrium cell was made from 316 stainless steel and its internal volume was approximately 150 cm³. The phase equilibrium measurements of binary THF+He hydrates were carried out at 5.6, 3.0, 2.0 THF mol%. After the equilibrium cell was charged with these solutions, it was pressurized to the desired pressure with He and the main system was slowly cooled to 264 K. When the pressure depression caused by the hydrate formation was changed to steady-state condition, the temperature of the system increased at a rate of approximately 0.5 K/hr. The equilibrium pressure and temperature of the three phases (hydrate (H)-water-rich (L_w)-vapor (V)) were determined by tracing the P-T profiles from hydrate formation to dissociation.

2. Direct Release Measurement

The various THF solutions were frozen at 243 K for at least 1 day, and then ground to a fine powder (~120 μm). The powdered solid hydrate was placed in pressurized cells having 50 cm³ volumes and then was exposed to He gas, maintaining 120 bar and 268 K for 1 day for the complete conversion to the mixed clathrates. The thermal cycle steps were repeated at least four times in order to avoid the possible appearance of metastable structures and to approach the clathrate equilibrium. When the hydrate reaction was completed, after venting the residual He gas in the cell, we removed the He gas existing in the inside of cell and the surface of hydrate through vacuum pump under liquid nitrogen atmosphere. After the cell is maintained at room temperature, the dissociated He volume can be measured.

3. Hydrate-phase Compositions

The guest distributions in hydrate cages can be directly checked by determining hydrate compositions. For the composition measurement of the gases dissociated from the hydrate phase, a sampling valve with a loop volume of 1 μL was installed and connected to an online gas chromatograph. The gas chromatograph (Hewlett Packard, 5890 Series II) used a thermal conductivity detector (TCD) with a carboxisieve 100/120 1/8" SUS packed column (SUPELCO). The carrier gas was Ar. Finely pulverized ice was used as the starting material to form the mixed THF+He hydrate. During vigorous stirring of the ice particles at the desired pressure, the hydrate nucleated and grew, resulting in the system pressure decreasing continuously due to the enclathration of gas molecules into the hydrate cages. When the system pressure reached a steady state, the vapor phase was vacuumed at 243.1 K. Then, the valve was closed quickly to isolate the system, and the temperature was increased to 278.0 K, inducing the complete dissociation of the hydrate phase. The evolving gas was analyzed several times with a gas chromatograph directly attached to the reactor to eliminate any error that might have occurred during the sampling procedure and to confirm the reproducibility of the data. The overall experimental deviation in hydrate compositions was found to be within ±0.1%.

4. Hydrate Structure Analysis

The structure of the mixed THF+He hydrate was determined with a D/max-RB (Rigaku) diffractometer with CuKα1 radiation (λ=1.5406 Å), and 24 diffraction peaks at 1 bar and 123.15 K were observed. The X-ray diffraction data were collected by using a step

Table 1. Volumetric amount of binary THF+He hydrate system by direct releasing method

THF compositions	Helium amounts (per binary THF+He hydrate of total 5 g)
5.56 mol%	62.5 ml
3 mol%	40 ml
2 mol%	25 ml
1 mol%	7 ml

mode with a fixed time of 5 s and a step size of 0.05° 2 θ (10 to 65° in 2θ) at 1 bar and 123.15 K.

RESULTS AND DISCUSSION

1. Direct Release Measurement and Composition Determination by Gas Chromatography

In order to measure the amount of He gas absorbed in the THF+H₂O system, a direct release measurement followed by the on-line gas chromatography was conducted after dissolving the synthesized hydrates at room temperature. The resulting THF concentrations and released volumes by direct release measurement at 298 K are shown in Table 1. The largest He amount appeared at a 5.56 mol% THF solution in water, which gives a clathrate composition of THF·17H₂O when cooled below the melting point of 277.3 K. We note that the excess ice increases as the THF concentration decreases. Thus, the total released He volume must significantly decrease and the corresponding stored He wt% thereby becomes smaller. To cross-check the absorbed He amount in the system, gas chromatography was adopted through the on-line sampling and analysis system. In the gas chromatography of the THF+He binary system, the He peak was detected at 42 s, which is the detection time of He under condition of carrier gas Ar, and its peak area was increased according to the high THF concentration. Fig. 2 represents the He wt% stored in the hydrate as a function of the THF concentration for both cases of the direct release measurement and gas chromatography. Based on the total released He volume from Table 1, the direct re-

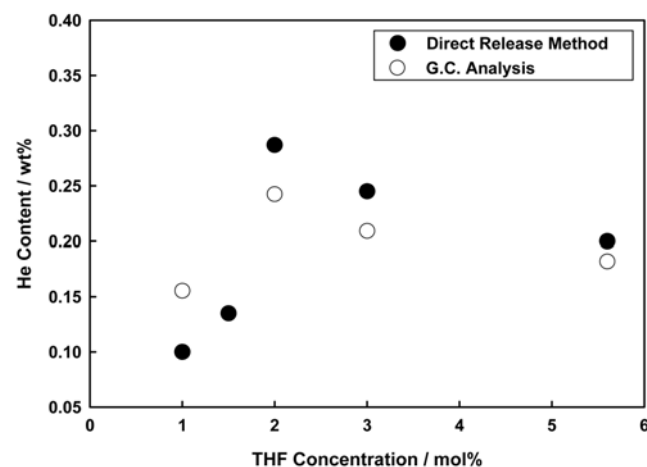


Fig. 2. Comparisons of He content by direct releasing method and gas chromatography measurement (He gas content is calculated from g of He per g of hydrate excluding ice phase, and expressed as wt%).

lease results measured at 5.56, 3, 2, 1.5, and 1 THF mol% samples were 0.2, 0.245, 0.287, 0.135, and 0.1 He wt%, respectively, where the He gas content is calculated from g of He per g of hydrate phase excluding ice phase. In this case, we assumed that the complete hydrate phase without ice phase was formed in 5.56 THF mol%, which is the ideal concentration for forming complete hydrate phase in sII type hydrate. As the concentration of THF is decreased, the amount of the hydrate phase created is decreased. Therefore, according to decreasing the THF concentration, the He content had a tendency to be increased to some concentrations. Also, the He contents through GC results were performed as some calculation. The He content by gas chromatography showed a similar tendency to that by direct release measurements. Particularly, the highest He content per g of hydrate was shown at 2 THF mol%. This point might be the critical guest concentration (CGC) suggested by tuning phenomenon in the binary hydrates [8,9]. However, more detailed macroscopic and microscopic approaches are needed in order to provide definite evidence of the CGC existence caused by the liquid guest-dependent tuning pattern.

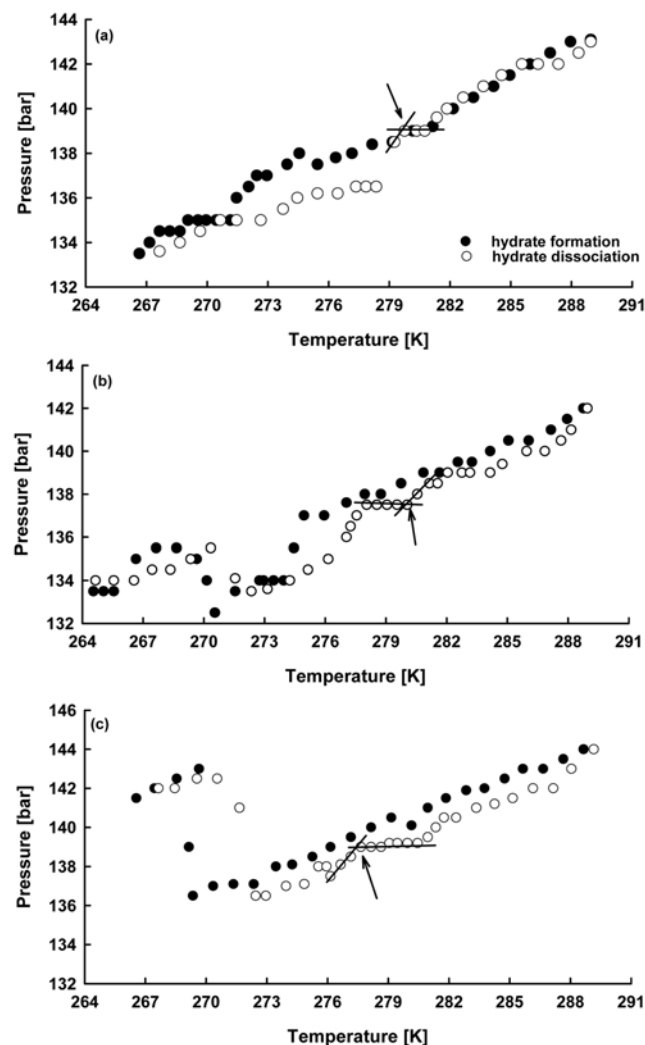


Fig. 3. P-T trajectory representing hydrate formation/dissociation by THF concentrations of (a) 5.6 mol%, (b) 3 mol% and (c) 2 mol%.

2. Phase Equilibrium Data

As an indirect measure of the hydrate formation, the pressure-temperature (P-T) trajectory, which represents the hydrate nucleation, growth, and dissociation stages, was measured experimentally. The resulting closed loop produced from the hydrate formation and dissociation processes is shown in Fig. 3. In Fig. 3(a), the binary THF+He hydrate started to form directly after the conditions of 280.6 K and 139 bar, and a rapid pressure reduction occurred upon the complete transformation of the 5.6 mol% aqueous (THF·17H₂O) to the hydrate. The system pressure continued to decrease with the temperature, but a minor pressure increase at 275 K was detected. Subsequently, further cooling initiated a second pressure drop below 268 K. Interestingly, this two-stage pressure drop might indicate the formation of pure He hydrate even though its actual amount seems to be small when compared with the binary He hydrate. As the temperature was again raised, the pure He hydrate first dissociated followed by the dissociation of the mixed He hydrate. Similar P-T trajectories were observed for the 3 and 2 THF mol%, as shown in Figs. 3(b) and (c), respectively. During hydrate formation process an unusual pressure increase appeared as the THF concentration lowered much below the stoichiometric 5.56 THF mol%. This rising pressure might be expected especially for the hydrate systems that absorb only a small amount of gaseous guest molecules. In such guest-depleted hydrate mixtures, the large excess ice phase inevitably exists. Accordingly, in a reactor with a constant volume for preparing hydrates, the volume expansion occurs due to the phase change of water to ice, making the residual He gas to be more pressurized. It is thus well understood that the pressure increase in the 2 mol% THF solutions is much larger than that in the 3 mol% THF solutions. Unlike the phase equilibrium shape of pure CH₄ hydrate having large pressure drop at the hydrate formation conditions of particular temperature and pressure, the THF+He binary hydrate indicated little pressure drop due to absorbing small amount of He. At this stage it might be worthwhile to remember that much literature exists regarding the three-phase equilibria (H-L_v-V) of the binary water and small guests (H₂, He, and probable Ne). However, extreme pressures are generally required to produce hydrate states in those binary systems. Of course, the presence of water-soluble liquid

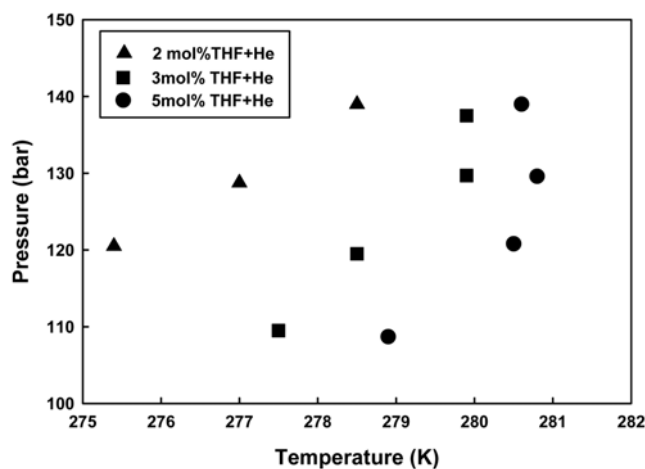
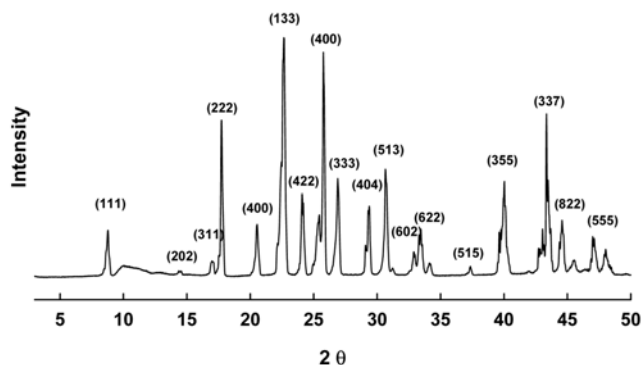


Fig. 4. Equilibrium conditions of gas hydrate from binary THF+He hydrate system.

Table 2. Hydrate phase equilibria of the binary THF+He mixtures

THF concentrations	Temperature (K)	Pressure (bar)
2 mol%	275.4	120.50
	277.0	128.75
	278.5	139.00
3 mol%	277.5	109.50
	278.5	119.50
	279.9	129.70
	279.9	137.00
5.56 mol%	278.9	108.70
	280.5	120.80
	280.8	129.60
	280.6	139.00

**Fig. 5. X-ray diffraction of binary THF+He hydrate system formed from 5.56 mol% THF concentration.**

guests can induce the hydrate-forming condition to be more favorable by lowering the pressure and raising the temperature required to form the binary hydrates compared with the corresponding condition of a pure hydrate. Fig. 4 and Table 2 clearly support this well-defined promotion effect. THF itself can play an important role in forming cubic structure II hydrates as a guest molecule and it can only occupy the large cages because of its size.

3. X-Ray Diffraction Measurements

Fig. 5 shows the X-ray powder diffraction pattern of the binary 5.56 mol% THF+He hydrate system. The X-ray diffraction data identify the binary hydrate with an exemplary sII crystal structure.

Also, it can be indexed with a regular cubic unit cell (space group $Fd-3m$) with a unit cell parameter of 17.21 ± 0.01 Å. This result agrees with the reported values for the unit cell parameters of sII THF clathrate hydrate [9].

CONCLUSION

The storage capacity and equilibrium condition of gas hydrates formed from the THF+He binary guests were determined experimentally by using a direct volumetric measuring method together with the on-line GC under varying THF concentrations. The storage capacity of the 5.56 mol% THF solution was 0.2 wt% He. The X-ray diffraction data identify the THF+He binary hydrate as an exemplary sII crystal structure (space group $Fd-3m$) with a unit cell parameter of 17.21 ± 0.01 Å.

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