# Experimental Measurements of Hydrate Phase Equilibria for Carbon Dioxide in the Presence of THF, Propylene Oxide, and 1,4-Dioxane

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Hydrate phase equilibria have been measured for carbon dioxide + cyclic ethers + water in the temperature range of (270 to 290) K and in the pressure range of (0.2 to 4.7) MPa. Three cyclic ethers, THF, propylene oxide, and 1,4-dioxane, were selected at a mole fraction of 0.03. The stabilization effect of the mixed hydrate was found to be the highest for THF followed by propylene oxide, while no stabilization effect was observed for 1,4-dioxane in the studied temperature and pressure range. The mole fraction effect on hydrate phase equilibria has also been investigated for THF and propylene oxide in the range of $x = (0.01 \text{ to } 0.10)$.

## Introduction

Gas hydrates are crystalline compounds formed when guest molecules are incorporated in host cages formed by water molecules through hydrogen bonding. Low molecular weight gas molecules, such as methane, nitrogen, and carbon dioxide, are captured into these cages, and each hydrate lattice consists of at least two types of polyhedral cages. With differences in cage sizes and shapes, gas hydrates are divided into three distinct structures termed structure I, II, and H.[1] The physical and thermal properties of gas hydrates have been extensively measured by many researchers from different perspectives. Among possible applications of gas hydrate, carbon dioxide capture and storage is gathering particular attention because of a growing concern of carbon dioxide emission. It is identified that the principal sources of carbon dioxide emissions are from the burning of fossil fuels and power generation. They dominate the emissions accounting for 40 % of energy related greenhouse gas emission.[2] Three principal methods have been proposed to capture carbon dioxide from power generation plant, which are termed postcombustion, precombustion, and oxyfuel combustion. Post combustion separates carbon dioxide from flue gas emitted by the burning of fossil fuel, which is mainly composed of nitrogen and carbon dioxide. Recently, the integrated gasification combined cycle (IGCC) plant that converts fossil fuel into syngas, a mixture of hydrogen and carbon monoxide, has become popular in the power generation sector. In this cycle, the syngas goes through the water gas shift reaction, and resulting carbon dioxide is separated from the hydrogen, which is termed precombustion. Carbon dioxide is a well-known gas hydrate guest, and the hydrate is easy to form. Nitrogen and hydrogen require higher pressure to form gas hydrates than that of carbon dioxide at the same temperature. Accordingly, the carbon dioxide molecules should dominate the gas hydrate cages when carbon dioxide and nitrogen or carbon dioxide and hydrogen gas mixtures form gas hydrate. These physical properties of gas hydrate provide the feasibility of gas hydrate application to carbon dioxide capture and storage.

Kang and Lee thermodynamically verified a new process for effectively removing and recovering carbon dioxide from multicomponent flue gas and suggest the use of THF as a hydrate stabilizer that can reduce the hydrate formation pressure and promote the formation rate.[3] Seo et al. proposed that the recovery rate of carbon dioxide from flue gas can be enhanced by dispersing water in a porous media.[4] Sabil et al. studied the hydrate equilibrium conditions of carbon dioxide hydrate in the presence of THF and sodium chloride, suggesting that the presence of THF shows a significant hydrate pressure reduction up to a THF mole fraction of about (0.05 to 0.07) in the water phase.[5] As anticipated, the addition of sodium chloride into the mixed carbon dioxide + THF hydrate reduces the promotion effect of THF because of the ionic clustering between ions and water molecules and the salting-out effect. Delahaye et al. investigate the formation conditions and the latent heat of dissociation of mixed carbon dioxide + THF hydrate to study the possible use of the corresponding hydrate slurries as secondary refrigerants.[6] The results indicated that, at fixed temperature, adding THF resulted in a drastic reduction of carbon dioxide hydrate equilibrium pressure. Linga et al. reported the postcombustion carbon dioxide capture process based on three hydrate stages coupled with a membrane process where it is possible to reduce the compression costs from (75 to 53) % of the power produced for a typical 500 MW power plant.[7] They also used THF to reduce the incipient hydrate equilibrium conditions of the carbon dioxide and nitrogen gas mixture. A similar conceptual process has been proposed for precombustion carbon dioxide capture, in which two hydrate

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stages are coupled with a membrane process to obtain 0.99 mol fraction of carbon dioxide in the stream.[8,9] Hashimoto et al. have studied the hydrate equilibrium conditions of the hydrogen and carbon dioxide gas mixture in the presence of THF and investigated the hydrate phase with Raman spectroscopy.[10] For these conceptually designed processes, the critical disadvantage that must be resolved prior to real application is the high pressure required in the first stage of hydrate formation at the time of either postcombustion or precombustion. Therefore, the simplest and most convenient idea is to use water-soluble liquid hydrocarbons such as THF to lower the formation pressure. Of course, the physical function as a hydrate stabilizer has been widely adopted in the natural gas industry.[11,12] In this connection, cyclic ether compounds such as THF, propylene oxide, and 1,4-dioxane are studied in the present work because of their remarkable stabilization effect leading to lowering pressure or increasing temperature at the corresponding equilibrium conditions. Herein, we report the experimental measurements of hydrate phase equilibria for carbon dioxide in the presence of THF, propylene oxide, and 1,4-dioxane. Moreover, the upper limit of hydrate equilibrium conditions particularly is examined to identify the hydrate stability region.

**Table 1. Hydrate Equilibrium Conditions of the Carbon Dioxide + 0.03 Mole Fraction Cyclic Ether + Water System**

| system | *T*/K | *P*/MPa |
|---|---|---|
| carbon dioxide + THF + water | 279.75 | 0.35 |
| | 281.05 | 0.49 |
| | 286.45 | 1.43 |
| | 288.65 | 2.37 |
| | 290.05 | 3.08 |
| carbon dioxide + propylene oxide + water | 271.95 | 0.38 |
| | 273.95 | 0.67 |
| | 275.85 | 0.97 |
| | 277.95 | 1.46 |
| | 279.75 | 2.06 |
| | 281.45 | 3.00 |
| carbon dioxide + 1,4-dioxane + water | 274.65 | 1.08 |
| | 277.25 | 1.69 |
| | 279.35 | 2.53 |
| | 280.35 | 3.10 |
| | 280.95 | 3.76 |
| carbon dioxide + acetone + water | 270.05 | 0.81 |
| | 274.05 | 1.60 |
| | 277.05 | 2.64 |
| | 279.15 | 3.54 |

## Experimental Section

***Materials.*** Carbon dioxide with a minimum purity of 0.9999 mol fraction was supplied by World Gas Co. HPLC-grade water was supplied by Sigma-Aldrich Chemicals Co. with a purity of 0.9999 mol fraction. Research grade THF, 1,4-dioxane, and propylene oxide with a mole fraction purity of 0.9997 was obtained from Sigma-Aldrich Chemicals Co. All chemicals are used without further purification.

***Apparatus.*** The experimental apparatus for the hydrate equilibrium measurement is described in our previous works.[12,13] The high-pressure cell, made of 316 stainless steel, was equipped with two thermally reinforced sight glasses for visual observation and had the internal volume of 50 $\mathrm{cm}^3$. The working pressure was 10 MPa. The cell contents were agitated by a magnetic spin bar that was coupled with an immersion magnet placed under the cell, which was immersed in the bath containing 30 L of liquid mixture of ethylene glycol and water. The temperature of the bath was controlled by an externally circulating refrigerator/heater (Jeio Tech, MC-31) with an uncertainty of ± 0.05 K, and a K-type thermocouple probe with a digital thermometer (Cole-Parmer, 8535-26) was inserted into the cell to measure the temperature of its inner content within an uncertainty of ± 0.05 K. A Heise Bourdon tube pressure gauge (CMM 104957, (0 to 20) MPa range) with an estimated maximum uncertainty of ± 0.01 MPa in the full scale range was used to measure the system pressure.

***Procedure.*** Approximately 25 mL of aqueous solution of cyclic ether was prepared with uncertainties in mole fraction of ± 0.0001. The solution was introduced into the evacuated high-pressure cell, and then it was charged with carbon dioxide. After the cell was pressurized to a desired pressure, the system was cooled to about 5 K below the anticipated hydrate equilibrium temperature. Hydrate nucleation and growth was then induced in the aqueous solution, and the system pressure continuously decreased due to the formation of gas hydrate. After the system pressure reached a steady state, the cell temperature was gradually elevated to dissociate the formed hydrate. The external heater was used to increase the system temperature at a rate of 0.1 $\mathrm{K \cdot h^{-1}}$. A little increment of the cell temperature made the hydrate phase dissociate and caused a corresponding increase in the pressure. The three phases of hydrate, water-rich liquid, and vapor coexist at hydrate equilibrium condition, which was determined by a visual observation method supplemented by a temperature−pressure plot. From the visual observation on the hydrate phase, when a minute amount of crystals remained and system pressure was kept constant at least for 10 h after the system temperature was stabilized, the resulting temperature and pressure were considered as the hydrate phase equilibrium conditions. To supplement the visual observation method, a temperature−pressure plot was used to determine the equilibrium conditions. If the temperature increased below hydrate equilibrium temperature, a substantial increase of system pressure is detected due to the dissociation of the hydrate phase resulting in the release of carbon dioxide. However, when the temperature was increased above hydrate equilibrium conditions, only a small pressure increase was observed due to thermal expansion. Therefore, the temperature and pressure at which the slope of the temperature−pressure plot changed sharply was considered as the hydrate equilibrium conditions. In addition, the upper quadruple point at which four phases of hydrate, water-rich liquid, carbon dioxide-rich liquid, and vapor coexist was also determined to establish the upper limit of hydrate equilibrium conditions.

## Results and Discussion

Three phases of hydrate, water-rich liquid, and vapor equilibrium of carbon dioxide + 0.03 mol fraction THF + water, carbon dioxide + 0.03 mol fraction propylene oxide + water, and carbon dioxide + 0.03 mol fraction 1,4-dioxane + water systems were measured, and the results are given in Table 1 and Figure 1. For the carbon dioxide + 0.03 mol fraction THF + water system, it is quite clear that the presence of THF-induced hydrate forming conditions was more favorable by lowering the pressure and raising the temperature when compared with the corresponding condition of the carbon dioxide + water system. The addition of THF to water is known to form the pure structure II hydrate, and its direct exposure to pressurized carbon dioxide gas allows carbon dioxide molecules to occupy the empty small cages, still maintaining the mixed sII hydrate with the equilibrium shift to higher temperature and lower pressure. Meanwhile, the stabilization effect might be considered as the difference of hydrate equilibrium temperature between pure carbon dioxide and mixed carbon dioxide + THF hydrates, and in that case, the temperature

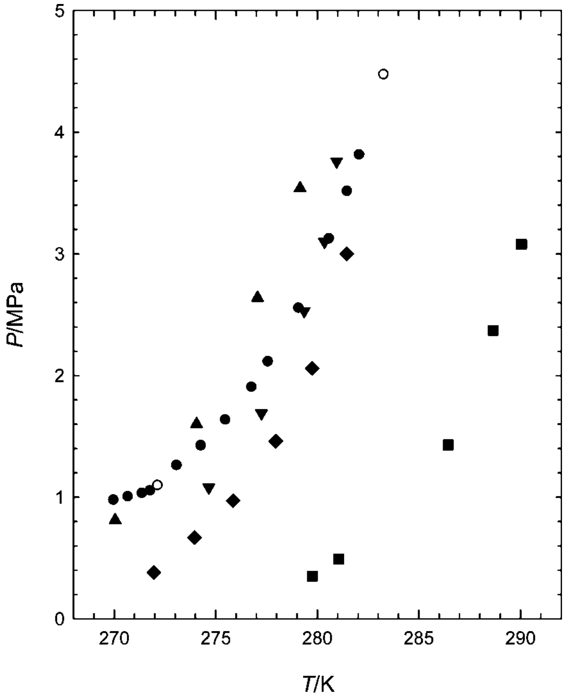

**Figure 1.** Experimental hydrate dissociation pressures for ●, carbon dioxide + water; ▲, carbon dioxide + 0.03 mol fraction acetone aqueous solution; ▼, carbon dioxide + 0.03 mol fraction 1,4-dioxane aqueous solution; ♦, carbon dioxide + 0.03 mol fraction propylene oxide aqueous solution; and ■, carbon dioxide + 0.03 mol fraction THF aqueous solution. Upper quadruple points for the carbon dioxide + water system are represented as open symbols.

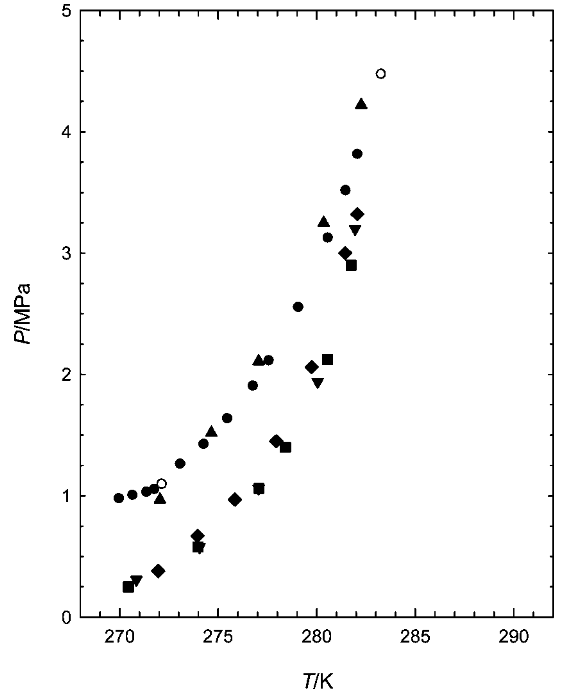

**Figure 2.** Experimental hydrate dissociation pressures for ●, carbon dioxide + water; and carbon dioxide + propylene oxide aqueous solution. ▲, 0.01 mol fraction; ♦, 0.03 mol fraction, ▼, 0.05 mol fraction; and ■, 0.10 mol fraction. Upper quadruple points for the carbon dioxide + water system are represented as open symbols.

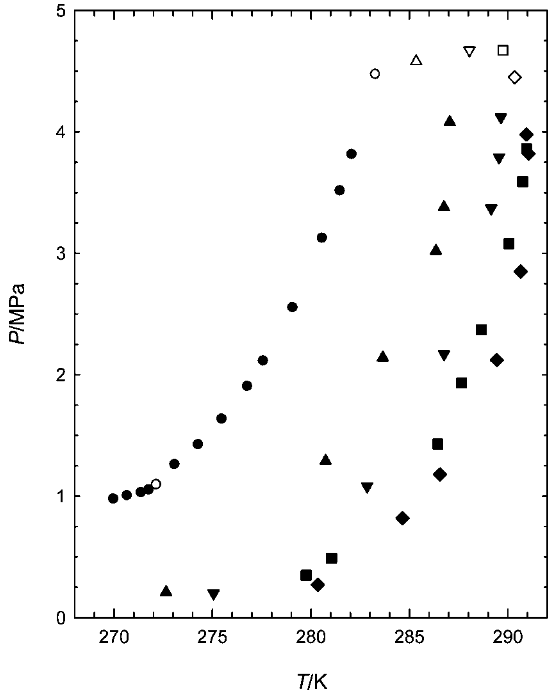

**Figure 3.** Experimental hydrate dissociation pressures and upper quadruple points for ●, carbon dioxide + water; and carbon dioxide + THF aqueous solution. ▲, 0.01 mol fraction; ▼, 0.02 mol fraction; ■, 0.03 mol fraction; and ♦, 0.05 mol fraction. Upper quadruple points at each mole fraction are represented as open symbols.

**Table 2. Hydrate Equilibrium Conditions of the Carbon Dioxide + Propylene Oxide + Water System Measured at Four Different Mole Fractions *x* of propylene oxide**

| *x* | *T*/K | *P*/MPa |
|---|---|---|
| 0.01 | 272.05 | 0.97 |
| | 274.65 | 1.52 |
| | 277.05 | 2.11 |
| | 280.35 | 3.25 |
| | 282.25 | 4.22 |
| 0.03 | 271.95 | 0.38 |
| | 273.95 | 0.67 |
| | 275.85 | 0.97 |
| | 277.95 | 1.45 |
| | 279.75 | 2.06 |
| | 281.45 | 3.00 |
| | 282.05 | 3.32 |
| 0.05 | 270.85 | 0.31 |
| | 274.05 | 0.58 |
| | 277.05 | 1.06 |
| | 280.05 | 1.94 |
| | 281.95 | 3.20 |
| 0.10 | 270.45 | 0.25 |
| | 273.99 | 0.58 |
| | 277.06 | 1.06 |
| | 278.41 | 1.40 |
| | 280.55 | 2.13 |
| | 281.75 | 2.90 |

difference is about 10.55 K at 3.1 MPa and 12.15 K at 1.4 MPa, indicating that the stabilization effect increases as the pressure is decreased. For the carbon dioxide + 0.03 mol fraction propylene oxide + water system, the stabilization effect appears to be around 3.85 K at 1.25 MPa and decreases at higher pressure. However, for the carbon dioxide + 0.03 mol fraction 1,4-dioxane + water system, the stabilization effect is not significant in the pressure range of (1 to 3) MPa, and the inhibition effect is observed at 3.76 MPa, indicating that the equilibrium temperature of the mixed carbon dioxide + 1,4-dioxane hydrate is lower than that of pure carbon dioxide hydrate at a specified pressure. Moreover, for the carbon dioxide + 0.03 mol fraction acetone + water system, the inhibition effect is observed in the pressure range of (1.5 to 3.5) MPa. Therefore, as well accepted in the hydrate community, the mixed carbon dioxide + THF hydrate appears to be the most favorable with

**Table 3. Hydrate Equilibrium Conditions of the Carbon Dioxide + THF + Water System Measured at Four Different Mole Fractions *x* of THF**

| *x* | *T*/K | *P*/MPa |
|---|---|---|
| 0.01 | 272.65 | 0.21 |
| | 280.75 | 1.29 |
| | 283.65 | 2.14 |
| | 286.35 | 3.02 |
| | 286.75 | 3.38 |
| | 287.05 | 4.08 |
| 0.02 | 275.05 | 0.20 |
| | 282.85 | 1.08 |
| | 286.75 | 2.17 |
| | 289.15 | 3.37 |
| | 289.55 | 3.79 |
| | 289.65 | 4.12 |
| 0.03 | 279.75 | 0.35 |
| | 281.05 | 0.49 |
| | 286.45 | 1.43 |
| | 287.65 | 1.93 |
| | 288.65 | 2.37 |
| | 290.05 | 3.08 |
| | 290.75 | 3.59 |
| | 290.95 | 3.86 |
| 0.05 | 280.35 | 0.27 |
| | 284.65 | 0.82 |
| | 286.55 | 1.18 |
| | 289.45 | 2.12 |
| | 290.65 | 2.85 |
| | 290.95 | 3.98 |
| | 291.05 | 3.82 |

**Table 4. Upper Quadruple Points of the Carbon Dioxide + THF + Water System Measured at Four Different Mole Fractions *x* of THF**

| *x* | *T*/K | *P*/MPa |
|---|---|---|
| 0.01 | 285.35 | 4.58 |
| 0.02 | 288.05 | 4.67 |
| 0.03 | 289.75 | 4.67 |
| 0.05 | 290.35 | 4.45 |

the order of THF > propylene oxide > 1,4-dioxane. A notable feature is that all the cyclic ethers clearly exhibit the highly promoting trend for hydrate formation when methane or nitrogen is participated as the coguest,[12] while in the case of carbon dioxide, THF only acts as a promising stabilizer and the role of the two other cyclic ethers of 1,4-dioxane and propylene oxide appears to be quite inconspicuous. The overall general picture is shown in Figure 1.

Table 2 shows the measured hydrate equilibrium conditions of the carbon dioxide + propylene oxide + water system at (0.01, 0.03, 0.05, and 0.10) mol fractions of propylene oxide. Here, we again note that the mixed carbon dioxide + propylene oxide hydrate forms structure II with stoichiometric concentration of 0.056 propylene oxide mole fraction. As shown in Figure 2, the stabilization effect appears to be the highest at 0.05 mol fraction of propylene oxide. An increase of propylene oxide composition to 0.10 mol fraction does not show any noticeable effect. At 0.10 mol fraction of propylene oxide, the stoichiometric amount of propylene oxide, of course, participates in forming the mixed structure II hydrate with carbon dioxide, and the remaining propylene oxide exists as free molecules in the aqueous phase.

In contrast to propylene oxide, THF shows a stabilization effect at all mole fractions as shown in Table 3, and the effect appears to be highest at 0.05 mol fraction of THF. With decreasing the mole fraction of THF, the stabilization effect is about 6 K in a pressure range of (1 to 4) MPa at 0.01 mol fraction of THF. At 0.03 mol fraction of THF, the hydrate equilibrium conditions are similar to those of 0.05 mol fraction of THF, which indicate that the added amount could be lowered below the stoichiometric mole fraction to maintain the stabilization effect. It is noted that the hydrate equilibrium data at (0.01 to 0.03) mole fractions of THF show a deviation with the literature data obtained by using the Caillete apparatus and thermal techniques.[5,6] Among the studied cyclic ethers, THF has proven to be the best for stabilizing the mixed hydrates, and moreover, the mole fraction of THF can be adjusted to reduce the amount added when applied to the carbon dioxide capture process. However, the precise study on phase behavior is needed because the upper limit of hydrate equilibrium conditions could exist in the carbon dioxide containing system as studied in our previous work.[13] Table 4 shows the upper quadruple point at each mole fraction of THF, which is regarded as the upper pressure and temperature limit of the three-phase equilibrium curve in Figure 3. At the quadruple point, one additional carbon dioxide-rich liquid phase coexists with the hydrate, water-rich liquid, and vapor phases. Our previous results related to the mixed carbon dioxide and methane hydrates are concerned with the quadruple point locus at different carbon dioxide mole fractions.[14] The three-phase equilibrium temperature increases continuously with the pressure increase and eventually connects to the quadruple point. However, we particularly note that for the mixed carbon dioxide + THF hydrate the three-phase equilibrium temperature increases continuously with the pressure increase below 4 MPa but decreases with the pressure increase above 4 MPa. Therefore, the stabilization effect is lowered around the quadruple point. It might be expected that the competition in forming hydrate structure occurs, inducing the THF aqueous solution and carbon dioxide-rich liquid to favorably form the structure II and structure I hydrates, respectively.

## Conclusions

This work presents the three-phase hydrate equilibria for carbon dioxide + cyclic ethers + water. The addition of cyclic ethers results in the formation of mixed hydrate and the shift of hydrate equilibrium conditions to the higher temperature and lower pressure region. The THF is found to exhibit the highest stabilization effect among the studied cyclic ethers, while for 1,4-dioxane, no clear stabilization effect appears in the temperature and pressure range studied. For propylene oxide, a weak stabilization effect is observed at 0.03 mol fraction but increases with an increase in mole fraction up to 0.05 and eventually terminates at 0.10 mol fraction. The THF appears to be the most favorable stabilizer for the full mole fraction range of (0.01 to 0.05), although the stabilization effect weakens near the quadruple point that is regarded as the upper limit of the three-phase hydrate equilibria with the appearance of an additional carbon dioxide-rich liquid phase.

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