



In situ Raman spectroscopic study of the pressure effect on the concentration of CO₂ in water at hydrate-liquid water equilibrium up to 900 bar



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ABSTRACT

CO₂ hydrate may form during the injection of CO₂ into the submarine environment for CO₂ storage or enhanced recovery of CH₄ hydrate. The growth of CO₂ hydrate in seawater is dependent on the concentration of CO₂ in seawater in equilibrium with hydrate. However, such data are currently only available at pressures below 250 bar, and the pressure effect on the concentration of CO₂ in water at hydrate-liquid water equilibrium still remains controversial. In this study, Raman spectroscopy was applied to measure the concentration of CO₂ in water in equilibrium with hydrate from 276.15 to 289.05 K and from 30 to 900 bar. Our results show that the concentration of CO₂ in water at hydrate-liquid water equilibrium increases with increasing temperature (−0.081 mol/(kg K) on average), but decreases slightly with increasing pressure (−0.016, −0.021 and −0.034 mol/(kg·100 bar) at 276.15, 280.15 and 285.15 K, respectively). An equation that can well reproduce the current and previous measurements of CO₂ concentration in water at hydrate-liquid water equilibrium was proposed.

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1. Introduction

Disposal of greenhouse gas CO₂ and exploitation of CH₄ hydrate are two crucial issues of global concern. Direct injection of CO₂ into the deep ocean [1] (more than 3000 m below sea level) has been considered as an efficient method for CO₂ storage. On the other hand, a novel technique, in which CH₄ in natural hydrates was replaced by CO₂ as demonstrated by Ohgaki et al. [2], provides twin advantages: sequestering CO₂ and enhancing CH₄ hydrate recovery.

In the past decades, experiments of the H₂O–CO₂ system at hydrate (H)–liquid water (Lw)–vapor/liquid CO₂ (V_{CO₂}/L_{CO₂}) equilibrium (HLVE/HLLE), particularly at temperatures below 283.15 K were extensively conducted and have been well documented in Sloan and Koh's book [3]. Owing to pressure and temperature in most submarine conditions are more conducive to hydrate-liquid water equilibrium (HLE) than HLVE/HLLE (Fig. 1), the concentration of CO₂ (C_{CO₂}) in seawater plays the key role in driving CO₂

hydrate growth or dissolution. However, current measurements of C_{CO₂} in water at HLE [4–9] are limited below 250 bar (Fig. 1), and the pressure effect on C_{CO₂} in water at HLE still remains controversial. For instance, Servio and Englezos [5] measured C_{CO₂} in water at HLE from 273 to 284 K and from 20 to 60 bar, and suggested that pressure is not a strong factor on C_{CO₂} in water at HLE. Kim et al. [6] extended the experimental pressure to 201 bar and concluded that the pressure effect on C_{CO₂} at HLE is very weak. In addition, according to the measurements of C_{CO₂} in water at HLE from 49.9 to 142 bar at 280 K and the predictions, Yang et al. [4] suggested that C_{CO₂} in water at HLE decreases slightly with increasing pressure. Moreover, both experimental and theoretical results from 273 to 281 K below 250 bar reported by Zhang et al. [7] shown a negative effect of pressure on C_{CO₂} in water at HLE as well. In contrast, the theoretical derivation proposed by Bergeron et al. [10] and the semi-empirical model of Hashemi et al. [11] indicated that C_{CO₂} in water at HLE should increase with increasing pressure.

In an effort to overcome the existing controversy of the pressure effect on C_{CO₂} in water at HLE and extend our knowledge of the CO₂–H₂O system high-pressure phase equilibria, we measured C_{CO₂} in water in equilibrium with hydrate from 276.15 to 289.05 K and from 30 to 900 bar using Raman spectroscopy.

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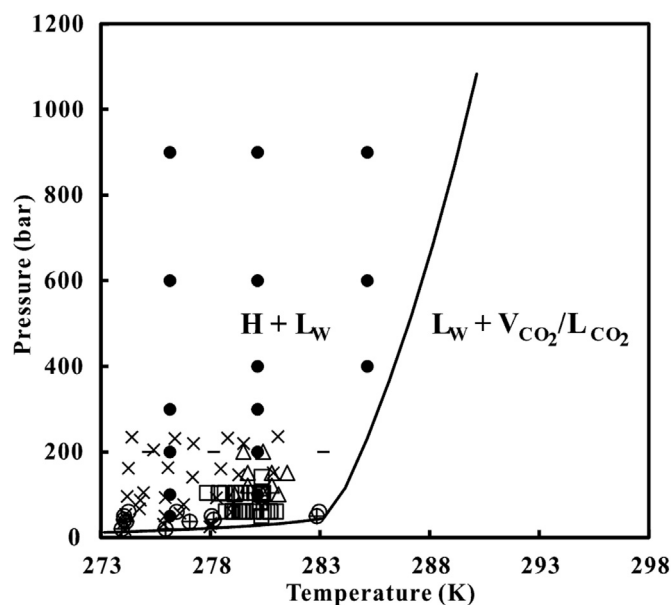


Fig. 1. Pressure-temperature conditions of previous experimental data and our new measurements of the concentration of CO₂ in liquid water (L_w) in equilibrium with hydrate (H) in the absence of vapor/liquid CO₂ (V_{CO₂}/L_{CO₂}); (□) Yang et al. [4]; (○) Servio and Englezos [5]; (△) Kim et al. [6]; (×) Zhang et al. [8]; (+) Sun et al. [8]; (–) Guo et al. [9]; (●) this study; (curve) the calculated dissociation pressures of CO₂ hydrate from the model of Sun and Duan [16].}}

2. Experimental

2.1. Materials

CO₂ with a purity of 99.99% supplied by Air Products and ultra-purified water with a resistivity of 18.24 MΩ cm (Table 1) were used in this study. The water was boiled for several minutes to expel possible dissolved air before sample preparation.

2.2. Apparatus and procedures

The experimental apparatus (Fig. 2) used in this study are similar to those we used previously for quantifying the diffusion coefficients of CO₂ in water [12] and geo-fluids high-pressure phase equilibria [9,13]. Briefly, a high pressure optical capillary cell [14] combined with a Linkam CAP500 heating-cooling stage were used. The temperature was measured by a K-type thermocouple with accuracy of ±0.1 K. The pressure in the cell was maintained with CO₂, strong brine, or both in the pressure line, adjusted by a pressure generator, and read from a Setra 204D digital pressure transducer (690 bar full scale; accurate to ± 0.14%) with Datum 2000™ manometer below 600 bar, and from a Omega PX91N0-30KSV pressure transducer (2000 bar full scale; accurate to ± 0.5%) from 600 to 900 bar.

The procedures for measurements of C_{CO₂} in water in equilibrium with hydrate include: (1) load a small quantity of water in the closed end of the capillary cell and connect the open end of the cell

to the high-pressure valve in the pressure line; (2) insert the cell horizontally to the Linkam CAP500 heating-cooling stage; (3) evacuate the pressure line and the cell and load it with CO₂; (4) repeat procedure (3) three times; (5) pressurize the line with a section of strong brine at ~200 bar for several days to let enough CO₂ be dissolved in the water; (6) adjust the pressure in the cell to a fixed value; (7) decrease the temperature rapidly to form CO₂ hydrate crystals (usually at 248 K); (8) increase the temperature to 273.15 K and maintain it for several days to grow hydrate crystals until the vapor/liquid CO₂ is completely consumed; (9) locate some crystals and move them to the window of the heating-cooling stage for Raman study; (10) slowly increase temperature to closely near the hydrate dissolution level; (11) adjust temperature repeatedly until there is no change in crystal size, and then keep the cell under this condition for more than 15 min to ensure the system reaches HLE; (12) collect Raman spectra of the aqueous solution between two hydrate crystals (Fig. 3a) and record the pressure and temperature (Table 2). For measuring C_{CO₂} in water at HLVE/HLE, the main differences from the procedures described above are reserving some vapor/liquid CO₂ in procedure (8) and collecting Raman spectra between hydrate crystals and vapor/liquid CO₂ (Fig. 3b) in procedure (12).

2.3. Spectra collection and calculation of C_{CO₂} in water

Raman spectra were collected with a JY/Horiba LabRam HR800 system equipped with a frequency doubled Nd:YAG laser (532.06 nm) with the output laser power of 45 mW. A 50 × long-work-distance Olympus objective with 0.5 numerical aperture and a 300-groove/mm grating were used with a spectral resolution of about 4 cm⁻¹. Raman spectra were collected from 1150 to 4000 cm⁻¹ (Fig. 4, Fig. S1 and Fig. S2) for 20–30 s with two accumulations per spectrum to maintain high signal to noise ratio. The Raman peak heights of the upper band of CO₂ Fermi diad (H_{CO₂}, at ~1390 cm⁻¹) and the OH stretching band of water (H_{H₂O}, at ~3480 cm⁻¹) were obtained for calculating the Raman peak intensity ratio (HR, stands for (H_{CO₂}/H_{H₂O})) using the software GRAMS/AI (Thermo Galactic). In this study, three spectra were collected for each pressure-temperature condition and the average values of HR were used to quantify C_{CO₂} in water. Based on the quantitative relationship between HR and C_{CO₂} in water (molality of CO₂, mCO₂ in mol/kg) proposed by Guo et al. [9] for determining CO₂ solubility in water from 273.15 to 573.15 K and from 100 to 1200 bar using the same Raman system,

$$HR/mCO_2 = -5.38 \times 10^{-5}T + 0.126, 273.15K \leq T < 404.45K \quad (1)$$

C_{CO₂} in water in equilibrium with hydrate can be calculated.

3. Results and discussion

3.1. Measured C_{CO₂} in water at HLVE/HLE

Nine measurements of C_{CO₂} in water at HLVE/HLE from 30 to

Table 1
Sources and purity/resistivity of the compounds used in this study.

Compound	Formula	Source	Purity/Resistivity
Carbon dioxide	CO ₂	Air Products	0.9999 ^a
Water	H ₂ O	From Millipore water filtering system	DDI ^b (18.24 MΩ cm)

^a Mass percentage purity declared by the manufacturer.

^b Distilled and deionized water.

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