**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.

KEYWORDS: Carbon dioxide; Hydrate; High pressure phase equilibria; Raman spectroscopy

1. INTRODUCTION

Disposal of greenhouse gas CO_2 and exploitation of CH_4 hydrate are two crucial issues of global concern. Direct injection of CO_2 into the deep ocean [1] (more than 3000 m below sea level) has been considered as an efficient method for CO_2 storage. On the other hand, a novel technique, in which CH_4 in natural hydrates was replaced by CO_2 as demonstrated by Ohgaki et al. [2], provides twin advantages: sequestering CO_2 and enhancing CH_4 hydrate recovery.

In the past decades, experiments of the $\text{H}_2\text{O}-\text{CO}_2$ system at hydrate (H)-liquid water (Lw)-vapor/liquid CO_2 ($\text{V}_{\text{CO}_2}/\text{L}_{\text{CO}_2}$) 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 CO_2 (C_{CO_2}) in seawater plays the key role in driving CO_2 hydrate growth or dissolution. However, current measurements of C_{CO_2} in water at HLE [4-9] are limited below 250 bar (**Fig. 1**), and the pressure effect on C_{CO_2} in water at HLE still remains controversial. For instance, Servio and Englezos [5] measured C_{CO_2} 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_{CO_2} in water at HLE. Kim et al. [6] extended the experimental pressure to 201 bar and concluded that the pressure effect on C_{CO_2} at HLE is very weak. In addition, according to the measurements of C_{CO_2} in water at HLE from 49.9 to 142 bar at 280 K and the predictions, Yang et al. [4] suggested that C_{CO_2} 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_{CO_2} 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_{CO_2} in water at HLE should increase with increasing pressure.

In an effort to overcome the existing controversy of the pressure effect on C_{CO_2} in water at HLE and extend our knowledge of the CO_2 - H_2O system high-pressure phase equilibria, we measured C_{CO_2} in water in equilibrium with hydrate from 276.15 to 289.05 K and from 30 to 900 bar using Raman spectroscopy.

2. EXPERIMENTAL

2.1 Materials

CO_2 with a purity of 99.99% supplied by Air Products and ultra-purified water with a resistivity of 18.24 M Ω 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 CO_2 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 CO_2 , 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 $\pm 0.14\%$) with Datum 2000TM manometer below 600 bar, and from a Omega PX91N0-30KSV pressure transducer (2000 bar full scale; accurate to $\pm 0.5\%$) from 600 to 900 bar.

The procedures for measurements of C_{CO_2} 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 CO_2 ; (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 CO_2 be dissolved in the water; (6) adjust the pressure in the cell to a fixed value; (7) decrease the temperature rapidly to form CO_2 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 CO_2 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_{CO_2} in water at HLVE/HLLE, the main differences from the procedures described above are reserving some vapor/liquid CO_2 in procedure (8) and collecting Raman spectra between hydrate crystals and vapor/liquid CO_2 (**Fig. 3b**) in procedure (12).

2.3 Spectra collection and calculation of C_{CO_2} 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 CO_2 Fermi diad (H_{CO_2} , at $\sim 1390\text{ }cm^{-1}$) and the OH stretching band of water (H_{H_2O} , at $\sim 3480\text{ }cm^{-1}$) were obtained for calculating the Raman peak intensity ratio (HR, stands for (H_{CO_2}/H_{H_2O})) 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_{CO_2} in water. Based on the quantitative relationship between HR and C_{CO_2} in water (molality of CO_2 , m_{CO_2} in mol/kg) proposed by Guo et al. [9] for determining CO_2 solubility in water from 273.15 to 573.15 K and from 100 to 1200 bar using the same Raman system,

$$HR/m_{CO_2} = -5.38 \times 10^{-5}T + 0.126, 273.15\text{ K} \leq T < 404.45\text{ K} \quad (1)$$

C_{CO_2} in water in equilibrium with hydrate can be calculated.

3. RESULTS AND DISCUSSION

3.1 Measured C_{CO_2} in water at HLVE/HLLE

Nine measurements of C_{CO_2} in water at HLVE/HLLE from 30 to 900 bar were obtained (**Table 2**). The uncertainties of m_{CO_2} for each C_{CO_2} at HLVE/HLLE are 0.17%

on average with a maximum of 0.34% at 200 bar. It can be seen from **Table 2** that C_{CO_2} in water at HLVE/HLLE increases from 1.328 to 2.386 mol/kg with increasing observation temperature (shown in **Table 2** as the dissociation temperature). Both our experimental dissociation temperature of CO_2 hydrate (**Fig. 5a**) and C_{CO_2} in water at HLVE/HLLE (**Fig. 5b**) are consistent with previous measurements [15, 5] and predictions [16].

3.2 Measured C_{CO_2} in water at HLE

Fifteen measurements of C_{CO_2} in water at HLE from 50 to 900 bar at 276.15, 280.15 and 285.15 K were obtained (**Table 2**). The uncertainties of mCO_2 for each C_{CO_2} at HLE are 0.45% on average with a maximum of 1.75% at 100 bar and 280.15 K. Our results show that C_{CO_2} increases with increasing temperature, but decreases slightly with increasing pressure (**Fig. 6**) over the experimental pressure-temperature conditions. Furthermore, the averaged C_{CO_2} in water at HLE from 50 to 900 bar at 276.15, 280.15 and 285.15 K are 1.024 ± 0.049 , 1.276 ± 0.060 and 1.750 ± 0.087 mol/kg, respectively, yielding an average increment of ~ 0.081 mol/(kg K). The average decreases caused by pressure at 276.15, 280.15 and 285.15 K are 0.016, 0.021 and 0.034 mol/(kg·100 bar), respectively. In addition, the measured C_{CO_2} in water at HLE were also compared with those from experiments reported in literature, as shown in **Fig. 7**.

Due to the measured values of C_{CO_2} in water at HLE (**Table 2**) vary with temperature and pressure, they can be fitted using the following equation:

$$mCO_2 = \exp[18.451 + 0.000129P - (5078.5 + 0.07734P)/T] \quad (2)$$

where P is pressure in bar and T is temperature in K. As shown in **Table 3**, Eq. (2) can well reproduce the measurements of C_{CO_2} in water at HLE reported in the literature and in this study with an overall average absolute deviation of 3.53%.

3.3 The pressure effect on C_{CO_2} in water at HLE

Our measurements shown in **Table 2** and **Fig. 6** verified that C_{CO_2} in water at HLE decreases slightly with increasing pressure [4]. For the CO_2 hydrate dissolution reaction:

where n is the hydration number, subscripts (s) and (aq) denote the solid phase and aqueous solution phase, respectively. Following Lu et al. [17], the variation of C_{CO_2} in water (mCO_2) at HLE as a function of pressure can be simplified as:

$$\partial[\ln(mCO_2)]/\partial P = -\Delta V/(RT) \quad (4)$$

Interpreting Eq. (2) and substituting in to Eq. (4) yield:

$$\Delta V = R(0.07734 - 0.000129T) \quad (5)$$

where R is the universal gas constant ($83.14467 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$), and ΔV , the molar volume change of reaction (3), is related to the hydration number (n), volume of CO_2 hydrate per mole of water (V_H , here we assume it is equal to molar volume of water in the hydrate lattice), molar volume of liquid water (V_W) and the apparent molar volume of dissolved CO_2 in water (V_{ϕ,CO_2}) at given pressure and temperature conditions according to the following equation:

$$\Delta V = V_{\phi,CO_2} + n(V_W - V_H) \quad (6)$$

Thus, the hydration number, n , can be derived from:

$$n = (V_{\phi, \text{CO}_2} - \Delta V) / (V_H - V_W) \quad (7)$$

Based on Eq. (5), we calculated the molar volume changes (ΔV) of reaction (3), and they were listed in **Table 4**. It can be seen that the molar volume changes vary from 3.372 to 3.469 cm³ per mole of hydrate in the temperature range of 276.15-285.15 K, which are about 3.7 times smaller than those (range: 11.848-13.225 cm³ per mole of hydrate) for CH₄ hydrate dissolution estimated by Lu et al. [17]. Therefore, the positive but relatively small values of the molar volume changes of CO₂ hydrate dissolution reaction lead to that C_{CO₂} in water at HLE decreases slightly with increasing pressure.

Additionally, combined with the models for predicting the apparent molar volume of dissolved CO₂ in water (V_{ϕ, CO_2}) [18], molar volume of liquid water (V_W) [19] and volume of CO₂ hydrate per mole of water (V_H) [16], the hydration numbers (n) of CO₂ hydrate were derived (**Table 4**) according to Eq. (7). The hydration numbers are in the range of 5.81-6.06 from 276.15 to 285.15 K and from 100 to 900 bar, and they are consistent with the estimates (5.63 ± 0.3 to 6.25 ± 0.3) of Anderson [20] from 276.15 to 283.15 K using the Clausius-Clapeyron equation, and with the measurements (6.2 ± 0.15) of Udachin et al. [21] at 276 K and 38 bar using X-ray diffraction. It can also be seen from **Table 4** that hydration number decreases slightly with increasing pressure and increases slightly with increasing temperature at constant pressure, indicating that the cage occupancy of CO₂ hydrate increases slightly with increasing pressure, and decreases slightly with increasing temperature.

4. CONCLUSION

Raman spectroscopy was applied to measure C_{CO_2} in water in equilibrium with hydrate in order to study the pressure effect on C_{CO_2} in water at HLE. Fifteen measurements of C_{CO_2} in water at HLE from 276.15 to 285.15 K and from 50 to 900 bar as well as nine measurements of C_{CO_2} in water at HLVE/HLLE from 276.15 to 289.05 K were obtained. We concluded that C_{CO_2} in water at HLE increases with increasing temperature, but decreases slightly with increasing pressure.

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FIGURE CAPTIONS

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]; (Δ) 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].

Fig. 2 Schematic diagram of the experimental apparatus for high-pressure observations.

Fig. 3 Photos of hydrate crystals in the cell showing the H₂O-CO₂ system at hydrate (H)-liquid water (L_w) equilibrium at 285.15 K and 900 bar (a), and at hydrate-liquid water-vapor CO₂ (V_{CO₂}) equilibrium at 280.45 K and 30 bar (b). Black arrows indicate the spots from which Raman spectra were collected.

Fig. 4 Raman spectra of dissolved CO₂ and H₂O collected from 50 to 900 bar at 276.15 K. The dashed lines added on the spectrum for 50 bar are the base lines used for calculating the Raman peak heights of CO₂ (H_{CO_2} , at ~1390 cm⁻¹) and H₂O ($H_{\text{H}_2\text{O}}$, at ~3480 cm⁻¹). The insert shows the magnified upper band of CO₂ Fermi diad, the peak height of which decreases slightly with increasing pressure.

277

278 **Fig. 5 Comparison of measured and calculated dissociation temperatures (a) and**
279 **concentrations of CO₂ in water at corresponding dissociation temperatures (b):**
280 **(Δ) Takenouchi and Kennedy [15]; (□) Servio and Englezos [5]; (○) this study;**
281 **(curve) the calculated values from the model of Sun and Duan [16].**

282

283 **Fig. 6 The measured concentrations of CO₂ in water at HLE plotted with**
284 **pressure at (○) 276.15, (Δ) 280.15 and (□) 285.15 K.**

285

286 **Fig. 7 Comparison of the measured concentrations of CO₂ in water at HLE with**
287 **other experimental data reported in literature: black symbols, measured in this**
288 **study at (*) 50, (□) 100, (Δ) 200, (○) 300, (–) 400, (◇) 600 and (+) 900 bar. Gray**
289 **symbols, Yang et al. [4] at (○) 61 and (Δ) 104.4 bar; Servio and Englezos [5] at (+)**
290 **50 and (×) 60 bar; Kim et al. [6] at (□) 101, (◇) 151 and (–) 201 bar; Guo et al. [9]**
291 **at (*) 200 bar.**

292

TABLE CAPTIONS

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

Table 2. Concentrations of CO₂ in water measured by using Raman spectroscopy and calculated from Raman peak-height ratios (HR) from the spectra of aqueous solutions in equilibrium with hydrate at various pressures and temperatures.

Table 3. Average absolute deviations (AAD) between the calculated concentrations of CO₂ in water at hydrate-liquid water equilibrium using Eq. (2) and those obtained by experiments in literature and this study.

Table 4. Calculated molar volume changes (ΔV) for CO₂ hydrate dissolution reaction in water and the derived hydration numbers (n) for CO₂ hydrate at various temperatures and pressures.

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.

Table 2. Concentrations of CO₂ in water measured by using Raman spectroscopy and calculated from Raman peak-height ratios (HR) from the spectra of aqueous solutions in equilibrium with hydrate at various pressures and temperatures.

Phases ^a	<i>P</i> (bar)	<i>T</i> (K)	HR	QF ^b (HR/ <i>m</i> CO ₂)	<i>m</i> CO ₂ ^c (mol/kg)	<i>u</i> (mCO ₂) (mol/kg)
H-Lw	50	276.15	0.1221	0.11114	1.099	0.006
H-Lw	100	276.15	0.1169	0.11114	1.052	0.001
H-Lw	200	276.15	0.1146	0.11114	1.031	0.002
H-Lw	300	276.15	0.1134	0.11114	1.020	0.003
H-Lw	600	276.15	0.1082	0.11114	0.974	0.003
H-Lw	900	276.15	0.1075	0.11114	0.967	0.002
H-Lw	100	280.15	0.1519	0.11093	1.369	0.024
H-Lw	200	280.15	0.1461	0.11093	1.317	0.009
H-Lw	300	280.15	0.1419	0.11093	1.279	0.013
H-Lw	400	280.15	0.1382	0.11093	1.246	0.001
H-Lw	600	280.15	0.1378	0.11093	1.242	0.003
H-Lw	900	280.15	0.1335	0.11093	1.203	0.002
H-Lw	400	285.15	0.2042	0.11066	1.845	0.014
H-Lw	600	285.15	0.1916	0.11066	1.731	0.002
H-Lw	900	285.15	0.1852	0.11066	1.674	0.006
H-Lw-V _{CO2}	30	280.55 [*]	0.1473	0.11091	1.328	0.004
H-Lw-L _{CO2}	50	283.25 [*]	0.1822	0.11076	1.645	0.002
H-Lw-L _{CO2}	100	283.85 [*]	0.1866	0.11073	1.685	0.002
H-Lw-L _{CO2}	200	284.75 [*]	0.1961	0.11068	1.772	0.006
H-Lw-L _{CO2}	300	285.55 [*]	0.2051	0.11064	1.854	0.000
H-Lw-L _{CO2}	400	286.15 [*]	0.2122	0.11061	1.919	0.004
H-Lw-L _{CO2}	500	286.95 [*]	0.2208	0.11056	1.997	0.002
H-Lw-L _{CO2}	600	287.45 [*]	0.2449	0.11054	2.216	0.006
H-Lw-L _{CO2}	900	289.05 [*]	0.2635	0.11045	2.386	0.002

Standard uncertainties *u* are $u(T) = 0.1$ K for $273 \text{ K} < T < 373 \text{ K}$, $u(P) = 0.97$ bar for $P < 600$ bar, $u(P) = 10$ bar for $600 \text{ bar} \leq P < 1500$ bar and the uncertainties of CO₂ concentration $u(m\text{CO}_2)$ are estimated based on the average deviation of three measurements of HR at given pressure and temperature.

^a H, Lw, V_{CO2} and L_{CO2} are the hydrate phase, liquid water phase, vapor and liquid CO₂ phases, respectively.

^b Quantitative factor (QF = HR/*m*CO₂).

^c CO₂ concentration in molality: $m\text{CO}_2 = \text{HR}/\text{QF}$.

^{*} CO₂ hydrate dissociation temperature at corresponding pressure.

Table 3. Average absolute deviations (AAD) between the calculated concentrations of CO₂ in water at hydrate-liquid water equilibrium using Eq. (2) and those obtained by experiments in literature and this study.

References	P (bar)	T (K)	No. of data	AAD (%)
Yang et al. [4]	49.9 - 142	277.84 - 280.98	32	6.37
Sevrio and Englezos [5]	20 - 60	273.95 - 282.95	12	3.31
Kim et al. [6]	101 - 201	279.5 - 281.5	10	2.55
Zhang et al. [7]	18.74 - 235.98	274.06 - 281.08	30	2.82
Sun et al. [8]	20 - 50	273.95 - 282.85	7	3.28
Guo et al. [9]	200	275.15 - 283.15	4	4.68
This study	50 - 900	276.15 - 285.15	15	1.73

Table 4. Calculated molar volume changes (ΔV) for CO₂ hydrate dissolution reaction in water and the derived hydration numbers (n) for CO₂ hydrate at various temperatures and pressures.

P (bar)	T (K)	ΔV (cm ³ /mol)	V_W^a (cm ³ /mol)	V_H^b (cm ³ /mol)	V_{ϕ,CO_2}^c (cm ³ /mol)	n
100	276.15	3.469	17.928	22.543	31.191	6.01
300	276.15	3.469	17.760	22.455	31.788	6.03
500	276.15	3.469	17.602	22.373	32.019	5.98
700	276.15	3.469	17.453	22.296	32.045	5.90
900	276.15	3.469	17.313	22.225	32.02	5.81
100	278.15	3.447	17.930	22.555	31.293	6.02
300	278.15	3.447	17.763	22.466	31.821	6.03
500	278.15	3.447	17.607	22.384	32.025	5.98
700	278.15	3.447	17.460	22.308	32.046	5.90
900	278.15	3.447	17.321	22.236	32.019	5.81
100	280.15	3.426	17.932	22.566	31.398	6.04
300	280.15	3.426	17.767	22.478	31.858	6.04
500	280.15	3.426	17.612	22.396	32.035	5.98
700	280.15	3.426	17.467	22.319	32.051	5.90
900	280.15	3.426	17.329	22.247	32.022	5.81
100	283.15	3.393	17.937	22.583	31.563	6.06
300	283.15	3.393	17.775	22.495	31.919	6.04
500	283.15	3.393	17.622	22.413	32.058	5.98
700	283.15	3.393	17.478	22.336	32.068	5.90
900	283.15	3.393	17.342	22.264	32.036	5.82
300	285.15	3.372	17.780	22.506	31.965	6.05
500	285.15	3.372	17.629	22.424	32.078	5.99
700	285.15	3.372	17.486	22.347	32.084	5.91
900	285.15	3.372	17.351	22.275	32.051	5.82

^a Calculated with the IAPWS-97 model [19].

^b Calculated from Eq. (10) of Sun and Duan [16].

^c Calculated from Eq. (11) of Hu et al. [18].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5a

Figure 5b

Figure 6

Figure 7