**Determination of P - V - T - x properties of the CO₂-H₂O system up to 573.15 K and
120 MPa—Experiments and model**

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Abstract: A new method is being developed as part of this study to measure the Pressure-Volume-Temperature-composition (P - V - T - x) properties of the CO_2 - H_2O system at temperatures from 273.15 to 513.15 K and pressures from 30 to 120 MPa. The density of a CO_2 - H_2O solution is determined by measuring the volumetric change of the solution sealed in a capillary High-Pressure Optical Cell (HPOC), through a systematic correction. This study partially fills the current density/molar volume data gap for dilute CO_2 - H_2O systems. Data show that the density of CO_2 - H_2O mixture ($\rho_{\text{CO}_2\text{-H}_2\text{O}}$) changes little below 298.15 K, then decreases more rapidly than $\rho_{\text{H}_2\text{O}}$ with increasing temperature at constant pressure, and eventually becomes lower than $\rho_{\text{H}_2\text{O}}$ in high temperature range (for example, above 489 K at 30 MPa). This pivoting temperature (T_p , above which $\rho_{\text{CO}_2\text{-H}_2\text{O}}$ becomes lower than $\rho_{\text{H}_2\text{O}}$) monotonously increases with increasing pressure (to 575 K as the pressure reaches 120 MPa). The calculated apparent molar volume of CO_2 in water (V_{Φ,CO_2}) is independent of CO_2 concentration, but is negatively correlated to pressure when the temperature is above 298.15 K. A revised V_{Φ,CO_2} model for dilute CO_2 - H_2O systems is proposed based on this study. This revised model can reproduce both the current and previous density data with an acceptable error range at temperatures up to 573.15 K and pressures up to 120 MPa. It can be used reliably to simulate geological sequestration of CO_2 into water aquifers, and in the study of P - V - T - x evolution of geo-fluids (e.g., CO_2 -bearing aqueous ore forming fluids).

Key words: P - V - T - x ; CO_2 - H_2O system; measurements; model

1. Introduction

Accurate estimation of P - V - T - x properties of the binary CO_2 - H_2O system is crucial for understanding behaviors of CO_2 -bearing aqueous fluids. For example, studies of fluid inclusions need to construct Pressure-Temperature (P - T) curves along the isochores (Schmidt and Bodnar, 2000); studies of CO_2 sequestration require evaluating CO_2 effects on the density of water (Bachu and Adams, 2003), etc. Moreover, determining the molar volume of CO_2 - H_2O system controlled by pressure (P), temperature (T) and composition (x) is a fundamental scientific research problem (Bakker and Diamond, 2000).

As of today, numerous papers have been published in experimental studies (Blencoe et al., 2001a; Blencoe et al., 1999; Capobianco et al., 2013; Crovetto and Wood, 1992; Hebach et al., 2004; Hnědkovský et al., 1996; King et al., 1992; Li et al., 2004; Nighswander et al., 1989; Ohsumi et al., 1992; Parkinson and De Nevers, 1969; Patel and Eubank, 1988; Seitz and Blencoe, 1999; Singh et al., 2000; Song et al., 2003; Song et al., 2013; Sterner and Bodnar, 1991; Teng et al., 1997; Yaginuma et al., 2000; Yan et al., 2011; Zawisza and Malesinska, 1981) and theoretical modeling (Akinfiev and Diamond, 2003; Akinfiev and Diamond, 2004; Andersen et al., 1992; Bachu and Adams, 2003; Blencoe et al., 1999; Duan et al., 2008; Ellis and McFadden, 1972; Enick and Klara, 1990; Garcia, 2001; Iglesias and Moya, 1992; Ji et al., 2005; Li et al., 2011; Plyasunov et al., 2000; Sedlbauer et al., 2000; Sun and Dubessy, 2010) of P - V - T - x properties of the H_2O -rich phase of CO_2 - H_2O system. Before 2007, most

P - V - T - x data were obtained below 35 MPa in pressure; data obtained over 35 MPa in pressure and below 493.15 K in temperature was lacking (Hu et al., 2007). Despite some newly reported data (Yan et al., 2011; Song et al., 2013; Capobianco et al., 2013), the pressure and/or temperature ranges in these experiments remain limited (In Yan: $T = 323.15, 373.15$, and 413.15 K, $P = 5$ – 40 MPa; In Song: $T = 333.15$ – 413.15 K, $P = 10$ – 18 MPa; and In Capobianco: $T = 473.15$ and 523.15 K, $P = 20$ – 80 MPa). The data measured near or above the critical temperature of H_2O (T_C) are scarce, which include those reported by Crovetto and Wood (1992) ($T = 622.75$ – 642.70 K, $P = 19.64$ – 28.13 MPa, x_{CO_2} (mol fraction of CO_2) = 0.0048 – 0.008745), Sterner and Bodnar (1991) ($T = 673.15$ – 973.15 K, $P = 200$ – 600 MPa, $x_{CO_2} = 0.1234$ – 0.7473), Seitz and Blencoe (1999) ($T = 673.15$ K, $P = 9.94$ – 99.93 MPa, $x_{CO_2} = 0.1$ – 0.9), and Blencoe et al. (1999) ($T = 673.15$ K, $P = 79.93$ MPa, $x_{CO_2} = 0.02$ – 0.2). So it can be seen that there are no P - V - T - x data at conditions over 40 MPa and below 473.15 K for CO_2 - H_2O system.

Due to the limitation of experiment, measuring all the P - V - T - x data of CO_2 - H_2O system at high pressures and temperatures is not practical. One key aspect of the issue is the CO_2 - H_2O density ($\rho_{CO_2-H_2O}$) dependency on P , T , and x . It is generally agreed that the increase of CO_2 concentration will raise the ratio of the density of CO_2 - H_2O solution to the density of pure water at low temperatures, as illustrated by the relationship:

$$\rho_{CO_2-H_2O} = \rho_{H_2O}(1 + \beta w_{CO_2}) \quad (1)$$

where $\rho_{\text{CO}_2\text{-H}_2\text{O}}$ is the density of $\text{CO}_2\text{-H}_2\text{O}$ system; $\rho_{\text{H}_2\text{O}}$ is the density of pure water; w_{CO_2} is the mass fraction of CO_2 in H_2O ; and β is defined as the “density changing coefficient”. $\beta = 0.275$ was proposed by Song et al. (2003), and an approximate value of 0.284 (i.e., density increases by 0.284 g/cm³ when 1 weight% CO_2 was added) was given by Ohsumi et al. (1992).

However, the experimental data of Hnědkovský et al. (1996), Yan et al. (2011) and Song et al. (2013) show that $\rho_{\text{CO}_2\text{-H}_2\text{O}}$ becomes lower than $\rho_{\text{H}_2\text{O}}$ at temperatures beyond approximately 483 K, defined as the pivoting temperature (T_p). This pivoting temperature (T_p) tends to be reduced by increasing pressure (Yan et al., 2011). Despite the recent $\rho_{\text{CO}_2\text{-H}_2\text{O}}$ data mentioned above, several questions remain unanswered: (a) How does CO_2 affect water density at temperatures higher than 483 K? (b) How is T_p affected by pressure in a wider P range covering beyond 40 MPa? And (c) How are molar volume of $\text{CO}_2\text{-H}_2\text{O}$ and apparent molar volume of CO_2 (V_{Φ,CO_2}) in water affected by P , T , and x ? Many authors chose to neglect the effects of pressure and CO_2 concentration on V_{Φ,CO_2} and only provided $V_{\Phi,\text{CO}_2}\text{-}T$ correlation models (e.g. Andersen et al., 1992; Garcia, 2001; Iglesias and Moya, 1992; Plyasunov et al., 2000; Sedlbauer et al., 2000). However, these models are not able to accurately reproduce experimental results (Hu et al., 2007), though ignoring the effect of CO_2 concentration on V_{Φ,CO_2} appears to be reasonable in a fairly wide range of CO_2 concentration (Duan et al., 2008). The pressure influence has not been investigated in pressures beyond 40 MPa. More data, systematically measured in wide $P\text{-}T$ ranges, are in an urgent need for completely understanding the $\text{CO}_2\text{-H}_2\text{O}$ system behavior.

Obtaining the density data of CO₂-H₂O system under high-pressure and -temperature conditions relies on experiment equipment that can be operated under extreme conditions safely while maintaining their accuracy. Since 1960s, various methods have been developed for measuring P - V - T - x data of CO₂-bearing fluids, such as the widely used vibration tube densitometry (Blencoe et al., 2001b; Crovetto and Wood, 1992; Hnědkovský et al., 1996; Ohsumi et al., 1992; Seitz and Blencoe, 1999) and synthetic fluid inclusion technique (Sterner and Bodnar, 1991; Zhang and Frantz, 1992). However, some intrinsic flaws restrict their usage in measuring P - V - T - x data, which include: (1) sampling procedures in some methods for determining compositions may cause the system to lose the equilibrium state and result in large error ; and (2) the material defects of some apparatus such as the expansion of quartz in synthetic fluid inclusions may introduce error of measured volume (Corti and Abdulagatov, 2008). A promising method is to integrate micro-fluid technique with *in situ* measurement. The High-Pressure Optical Cell (HPOC) developed by Chou et al. (2005) is an excellent tool and has been extensively applied for studying various fluid systems with *in situ* techniques (Caumon et al., 2014; Hu et al., 2013; Lu et al., 2008; Lu et al., 2013; Wang et al., 2013). Recently, we have reported the solubilities of CO₂ in H₂O measured in HPOCs with *in situ* Raman spectroscopy from 273.15 to 573.15 K and up to 120 MPa (Guo et al., 2014). Based on this report, the HPOC functionality is extended to measure P - V - T - x data of CO₂-H₂O system presented in this paper.

2. Experiment

2.1 Equipment and method

All the measurements are performed in the HPOC. The core section of the HPOC is a capillary tube, which is made of fused quartz. The tube can be connected to a high-pressure system in which pressure is maintained by a pump (*HiP* # 37-5.75-60) using water as the pressure medium. Pressure is read from an Omega PX91N0-50 KSV transducer (accurate to 0.5%) with an Omega DP41-S-230 strain gauge indicator (accurate to 0.005%). The sample is inserted into a Linkam CAP500 heating-cooling stage where the temperature is maintained by electrical heater or liquid nitrogen, and measured by a K-type thermocouple with accuracy of ± 0.1 K. The schematic plot of the experiment system is shown in Figure 1.

Following the procedures described in previous work (Guo et al., 2014; Lu et al., 2007), a series samples of CO₂ aqueous solution were sealed by mercury in the capillary tubes and homogenized at high pressure, to prepare CO₂ homogeneous aqueous solutions with knowing CO₂ concentration for *P-V-T-x* measurements. Samples were generally around 25 mm in length, to ensure the entire sample sealed by mercury in the capillary cell can be observed using reflected light from the top slit of the silver cover, where temperature was well controlled by the heating-cooling stage. Volumetric changes of the homogenized solutions were observed by an Olympus microscope at several temperatures and pressures. As shown in Figure 1, the lengths of the CO₂-H₂O columns, which expand or contract as temperature rises or drops, were measured by a motorized precision translation stage (MPTS, HTKY CO.,

LTD) with accuracy of 3 μm .

2.2 A test experiment— P - V - T measurement of H_2O

To assess the reliability of the method presented in Section 2.1, P - V - T measurements of water at 273.15–513.15 K and 30–120 MPa were performed. Water P - V - T measurements include obtaining volumes of water samples and the corresponding pressures and temperatures. Volumes of water sample columns ($V_{\text{H}_2\text{O}}^{\text{tot}}$, the total volume, distinguished from the molar volume $V_{\text{m},\text{H}_2\text{O}}$) was calculated by formula $V_{\text{H}_2\text{O}}^{\text{tot}} = \pi r^2 L_{\text{H}_2\text{O}}$, where r is the inner radius of the tube and $L_{\text{H}_2\text{O}}$ is the measured length of the water column. It was found that there was no observable change in r when changing pressure and temperature; as a result, $L_{\text{H}_2\text{O}}$ became the only indicator of water density. Without considering the change in r , water column lengths at pressures from 30 to 120 MPa and temperatures from 273.15 to 513.15 K were measured and the length change ratios ($LCR_{\text{H}_2\text{O}}$; $LCR_{\text{H}_2\text{O}} = L_{\text{H}_2\text{O}}/L_{\text{H}_2\text{O}}^0$, where $L_{\text{H}_2\text{O}}^0$ is the length of water sample at 298.15 K) were determined. Then, all the measured $LCR_{\text{H}_2\text{O}}$ values were compared with those length change ratios calculated from the widely accepted IAPWS-97 model (Wagner and Pruß, 2002) for pressures between 30 to 90 MPa and the WM-Hu model developed by Hu et al. (2007) for pressure at 120 MPa. The length change ratios estimated by models are denoted as $LCR_{\text{H}_2\text{O}}^{\text{WP}}$. As shown in Figure 2, ratio of $LCR_{\text{H}_2\text{O}}^{\text{WP}}$ to $LCR_{\text{H}_2\text{O}}$ (R_{TC} ; $R_{\text{TC}} = LCR_{\text{H}_2\text{O}}^{\text{WP}}/LCR_{\text{H}_2\text{O}}$) increases with increasing temperature, which indicates that water densities measured by HPOC have systematic positive deviations from those predicted by IAPWS-97 and

WM-Hu.

Despite the systematic deviation in R_{TC} , all measurements show good reproducibility.

After experiment, the length of water trapped by the mercury tap is identical within the measurement uncertainty to the initial length at 298.15 K and 1 atm.

3. Results and discussion

3.1. Determination of water densities by HPOC

Through measuring LCR_{H_2O} , the density of pure water can be determined with high accuracy using the HOPC. As shown in Figure 2, the average value of R_{TC} ($R_{TC,A}$) is related to temperature (T ; K) and pressure (P ; MPa) between 273.15 and 513.15 K by:

$$R_{TC,A} = 1.01010 - 2.61420E-10T^2P - 7.43677E-5T + 1.33777E-7T^2 + 8.42321E-8TP \quad (2)$$

Using the empirical relationship provided by Equation (2), the raw LCR_{H_2O} were corrected to produce $LCR_{H_2O,cor}$ as listed in Column 2 of the Table 1. Taking the densities at 298.15 K estimated by IAPWS-97/WM-Hu models as the reference density ($\rho_{CO_2-H_2O}^0$ s), the densities of water were determined based on $LCR_{H_2O,cor}$. These densities are in good agreement with those calculated by IAPWS-97 and WM-Hu with an Average Absolute Deviation (AAD) of 0.0162 %, which shows that the water density measurements data are accurate after the bias correction using equation (2).

3.2. Determination of CO₂-H₂O densities by the HPOC

Following the procedures for measuring pure water, P - V - T - x of CO₂ aqueous solutions

were measured with x_{CO_2} ranging from 0.00678 to 0.0356. The LCR of $\text{CO}_2\text{-H}_2\text{O}$ homogeneous solutions ($LCR_{\text{CO}_2\text{-H}_2\text{O}}$) are first measured at pressures from 30 to 120 MPa and temperatures from 273.15 to 513.15 K. Then, the $LCR_{\text{CO}_2\text{-H}_2\text{O}}$ were corrected by equation (2), assuming low concentrated and inert CO_2 solutions had the same systematic deviation as those for pure water. The $LCR_{\text{CO}_2\text{-H}_2\text{O,cor}}$ are presented in Table 1 side-by-side with $LCR_{\text{H}_2\text{O,cor}}$, which shows that adding CO_2 systematically increases LCR of the solution, i.e., $LCR_{\text{CO}_2\text{-H}_2\text{O}} > LCR_{\text{H}_2\text{O}}$ when T higher than 298.15 K.

Based on $LCR_{\text{CO}_2\text{-H}_2\text{O,cor}}$, the densities of $\text{CO}_2\text{-H}_2\text{O}$ solutions ($\rho_{\text{CO}_2\text{-H}_2\text{O}}$) are determined at pressures from 30 to 120 MPa and temperatures from 273.15 to 513.15 K using the reference densities at 298.15 K ($\rho_{\text{CO}_2\text{-H}_2\text{O}}^0$) calculated by the model of Duan et al. (2008). Then, the effect of CO_2 on density of CO_2 -bearing aqueous solution is estimated using the β in Equation (1). The calculated values of β were plotted with temperature (Figures 3a-e). Figures 3a-e show that β values change little below 298.15 K, but decrease with increasing temperatures above 313.15 K from positive values to negative values at temperature T_p that we designate as pivoting temperature. This indicates that $\rho_{\text{CO}_2\text{-H}_2\text{O}}$ values are lower than $\rho_{\text{H}_2\text{O}}$ above T_p .

The decreasing trend of β with increasing temperature has been indicated by previous studies, especially by the data of Hnědkovský et al. (1996), Yan et al. (2011) and Song et al. (2013), as illustrated in Figure 3f. Above 298.15 K, the decreasing trend of β shown by this study at 30 MPa is very close to that predicted by data of Hnědkovský et al. (1996) at 20 or 35 MPa. Though the pressures in previous experimental studies

are scattered below 35 MPa, pressure has little effect on β at temperatures lower than 423.15 K. Our data demonstrate that increasing pressure slightly reduces β at temperatures below 313 K and pressures up to 120 MPa. However, the reduction rate of β is greatly weakened with increasing pressure (Figure 3f). On the other hand, it is further confirmed by our data that x_{CO_2} has negligible influence on β at pressures beyond 40 MPa (see Figures 3a-d). This agrees with previous experimental works. In addition, it is indicated by measurement on sample with high CO_2 concentration (e.g., the sample with $w_{\text{CO}_2} = 0.0827$) that the maximum value of x_{CO_2} for which CO_2 concentration has little effect on β is saturated concentration. Noted that the averaged β values obtained for different CO_2 concentrations at the same T are used as valid indicators for evaluating effect of CO_2 concentration on density of CO_2 -bearing solution at 120 MPa, though measurements at 120 MPa showed a somewhat reducing effect of x_{CO_2} on β (Figure 3e).

T_p values can be fitted using a function correlated β to P and T (Figures 3a-e; Table 2). $T_p = 489$ K at 30 MPa is very close to its value at 473–483 K (5–40 MPa) recommended by Yan et al. (2011), 503 K (10–18 MPa) inferred by Song et al. (2013), and 476 K (35 MPa) derived from data of Hnědkovský et al. (1996). Furthermore, T_p has a positive and linear dependency on pressure with an extrapolated maximum value of 575 K at 120 MPa. This pressure dependency of T_p is in good agreement with that observed by Hnědkovský et al. (1996) (Figure 4), but is in conflict with data of Yan et al. (2011) who showed that T_p would drop from 483 K at 5 MPa to 473 K at 40 MPa.

3.3. Estimation of the uncertainties

The sources of the uncertainties of the determined densities of CO₂-H₂O solutions are mainly (1) the errors of the measured $LCR_{CO_2-H_2O}$ s, and (2) the errors of the calculated x_{CO_2} . Because the content of CO₂ relative to that of H₂O is much lower, the $LCR_{CO_2-H_2O}$ are thought to have similar measuring errors to that for LCR_{H_2O} . This can also be proved by the fact that no observable corrosion or dissolution of Hg occurred near the interface of Hg and the CO₂-H₂O solution during the measuring processes at any temperature and any pressure in this study, which is the same as that for water as indicated by our previous phase-equilibrium study of the CO₂-H₂O system (Guo et al., 2014). So, the errors estimated for $LCR_{CO_2-H_2O}$ are at the level of 0.015 %. Generally, the initially sealed length of the CO₂ gas is at least 20 cm, and measured by a ruler accurate to 1 mm. The length of the water column is measured by the MPTS and the corresponding length errors are 0.02 % at most. Thus, the maximum uncertainties of x_{CO_2} are estimated to be 0.5 %. Because the maximum x_{CO_2} is 0.0356, the errors in density caused by uncertainties of x_{CO_2} are less than 0.013 % according to Equation (1). As a result, the error of the CO₂-H₂O densities measured by the HPOC method is 0.015 %.

3.4. Determination of the apparent molar volume of CO₂ (V_{Φ,CO_2})

It is known that density of CO₂-H₂O is related to V_{Φ,CO_2} as follows:

$$\rho_{CO_2-H_2O} = (x_{H_2O}M_{H_2O} + x_{CO_2}M_{CO_2})/(x_{H_2O}V_{m,H_2O} + x_{CO_2}V_{\Phi,CO_2}) \quad (3)$$

where $x_{\text{H}_2\text{O}}$ and x_{CO_2} are molar fractions of H_2O and CO_2 , respectively; $M_{\text{H}_2\text{O}}$ is the molar mass of H_2O (18.0153 g/mol) and M_{CO_2} is the molar mass of CO_2 (44.01 g/mol). Molar volume of H_2O ($V_{\text{m,H}_2\text{O}}$) and apparent molar volume of CO_2 (V_{Φ,CO_2}) are both in cm^3/mol . x_{CO_2} could be expressed in the form containing mass fraction of H_2O ($w_{\text{H}_2\text{O}} = 1 - w_{\text{CO}_2}$) and w_{CO_2} :

$$x_{\text{CO}_2} = (w_{\text{CO}_2}/M_{\text{CO}_2})/[w_{\text{CO}_2}/M_{\text{CO}_2} + w_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}}] \quad (4)$$

Substituting Equation (4) into Equation (3), V_{Φ,CO_2} is calculated by:

$$\rho_{\text{CO}_2\text{-H}_2\text{O}} = \rho_{\text{H}_2\text{O}}/[1 - w_{\text{CO}_2}(1 - \rho_{\text{H}_2\text{O}}V_{\Phi,\text{CO}_2}/M_{\text{CO}_2})] \quad (5)$$

Then

$$V_{\Phi,\text{CO}_2} = [\rho_{\text{H}_2\text{O}} - (1 - w_{\text{CO}_2})\rho_{\text{CO}_2\text{-H}_2\text{O}}]/(\rho_{\text{H}_2\text{O}}w_{\text{CO}_2}\rho_{\text{CO}_2\text{-H}_2\text{O}}/M_{\text{CO}_2}) \quad (6)$$

Or replacing $\rho_{\text{CO}_2\text{-H}_2\text{O}}$ with $\rho_{\text{H}_2\text{O}}$ according to Equation (1), β and V_{Φ,CO_2} can be written as:

$$V_{\Phi,\text{CO}_2} = M_{\text{CO}_2}/\rho_{\text{H}_2\text{O}}[1 - \beta/(1 + \beta w_{\text{CO}_2})] \quad (7)$$

Using Equations (6) or (7), the estimated $\rho_{\text{CO}_2\text{-H}_2\text{O}}$ or β could be used to calculate V_{Φ,CO_2} . The final V_{Φ,CO_2} values are depicted in Figure 5. What can be seen from Figure 5 are (1) V_{Φ,CO_2} increases sharply with increasing temperature above 298.15 K, but is nearly not affected by temperature lower than 298.15 K; (2) the effect of CO_2 concentration on V_{Φ,CO_2} is small (shown as the error bars); and (3) increasing pressure in the range of 30-120 MPa reduces the increasing rate of V_{Φ,CO_2} with increasing

temperature. Therefore, we calculate the mean value of V_{Φ, CO_2} obtained for different CO_2 concentrations at each pressure-temperature experimental condition. The results are listed in Table 3. These estimated apparent molar volumes of CO_2 are compared with previous data in Figure 6.

As shown in Figure 6a, most of the previous experimental data are constrained below 423.15 K and 40 MPa and none of the data are measured at $P > 40$ MPa and $T < 473.15$ K. Our data partially fill this gap. Previous data have shown that CO_2 concentration has negligible influences on the values of V_{Φ, CO_2} , which is confirmed by our data up to 120 MPa. The V_{Φ, CO_2} data obtained by this study agree well with Hnědkovský et al. (1996) on the value of V_{Φ, CO_2} measured at 30 MPa and on the negative dependency of V_{Φ, CO_2} on pressure. However, many previous models did not account for the effect of pressure on V_{Φ, CO_2} (Figure 6b) (Andersen et al., 1992; Enick and Klara, 1990; Garcia, 2001; Iglesias and Moya, 1992; Plyasunov et al., 2000; Sedlbauer et al., 2000). In addition the model by Duan et al. (2008) predicts V_{Φ, CO_2} values independent of pressure under 450 K, which is not consistent with our data. This conflict is likely due to the insufficient experimental data base (limited in a narrow pressure range) used for the previous models.

Models developed by different authors have produced inconsistent V_{Φ, CO_2} predictions. The model of Enick and Klara (1990) is questionable because the predicted values above ~380 K show a strong negative correlation with temperature, which contradicts to most other data and models. The earlier models developed by Ennis-King, Iglesias

and Moya (1992), and Andersen et al. (1992) are in poor agreement with the later models by Sedlbauer et al. (2000), Garcia (2001), and Duan et al. (2008) (whose model is the same as the model of Li et al. (2011)). The early models predict systematically higher V_{Φ, CO_2} below 323 K and systematically lower V_{Φ, CO_2} above 323 K than the values predicted by latter models as shown in Figure 6b. Actually, the experimentally measured V_{Φ, CO_2} data by Hnědkovský et al. (1996) play a key role in revealing the limitations of those models in predicting V_{Φ, CO_2} before the year of 1996. Due to the scarce V_{Φ, CO_2} data at high pressure, no model is capable enough of predicting accurate V_{Φ, CO_2} data at pressures beyond 35 MPa though Duan et al. (2008) claimed that their model could be extrapolated to 100 MPa with reasonable accuracy. However, as can be seen from Figure 6b, the model of Duan et al. (2008) predicts a relationship between V_{Φ, CO_2} and pressure, where only above ~ 470 K does the pressure have pronounced effect on V_{Φ, CO_2} ; and the only basis for Duan's model above 35 MPa is the data of Blencoe et al. (2001a) who measured the volumetric properties of $\text{CO}_2\text{-H}_2\text{O}$ up to 100 MPa only at 573.15 K. Apparently, more P - V - T - x data are needed in the region of $P > 35$ MPa and $T < 573.15$ K to check the model of Duan et al. (2008).

3.5. A revised V_{Φ, CO_2} model

Several models for predicting V_{Φ, CO_2} in H_2O (Table 4) have been proposed by previous studies, including: (1) the empirical models by Enick and Klara (1990), Andersen et al. (1992), Iglesias and Moya (1992) and Garcia (2001); (2) thermodynamic models by

Sedlbauer et al. (2000) and Plyasunov et al. (2000); and (3) correlations by Bachu and Adams (2003), Duan et al. (2008) and Li et al. (2011). As shown in Table 4, none of the models considered the effect of CO₂ concentration on V_{Φ, CO_2} . All models but the one proposed by Duan et al. (2008) neglected the pressure effect on V_{Φ, CO_2} . Considering the insignificant influences of w_{CO_2} (up to saturation) but significant pressure effect on V_{Φ, CO_2} revealed by this study, it is feasible to treat the change of molar volume of H₂O due to the dissolution of CO₂ as a perturbation of pure water volume (see the discussion by Duan et al. (2008)). So, the apparent molar volume of CO₂ (V_{Φ, CO_2}) can be expressed as:

$$V_{\Phi, \text{CO}_2} = AV_{\text{m}, \text{H}_2\text{O}} \quad (8)$$

where the coefficient A is a function of T and P , unrelated to w_{CO_2} . An expression of A was suggested by Duan et al. (2008) as follows:

$$A = 1 + A_1 + A_2P$$

$$A_i = A_{i1}T^2 + A_{i2}T + A_{i3} + A_{i4}T^{-1} + A_{i5}T^{-2} \quad (i = 1, 2) \quad (9)$$

where A_i , and A_{i1} - A_{i5} are empirical fitting parameters.

As stated by Duan et al. (2008), positive power terms were more important at higher temperatures and negative powers were more important at lower temperatures in Equation (9). In addition, we found that adding higher power P terms could greatly improve the performance of Equation (9) by an order of magnitude in reproducing data of this study. Hu et al. (2007) proposed a model for calculating molar volumes of

water (V_{m,H_2O}) that could reproduce the water volumes of Wagner and Pruß (2002) with an average deviation of 0.005% in the range of 273.15–473.15 K and 0–200 MPa in the following form:

$$V_{m,H_2O} = k_0 + k_1P + k_2P^2 + k_3P^3$$

$$k_i = k_{i1}T^3 + k_{i2}T^2 + k_{i3}T + k_{i4} + k_{i5}T^{-1} \quad (i = 0, 1)$$

$$k_j = k_{j1}T^3 + k_{j2}T^2 + k_{j3} \quad (j = 2, 3) \quad (10)$$

Through extensive trials, we found that including the third power term of T would reduce the goodness-of-fit. Meanwhile, if the negative power term of T was incorporated into the coefficients of the higher power term of P , no remarkable improvement was achieved. As a result, based on the model of Duan et al. (2008) and Hu et al. (2007), we suggest a V_{Φ,CO_2} model that is given as follows:

$$V_{\Phi,CO_2} = AV_{m,H_2O}$$

$$A = 1 + A_1 + A_2P + A_3P^2 + A_4P^3$$

$$A_i = A_{i1}T^2 + A_{i2}T + A_{i3} + A_{i4}T^{-1} + A_{i5}T^{-2} \quad (i = 1, 2)$$

$$A_j = A_{j1}T^2 + A_{j2}T + A_{j3} + A_{j4}T^{-1} \quad (j = 3, 4) \quad (11)$$

where the unit of molar volume (V_{Φ,CO_2} ; V_{m,H_2O}) is cm^3/mol . T and P are in K and MPa, respectively. The molar volumes of water are calculated with IAPWS-97 (for 30~90 MPa) and WM-Hu (for 120 MPa) at temperatures from 273.15 to 513.15 K. Then, the values of A_i and A_j are regressed from the V_{Φ,CO_2} data in Table 3 and the calculated

V_{m,H_2O} data according to Equation (11). The parameters for Equation (11) are listed in Table 5. The correlation coefficient R^2 of the regression is 0.997. This revised model can well reproduce our experimental V_{Φ,CO_2} with an AAD of 0.412%.

This model can well reproduce previous volume/density data for CO_2 - H_2O solutions up to 573.15 K and 120 MPa. As can be seen from Figure 7, the $V_{\Phi,cal}$ calculated by Equation (11) deviates from previous experimental results by no more than 8% ($|D_{\Phi}|$; the deviation $D_{\Phi} = (V_{\Phi,cal} - V_{\Phi,exp})/V_{\Phi,exp}$), except two data of Yan et al. (2011) at $T = 373.15$, $P = 15$ MPa ($D_{\Phi} = 12.2\%$) and $T = 413.15$ K, $P = 15$ MPa ($D_{\Phi} = 21.5\%$), and most data of Teng et al. (1997). The deviations (also donated as D_{Φ} in Figure 7) between $V_{\Phi,cal}$ and those from model of Duan et al. (2008) are within $\pm 5\%$. Our model further supports that data of Teng et al. (1997) are of low quality (Hu et al., 2007). This model reproduces densities of previous studies by D_{ρ} ($D_{\rho} = (\rho_{cal} - \rho_{exp})/\rho_{exp}$ where ρ_{cal} is the calculated densities of CO_2 - H_2O solutions and ρ_{exp} is the experimental densities) values from -0.25% to 0.45% except data of Teng et al. (1997) as shown in Figure 8a. The densities measured by this study can be reproduced according to Equations (5) and (11) by D_{ρ} from -0.1% to 0.4% (AAD = 0.026 %) (Figure 8b). These errors are within the usual uncertainty range of the experimental data and modeling predictions (Hu et al., 2007; Ji et al., 2005). Additionally, the predicted molar volumes for CO_2 - H_2O (V_{m,CO_2-H_2O}) at 20 and 35 MPa are in excellent agreement with those reported by Hnědkovský et al. (1996) with AAD of 0.24% (Figure 9a). Using the V_{Φ,CO_2} calculated by this model from 30 to 90 MPa, the obtained V_{m,CO_2-H_2O} ($x_{CO_2} = 0.05$) are very close to those graphically reported by Blencoe et al. (2001a)

(Figure 9b). So the model is believed to be safe in predicting molar volumes of CO₂-H₂O solutions up to 573.15 K. However, one should take great care to extrapolate this model to pressures higher than 120 MPa because the predicted V_{Φ, CO_2} - T dependency above 120 MPa are not constrained by experimental data.

Presently, the V_{Φ, CO_2} -related data beyond 573.15 K has been provided by several studies including Sterner and Bodnar (1991), Crovetto and Wood (1992), Hnědkovský et al. (1996), Seitz and Blencoe (1999), Blencoe et al. (2001a), etc. Among these data, some were reported in the form of excess molar volume (V^{ex}) of the CO₂-H₂O system. In fact, the V^{ex} can be easily converted into V_{Φ, CO_2} by combining the following two relations:

$$V_{\text{m}, \text{CO}_2\text{-H}_2\text{O}} = x_{\text{H}_2\text{O}}V_{\text{m}, \text{H}_2\text{O}} + x_{\text{CO}_2}V_{\Phi, \text{CO}_2} \quad (12)$$

$$V_{\text{m}, \text{CO}_2\text{-H}_2\text{O}} = x_{\text{H}_2\text{O}}V_{\text{m}, \text{H}_2\text{O}} + x_{\text{CO}_2}V_{\text{m}, \text{CO}_2} + V^{\text{ex}} \quad (13)$$

Then, yield the relation:

$$V_{\Phi, \text{CO}_2} = V^{\text{ex}}/x_{\text{CO}_2} + V_{\text{m}, \text{CO}_2} \quad (14)$$

where $V_{\text{m}, \text{CO}_2}$ is the molar volume of pure CO₂. We tentatively included these data in estimating the parameters of Equation (11) by regression to test if Equation (11) could be used for predicting volume properties of CO₂-H₂O system beyond 573.15 K. However, the trial was not successful, because (1) the difference between V_{Φ, CO_2} and $V_{\text{m}, \text{H}_2\text{O}}$, illustrated by the coefficient A of Equation (8), would be significantly increased at temperatures beyond 623.15 K and pressures below 35 MPa (Figure 10);

and (2) there are no data below 673.15 K from 200 to 500 MPa. So, more experimental P - V - T - x data that are systematically measured beyond 573.15 K and/or 120 MPa are still needed for seeking an equation that can be widely used for describing CO_2 - H_2O system under normal and extreme conditions.

From the discussions above, it is clear that the V_{Φ, CO_2} model of Equation (11) is not suitable for predicting volumetric properties of aqueous solutions with high CO_2 concentrations. The upper limit of x_{CO_2} that is suitable for this model is 0.05. As shown in Figures 9b and 11, the calculated $V_{\text{m}, \text{CO}_2\text{-H}_2\text{O}}$ with x_{CO_2} higher than 0.05 have large deviations from the experimentally determined molar volumes of Blencoe et al. (2001a) (in the case of $x_{\text{CO}_2} = 0.1$) and Capobianco et al. (2013). On the other hand, the excellent agreement of the predicted $V_{\text{m}, \text{CO}_2\text{-H}_2\text{O}}$ with those measured by Capobianco et al. (2013) ($x_{\text{CO}_2} \leq 0.05$) as shown in Figure 11 further supports this model at pressures higher than 30 MPa.

4. Implications for geological storage of CO_2 and role of CO_2 in hydrothermal deposits

4.1 Geological storage of CO_2

Main questions regarding the CO_2 sequestration issue include: what are the suitable conditions, in what amount CO_2 can be injected into aqueous fluids; and how long CO_2 can be stored, etc. CO_2 sequestration in deep saline formations is considered more favorable than sequestration in deep sea and oil reservoirs (Cinar and Riaz, 2014; Leung et al., 2014; Riaz and Cinar, 2014). The formations can be classified into

“cold” and “hot” types, and the temperature may be over 393 K (Bachu and Adams, 2003; Song et al., 2013). Findings of this study may have significant implications to the geological storage of CO₂ in the “hot” formation.

As shown by this study, when temperature is above 373 K, though solubility of CO₂ in H₂O increases with rising temperature, the density of the CO₂-H₂O mixture remain closer to the density of pure water as a result of the decreasing values of β with temperature. At 30 MPa, the CO₂-H₂O mixture becomes lighter than water beyond 489 K (i.e. T_p). The T_p becomes less than 485 K when the pressures are less than 30 MPa. Furthermore, data of Yan et al. (2011) suggest that the presence of NaCl can greatly reduce T_p (by ~70 K when salinity increases from 0 to 6 mol/kg; Yan et al. (2011)). If the temperature in the CO₂ storage formations is higher than T_p , there are less chance for the solubility trapping mechanism which is more efficient and secure than other mechanisms (Bodnar et al., 2013). So, operation of CO₂ sequestration should avoid those formations where the temperatures are over T_p .

As stressed by Hu et al. (2007), an accurate prediction of densities of CO₂-bearing solutions is crucial for CO₂ sequestration modeling. Calculated volume changes (ΔV) of supercritical CO₂ (scCO₂) aqueous solution in a closed equilibrium system with the revised CO₂-H₂O model by this study suggests that using the model of Duan et al. (2008) would underestimate the CO₂ storage capacity of a real site. In the simulated closed system as shown in Figure 12, the total volume of the space is denoted as V_0 ; the volume of the water aquifer is denoted as RV_0 (R is the volume proportion relative

to V_0); and the volume of the rest structural/stratigraphic space equals to $(1 - R)V_0$, assuming that the temperature (T) and the pressure (P) of the system are constant and not affected by the injection of CO_2 . Because dissolution of CO_2 in H_2O is a much slower process than the injection of CO_2 into the structural/stratigraphic space, it is reasonable to assume that scCO_2 does not dissolve in water until the structural/stratigraphic space is filled with scCO_2 . For no reliable phase-equilibrium and volume data for the CO_2 -rich phase, dissolution of H_2O in scCO_2 and the resulted volume change of the scCO_2 -rich phase are not considered. So, immediately after injection of scCO_2 , the system volume equals to the initial volume of water plus the volume of injected scCO_2 (V_{CO_2}), i.e.,

$$V_{\text{CO}_2} = (1 - R)V_0 \quad (15)$$

Based on the solubility of CO_2 in H_2O (m_{CO_2} ; mol/kg) at T and P , the dissolved volume of scCO_2 (ΔV_{CO_2}) is

$$\Delta V_{\text{CO}_2} = \rho_{\text{H}_2\text{O}} R V_0 m_{\text{CO}_2} V_{\text{m,CO}_2} \quad (16)$$

The volume of scCO_2 -saturated CO_2 - H_2O solution is

$$V_{\text{CO}_2\text{-H}_2\text{O}} = (\rho_{\text{H}_2\text{O}} R V_0 + \rho_{\text{CO}_2} \Delta V_{\text{CO}_2}) / \rho_{\text{CO}_2\text{-H}_2\text{O}} \quad (17)$$

Then, the volume change ratio of scCO_2 + water ($\Delta V/V_0$) when the injected scCO_2 reaches equilibrium with water is computed as

$$\Delta V/V_0 = [(\rho_{\text{H}_2\text{O}} R V_0 + \rho_{\text{CO}_2} \Delta V_{\text{CO}_2}) / \rho_{\text{CO}_2\text{-H}_2\text{O}} + (1-R)V_0 - \Delta V_{\text{CO}_2} - V_0] / V_0$$

(18)

Rearrange

$$\Delta V/V_0 = R[(\rho_{H_2O}/\rho_{CO_2-H_2O}(1 + m_{CO_2}M_{CO_2}/1000) - \rho_{H_2O}m_{CO_2}V_{m,CO_2}/1000 - 1] \quad (19)$$

where the densities ρ_{H_2O} , ρ_{CO_2} , and $\rho_{CO_2-H_2O}$ are all in g/cm^3 , and calculated with model of IAPWS-97, Duan et al. (1992) and Equation (11), respectively; V_{m,CO_2} is in cm^3/mol ; and the molar mass of CO_2 (M_{CO_2}) is 44.01 g/mol. The volume change ratios ($\Delta V/V_0$) calculated at temperatures from 273.15 to 423.15 K and pressures from 10 to 50 MPa are shown in Figure 13 and compared with those calculated based on the model of Duan et al. (2008). Figure 13 shows that the calculated $\Delta V/V_0$ ratios are negative in the simulated P - T scope and decrease with increasing temperature/ R but increase with increasing pressure when the other conditions are the same. This indicates that the pressure change in time caused by gradual dissolution of CO_2 in water will be negative after $scCO_2$ is injected into the water formation, which ensures the security of solubility trapping. By comparison, those $\Delta V/V_0$ ratios below 20 MPa and in the range of $20 \text{ MPa} \leq P \leq 35 \text{ MPa}$, $390 \text{ K} \leq T \leq 423.15 \text{ K}$ calculated by both of the models are close; however, in the ranges of $P > 20 \text{ MPa}$, $273.15 \text{ K} \leq T < 390 \text{ K}$ and $P > 35 \text{ MPa}$, $390 \text{ K} \leq T \leq 423.15 \text{ K}$, the model of Duan et al. (2008) predicts systematical higher $\Delta V/V_0$ values than this model (Equation 19) by an average deviation of ~5% (this deviation shows little dependence on R); and furthermore, the deviation between $\Delta V/V_0$ values calculated by the two models

increases with increasing pressure. This observation could be explained by the newly revealed pressure dependence of V_{Φ, CO_2} by this study compared to that predicted by the model of Duan et al. (2008) as shown in Figure 6b.

4.2 Role of CO₂ in hydrothermal deposits

CO₂ is ubiquitous in various hydrothermal ore deposits (Belousov et al., 2012; Heinrich, 2007; Yardley and Cleverley, 2013). Generally, CO₂ plays roles in buffering pH ranges of the fluids (Phillips and Evans, 2004) and causing fluid immiscibility below 673 K (Liebscher, 2007; Takenouchi and Kennedy, 1964). Fluid density is an important factor affecting ore formation processes (Landtwing et al., 2010; Williams-Jones and Heinrich, 2005). As demonstrated by this study, CO₂ reduces densities of H₂O-bearing fluids beyond 489 K over 30 MPa, and the rate of density reduction is increased at elevated CO₂ concentrations ($x_{\text{CO}_2} > 0.05$) (Blencoe et al., 2001a; Seitz and Blencoe, 1999). This indicates that injection of CO₂ can make the aqueous fluids lighter and enhance their upward movements. Especially, adding CO₂ into the H₂O-rich fluids would promote micro-fracturing and attendant fluid infiltration in some ore systems (Blencoe et al., 1999). So, it can be expected that CO₂ plays important roles in promoting hydrothermal deposits by affecting evolution of fluids.

5. Conclusions

A reliable technique was developed to determinate the P - V - T - x properties of the CO₂-H₂O system, and accurate density data for CO₂ aqueous solutions were obtained

at temperatures from 273.15 to 513.15 K and pressures from 30 to 120 MPa. Equations for the density of CO₂-H₂O solutions and for the apparent molar volume of CO₂ in H₂O were also provided. Densities of CO₂-H₂O solutions ($\rho_{\text{CO}_2\text{-H}_2\text{O}}$) was found to be higher than densities of pure water ($\rho_{\text{H}_2\text{O}}$) until the system reaching a specific pivoting temperature, for example, above 489 K at 30 MPa. This pivoting temperature was pressure-dependent and it was predicted to rise to 575 K at 120 MPa. Based on these density data, the apparent molar volumes (V_{Φ,CO_2}) of CO₂ in water were estimated. It was shown that V_{Φ,CO_2} remained almost constant with changing pressure when temperature was below 298.15 K but it drastically decreased with increasing pressure when temperature was beyond 298.15 K. As a result, a V_{Φ,CO_2} model was revised and it reproduced density and molar volume data within a reasonable range of experimental errors. This model is valid for dilute CO₂ aqueous solutions up to 573.15 K and 120 MPa.

For sequestration of CO₂ into geological formations, accurate models are needed to calculate the essential parameters governing the volume changes due to dissolution of CO₂ in water aquifers. The revised model proposed in this study is proved to be more reliable than the model of Duan et al. (2008). The mechanism that CO₂ reduces the densities of the ore forming fluids is emphasized and it is noted that CO₂ may kinetically promote formation of hydrothermal deposits.

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FIGURE CAPTIONS

Figure 1. A schematic diagram showing the experiment system and method for P - V - T - x measurement of the CO_2 - H_2O system.

Figure 2. Deviations of water apparent densities measured by this study from those calculated by IAPWS-97 and WM-Hu represented by R_{TC} (Exp = experimental data points). Lines are R_{TC} as function of temperature and pressure (Eq. 2, i.e., Equation 2).

Figure 3. The effect of CO_2 on density of CO_2 -bearing aqueous solution with increasing temperature at pressures of: (a) 30 MPa; (b) 50 MPa; (c) 60 MPa; (d) 90 MPa; (e) and 120 MPa by this study; and (f) by previous reports below 35 MPa. The symbols represent various CO_2 - H_2O systems: $\blacklozenge$ ($w_{\text{CO}_2} = 0.0164$); $\blacksquare$ ($w_{\text{CO}_2} = 0.0332$); $\blacktriangle$ ($w_{\text{CO}_2} = 0.0368$); $\times$ ($w_{\text{CO}_2} = 0.0488$); $+$ ($w_{\text{CO}_2} = 0.0519$); and $\bullet$ ($w_{\text{CO}_2} = 0.0827$). The curves in (a)-(e) are from quadratic fitting between the average β [$= (\rho_{\text{CO}_2\text{-H}_2\text{O}} - \rho_{\text{H}_2\text{O}})/\rho_{\text{H}_2\text{O}}/w_{\text{CO}_2}$] of all the measured samples and temperature. The previous β values in (f) were calculated according to the volume/density data in the literatures.

Figure 4. The dependence of the pivoting temperature (denoted as T_p) on pressure. Note that the straight line just illustrate a trend.

Figure 5. The calculated apparent molar volume (V_{Φ, CO_2}) for CO_2 - H_2O system by this study at various pressures.

Figure 6. Comparison of the apparent molar volume (V_{Φ, CO_2}) data by this study with data by previous (a) experiments and (b) models. The V_{Φ, CO_2} data by King et al. (1992),

Teng et al. (1997), Yaginuma et al. (2000), Song et al. (2003), Li et al. (2004), Hebach et al. (2004), Yan et al (2011), Song et al. (2013) were calculated based on β shown in Figure 4f according to Equation (7). The model of Ennis-King can be found in Garcia (2001).

Figure 7. Deviations ($D_\Phi = (V_{\Phi,\text{cal}} - V_{\Phi,\text{exp}})/V_{\Phi,\text{exp}}$) between the predicted ($V_{\Phi,\text{cal}}$) and experimental ($V_{\Phi,\text{exp}}$) apparent molar volumes of CO₂ by Equation (11) and previous reports, respectively.

Figure 8. Deviations ($D_\rho = (\rho_{\text{cal}} - \rho_{\text{exp}})/\rho_{\text{exp}}$) between the calculated densities by this model and (a) densities by previous measurements, and (b) densities measured in this work.

Figure 9. Comparison between the molar volumes of CO₂-H₂O solutions ($V_{\text{m},\text{CO}_2\text{-H}_2\text{O}}$) calculated by Equation (11) and those (a) reported by Hnědkovský et al. (1996); and (b) graphically reported by Blencoe (2001) at 573.15 K.

Figure 10. The correlation coefficient (A) between apparent molar volume of CO₂ (V_{Φ,CO_2}) and molar volume of H₂O ($V_{\text{m},\text{H}_2\text{O}}$) determined by this study and those calculated with previous volume-related data beyond 573.15 K. The data of Crovetto and Wood (1992) and data of Sterner and Bodnar (1991) are mean values of A at the same P, T conditions.

Figure 11. Comparison between the molar volumes of CO₂-H₂O solutions ($V_{\text{m},\text{CO}_2\text{-H}_2\text{O}}$) calculated by this study and graphically reported by Capobianco et al., 2013.

Figure 12. Conceptual diagram for the solubility mechanism with respect to CO₂ sequestration into geological water aquifers. The left represents the case that supercritical CO₂ (scCO₂) is injected to the structural/stratigraphic space adjacent to the water whose volume proportion is R and dissolution of CO₂ has not begun. The right illustrates that scCO₂ reaches equilibrium with water. The “scCO₂” shown in both sub-graphs has a same density and no scCO₂ is supplemented to the system after the water is saturated with CO₂, so ΔV refers to the volume change of scCO₂ + water.

Figure 13. The volume change ratios of scCO₂ + water ($\Delta V/V_0$; V_0 is the total volume of the system) calculated by Equation (11) and by model of Duan et al. (2008). The $\Delta V/V_0$ are shown as isopleths. R is the volume proportion of water relative to V_0

Table 1. The corrected length change ratio (*LCR*) data measured for H₂O and CO₂-H₂O solutions.

w_{CO_2} (mass fraction)	0 (Pure water)	0.0164	0.0322	0.0368	0.0488	0.0519	0.0827
LCR	$LCR_{\text{H}_2\text{O,cor}}$	$LCR_{\text{CO}_2\text{-H}_2\text{O,cor}}$					
T (K)	30 MPa						
273.15	0.9957	0.9954	0.9955	0.9956	0.9954	0.9955	
278.15	0.9961	0.9958	0.9960	0.9958	0.9957	0.9959	
283.15	0.9966	0.9964	0.9964	0.9964	0.9963	0.9964	
288.15	0.9975	0.9972	0.9973	0.9972	0.9971	0.9974	
293.15	0.9983	0.9983	0.9985	0.9983	0.9983	0.9985	
298.15	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	
313.15	1.0052	1.0051	1.0053	1.0055	1.0055	1.0059	
333.15	1.0145	1.0148	1.0149	1.0150	1.0155	1.0160	
353.15	1.0259	1.0263	1.0271	1.0273	1.0289	1.0291	
373.15	1.0394	1.0404	1.0418	1.0424	1.0440	1.0440	
393.15	1.0551	1.0565	1.0586	1.0597	1.0614	1.0622	
413.15	1.0730	1.0751	1.0773	1.0791	1.0812	1.0815	
433.15	1.0933	1.0959	1.0990	1.1011	1.1035	1.1039	
453.15	1.1160	1.1199	1.1235	1.1250	1.1285	1.1287	
473.15	1.1419	1.1460	1.1510	1.1522	1.1567	1.1576	
493.15	1.1708	1.1757	1.1819	1.1827	1.1889	1.1896	
513.15	1.2036	1.2098	1.2175	1.2189	1.2260	1.2267	
T (K)	50 MPa						
273.15	0.9947	0.9946	0.9950	0.9953			
278.15	0.9953	0.9953	0.9953	0.9957			
283.15	0.9962	0.9960	0.9962	0.9962			
288.15	0.9972	0.9970	0.9973	0.9975			
293.15	0.9985	0.9985	0.9985	0.9988			
298.15	0.9999	0.9999	0.9999	0.9999			
313.15	1.0053	1.0053	1.0055	1.0054			
333.15	1.0144	1.0148	1.0150	1.0154			
353.15	1.0256	1.0266	1.0269	1.0279			
373.15	1.0388	1.0403	1.0411	1.0420			
393.15	1.0540	1.0562	1.0569	1.0584			
413.15	1.0710	1.0741	1.0749	1.0770			
433.15	1.0902	1.0942	1.0952	1.0978			
453.15	1.1116	1.1168	1.1178	1.1212			
473.15	1.1356	1.1418	1.1430	1.1472			

493.15	1.1625	1.1700	1.1714	1.1762			
513.15	1.1925	1.2015	1.2033	1.2088			
T (K)	60 MPa						
273.15	0.9945	0.9946	0.9946	0.9947	0.9942	0.9944	
278.15	0.9952	0.9953	0.9953	0.9954	0.9948	0.9950	
283.15	0.9961	0.9961	0.9962	0.9960	0.9956	0.9958	
288.15	0.9971	0.9971	0.9972	0.9972	0.9968	0.9973	
293.15	0.9984	0.9985	0.9985	0.9985	0.9982	0.9986	
298.15	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	
313.15	1.0056	1.0056	1.0055	1.0057	1.0053	1.0055	
333.15	1.0147	1.0153	1.0150	1.0152	1.0154	1.0157	
353.15	1.0258	1.0266	1.0273	1.0274	1.0276	1.0271	
373.15	1.0387	1.0397	1.0411	1.0415	1.0418	1.0412	
393.15	1.0537	1.0551	1.0567	1.0573	1.0578	1.0572	
413.15	1.0706	1.0724	1.0741	1.0747	1.0760	1.0767	
433.15	1.0893	1.0915	1.0939	1.0945	1.0963	1.0960	
453.15	1.1102	1.1129	1.1157	1.1163	1.1187	1.1186	
473.15	1.1333	1.1365	1.1401	1.1407	1.1437	1.1437	
493.15	1.1591	1.1629	1.1671	1.1677	1.1713	1.1718	
513.15	1.1876	1.1922	1.1972	1.1976	1.2024	1.2026	
T (K)	90 MPa						
273.15	0.9935	0.9937	0.9938	0.9939	0.9940	0.9937	0.9933
278.15	0.9945	0.9947	0.9947	0.9947	0.9948	0.9946	0.9939
283.15	0.9957	0.9959	0.9958	0.9958	0.9958	0.9956	0.9952
288.15	0.9970	0.9971	0.9971	0.9970	0.9970	0.9969	0.9965
293.15	0.9983	0.9984	0.9984	0.9984	0.9984	0.9983	0.9982
298.15	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
313.15	1.0056	1.0060	1.0059	1.0059	1.0060	1.0062	-
333.15	1.0150	1.0157	1.0160	1.0161	1.0163	1.0163	-
353.15	1.0258	1.0265	1.0271	1.0278	1.0281	1.0282	-
373.15	1.0383	1.0394	1.0401	1.0408	1.0408	1.0415	-
393.15	1.0522	1.0536	1.0548	1.0555	1.0556	1.0562	-
413.15	1.0679	1.0696	1.0712	1.0718	1.0725	1.0728	1.0774
433.15	1.0854	1.0876	1.0894	1.0902	1.0913	1.0914	1.0962
453.15	1.1045	1.1071	1.1093	1.1103	1.1118	1.1121	1.1181
473.15	1.1258	1.1288	1.1315	1.1323	1.1343	1.1347	1.1412
493.15	1.1491	1.1526	1.1556	1.1567	1.1587	1.1592	1.1672
513.15	1.1746	1.1786	1.1822	1.1830	1.1861	1.1864	1.1960
T (K)	120 MPa						
273.15	0.9925	0.9929	0.9934	0.9934	0.9930	0.9934	0.9931
278.15	0.9938	0.9941	0.9945	0.9945	0.9942	0.9943	0.9939

283.15	0.9951	0.9953	0.9958	0.9958	0.9956	0.9956	0.9952
288.15	0.9967	0.9969	0.9971	0.9969	0.9967	0.9968	0.9965
293.15	0.9983	0.9983	0.9987	0.9985	0.9983	0.9982	0.9983
298.15	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
313.15	1.0060	1.0059	1.0061	1.0064	1.0064	1.0064	1.0064
333.15	1.0151	1.0152	1.0152	1.0155	1.0156	1.0156	-
353.15	1.0258	1.0261	1.0261	1.0264	1.0266	1.0266	-
373.15	1.0379	1.0384	1.0385	1.0391	1.0393	1.0394	-
393.15	1.0512	1.0519	1.0524	1.0532	1.0538	1.0540	1.0572
413.15	1.0662	1.0671	1.0679	1.0684	1.0698	1.0699	1.0735
433.15	1.0825	1.0837	1.0849	1.0855	1.0872	1.0872	1.0926
453.15	1.1003	1.1019	1.1033	1.1036	1.1064	1.1066	1.1129
473.15	1.1198	1.1217	1.1237	1.1243	1.1263	1.1269	1.1345
493.15	1.1410	1.1433	1.1458	1.1464	1.1498	1.1499	1.1583
513.15	1.1641	1.1667	1.1697	1.1703	1.1743	1.1744	1.1847

“-” denotes that the data there could not be measured due to the saturation of CO₂ in solutions

Table 2. The parameters of the function ($\beta = a_1T^2 + a_2T + a_3 + (a_4T + a_5)P$; $R^2 =$ squared correlation coefficient) for the fitted lines in Figures 3a-e.

a_1	a_2	a_3	a_4	a_5	R^2
-2.74915E-06	5.64547E-04	3.41844E-01	8.22562E-06	-2.70591E-03	0.981

Table 3. The determined apparent molar volume of CO₂ (V_{Φ, CO_2}) data by this study.

T (K)	V_{Φ, CO_2} (cm ³ /mol)				
	30 MPa	50 MPa	60 MPa	90 MPa	120 MPa
273.15	31.8±0.3	32.3±0.3	32.1±0.2	32.1±0.2	32.4±0.3
278.15	31.8±0.3	32.2±0.2	32.1±0.2	32.1±0.2	32.2±0.3
283.15	31.9±0.2	32.1±0.1	32.0±0.2	32.0±0.2	32.2±0.3
288.15	31.9±0.2	32.2±0.2	32.1±0.2	31.9±0.1	32.0±0.3
293.15	32.4±0.1	32.2±0.1	32.2±0.1	32.1±0.1	31.9±0.2
298.15	32.4±0.0	32.3±0.0	32.2±0.0	32.0±0.0	31.9±0.0
313.15	32.7±0.3	32.5±0.1	32.3±0.1	32.7±0.2	32.2±0.2
333.15	33.6±0.2	33.4±0.1	33.4±0.4	33.8±0.2	32.6±0.2
353.15	35.1±0.6	34.6±0.3	34.7±0.4	34.8±0.2	33.4±0.1
373.15	37.2±0.5	36.0±0.3	36.2±0.4	35.8±0.2	34.2±0.2
393.15	39.1±0.8	37.3±0.3	37.6±0.5	37.1±0.3	35.7±0.4
413.15	41.3±0.7	39.0±0.3	39.2±0.1	38.6±0.3	36.8±0.5
433.15	43.7±0.8	40.9±0.4	40.9±0.3	40.1±0.3	38.3±0.7
453.15	46.6±0.3	43.1±0.4	42.8±0.2	41.9±0.3	39.7±0.9
473.15	49.2±0.8	45.4±0.5	45.3±0.3	43.5±0.2	41.4±0.8
493.15	52.6±1.1	48.0±0.5	47.7±0.3	45.4±0.3	43.3±1.0
513.15	57.3±1.2	51.1±0.6	50.6±0.5	46.7±0.4	45.1±1.2

Table 4. The previously reported models for predicting V_{Φ, CO_2} .

Authors	Models
Ennis-King ^{&}	$V_{\Phi, \text{CO}_2} = 35.663 - 9.960 \times 10^{-2}(T - 273.15) + 6.308 \times 10^{-4} \times (T - 273.15)^2$
Enick and Klara (1990)	$V_{\Phi, \text{CO}_2} = 1799.36 - 17.8218T + 6.59297 \times 10^{-2}T^2 - 1.0579 \times 10^{-4}T^3 + 6.200275 \times 10^{-8} \times T^4$
Andersen et al. (1992)	$V_{\Phi, \text{CO}_2} = 37.36 - 7.109 \times 10^{-2}(T - 273.15) - 3.812 \times 10^{-5}(T - 273.15)^2 + 3.296 \times 10^{-6}(T - 273.15)^3 - 3.702 \times 10^{-9}(T - 273.15)^4$
Iglesias and Moya (1992)	$V_{\Phi, \text{CO}_2} = \exp[154.7881 - 3582.452/T - 26.7757773 \ln(T) + 0.045234908T]$
Garcia (2001)	$V_{\Phi, \text{CO}_2} = 37.51 - 9.585 \times 10^{-2}(T - 273.15) + 8.740 \times 10^{-4}(T - 273.15)^2 - 5.044 \times 10^{-7}(T - 273.15)^3$
Sedlbauer et al. (2000)	$V_{\Phi, \text{CO}_2} = \kappa_0 RT - d(V_0 - \kappa_0 RT) + \kappa_0 RT \rho_0 (a + c \exp(\theta/T) + b(\exp(\theta \rho_0) - 1) + \delta(\exp(\lambda \rho_0) - 1))$
Plyasunov et al. (2000)	$V_{\Phi, \text{CO}_2} = NV_0 + \kappa_0 RT(1 - N) + \kappa_0 RT \rho_0 \{2\Omega[B_{12}(T) - NB_{11}(T)]\exp(-c_1 \rho_0) + (a/T^5 + b)[\exp(c_2 \rho_0) - 1]\}$
Bachu and Adams (2003)	$V_{\Phi, \text{CO}_2} = [\rho_{\text{H}_2\text{O}} + (1 - w_{\text{CO}_2})\rho_{\text{CO}_2\text{-H}_2\text{O}}]/(\rho_{\text{H}_2\text{O}}w_{\text{CO}_2}\rho_{\text{CO}_2\text{-H}_2\text{O}}M_{\text{CO}_2})$
Li et al. (2011)*	$V_{\Phi, \text{CO}_2} = V_0 \times (1 + 0.38384020 \times 10^{-3}T^2 - 0.55953850T + 0.30429268 \times 10^3 - 0.72044305 \times 10^5 T^{-1} + 0.63003388 \times 10^7 T^{-2} + (-0.57709332 \times 10^{-6} T^2 + 0.82764653 \times 10^{-3} T - 0.43813556 + 0.10144907 \times 10^3 T^{-1} - 0.86777045 \times 10^4 T^{-2})P)$

κ_0 , ρ_0 , V_0 are isothermal compressibility, specific density, and molar volume of water, respectively. T is in K and P is in MPa.

* Whose model is the same as the model of Duan et al. (2008) that is not shown here.

& The model of Ennis-King is from Garcia (2001).

Table 5. The regressed coefficients for Equation (11).

A_{11}	1.05517E-05	A_{25}	9.63658E-03
A_{12}	-1.39639E-03	A_{31}	-9.77266E-09
A_{13}	2.71734E-01	A_{32}	1.11357E-05
A_{14}	3.68475E+00	A_{33}	-3.27286E-03
A_{15}	1.82538E-01	A_{34}	2.48680E-01
A_{21}	1.29713E-07	A_{41}	6.20440E-11
A_{22}	-2.52694E-04	A_{42}	-6.67817E-08
A_{23}	6.25072E-02	A_{43}	1.97577E-05
A_{24}	3.73262E-01	A_{44}	-1.61999E-03