**Carbon dioxide solubility in aqueous solutions of sodium chloride at geological conditions:
Experimental results at 323.15, 373.15, and 423.15 K and 150 bar and modeling up to
573.15 K and 2000 bar**

Haining Zhao^{a,b,c}, Mark V. Fedkin^b, Robert M. Dilmore^c, and Serguei N. Lvov^{a,b,d,#}

^aJohn and Willie Leone Family Department of Energy and Mineral Engineering

^bElectrochemical Technologies Program, EMS Energy Institute

^cPetroleum and Natural Gas Engineering Program, EMS Energy Institute

^dDepartment of Materials Sciences and Engineering

The Pennsylvania State University

University Park, PA 16802, USA

^eU.S. Department of Energy

National Energy Technology Laboratory

626 Cochrans Mill Road

Pittsburgh, PA 15236, USA

[#]Corresponding author: lvov@psu.edu

Abstract

A new experimental system was designed to measure the solubility of CO₂ at pressures and temperatures (150 bar, 323.15-423.15 K) relevant to geologic CO₂ sequestration. At 150 bar, new CO₂ solubility data in the aqueous phase were obtained at 323.15, 373.15, and 423.15 K from 0 to 6 mol kg⁻¹ NaCl(aq) for the CO₂-NaCl-H₂O system. A $\gamma - \varphi$ (activity coefficient - fugacity coefficient) type thermodynamic model is presented for the calculation of both the solubility of CO₂ in the aqueous phase and the solubility of H₂O in the CO₂-rich phase for the CO₂-NaCl-H₂O system. Validation of the model calculations against literature data and other models (MZLL2013, AD2010, SP2010, DS2006, and OLI) show that the proposed model is capable of predicting the solubility of CO₂ in the aqueous phase for the CO₂-H₂O and CO₂-NaCl-H₂O systems with a high degree of accuracy (AAD < 3.9%) at temperatures from 273.15 to 573.15 K and pressures up to 2000 bar. A comparison of modeling results with experimental values revealed a pressure-bounded "transition zone" in which the CO₂ solubility decreases to a minimum then increases as the temperature increases. CO₂ solubility is not a monotonic function of temperature in the transition zone but outside of that transition zone, the CO₂ solubility is decrease or increase monotonically in response to increased temperature. A link of web-based CO₂ solubility computational tool can be provided by sending a message to Haining Zhao at hzz5047@gmail.com.

Key words: CO₂ solubility measurement, CO₂ solubility model, CO₂-NaCl-H₂O system, CO₂ sequestration, Equation of state, CO₂ solubility transition zone.

1. Introduction

The CO₂-H₂O and the CO₂-NaCl-H₂O fluid systems play an important role in various earth system and engineered geologic processes (Schmidt and Bodnar, 2000; Dubacq *et al.*, 2013). They represent the most commonly encountered fluids in geological environments (Hu *et al.*, 2007). In many technical applications, such as CO₂ storage and sequestration, CO₂-enhanced oil recovery, and CO₂-enhanced geothermal systems (Spycher and Pruess, 2010), dissolution, precipitation, and ion-exchange processes associated with these fluid systems can potentially impact the behavior of geologic media. Therefore, our knowledge of the phase equilibria and properties of these two systems over a wide pressure-temperature-composition (P - T - x) range is essential in the development of models for various geochemical and industrial processes.

Numerous studies have contributed to phase equilibrium data for CO₂-bearing binary and ternary systems. The main goal of many of those works has been to measure the CO₂ solubility in the aqueous phase and the water solubility in the CO₂-rich phase (*e.g.* Tödheide and Franck, 1963). In this study, research was oriented to CO₂ solubility experiments in support of geological CO₂ storage applications. The solubility of CO₂ in formation brines is a critical parameter to estimate the CO₂ storage capacity, the mechanism of trapping over site life, and the potential reactivity of the fluid-rock interface, as well as to understand the fate of the dissolved CO₂ in subsurface formations. Previous data (reported in this work) from experimental CO₂ solubility measurements in aqueous electrolyte solutions, along with reliable phase equilibrium models can serve as the foundation for modeling a variety of CO₂ storage and utilization processes.

Hu *et al.* (2007) have pointed out that many cubic equations of state (EoS) and virial EoS truncated at the second or third virial coefficient are adequate to predict the phase equilibria properties for the CO₂-H₂O and CO₂-NaCl-H₂O systems at low to medium pressures (up to 500 bar), but the deviations of these models from experimental values at high pressures were found to be unacceptable (Hu *et al.*, 2007; Spycher and Pruess, 2003). Spycher and Pruess's (2010) model allows computation of both the CO₂ solubility in the aqueous phase and the H₂O solubility in the CO₂-rich phase with high accuracy, but their model is limited to pressures up to 600 bar. Akinfiev and Diamond (2010) developed a highly accurate CO₂ solubility model for the CO₂-H₂O and CO₂-NaCl-H₂O systems, but the applicable temperatures and pressures of their model are limited to 251.15-373.15 K and 1-1000 bar. In addition, Akinfiev and Diamond's (2010) model only provides a rough estimate of water solubility in the CO₂-rich phase. The model developed by Duan *et al.* (2006) allows the CO₂ solubility in NaCl(aq) to be calculated up to 533.15 K, 2000 bar, and 4.5 mol kg⁻¹ of NaCl(aq), but their model is generally less accurate than the Akinfiev and Diamond (2010) and Spycher and Pruess (2010) models (see section 4.4, Table 10). Moreover, Duan *et al.*'s (2006) model does not allow calculation of the H₂O solubility in the CO₂-rich phase. The commercial software OLI studio 9.0 (Springer *et al.*, 2012) performs well at predicting the H₂O solubility in the CO₂-rich phase at low to moderate pressures, but its estimates of the CO₂ solubility in the aqueous phase are less accurate than those of other models mentioned above - Akinfiev and Diamond (2010), Spycher and Pruess (2010) and Duan *et al.* (2006) (see section 4.4, Tables 10 and 11). Additionally, Mao *et al.* (2013) developed a CO₂ solubility model for the CO₂-NaCl-H₂O system in the temperature range of 273.15-723.15 K, pressures from 1-1500 bar and NaCl molality from 0-4.5 mol kg⁻¹. Mao *et al.*'s (2013) model is in excellent agreement with experimental CO₂ solubility in the aqueous phase (see section 4.4,

Tables 10, 12, and 13), but this model does not allow calculation of H₂O solubility in the CO₂-rich phase. Note also that these models cannot be used for reliable phase equilibrium calculations in systems containing K⁺, SO₄²⁻ (e.g. CO₂-KCl-H₂O and CO₂-Na₂SO₄-H₂O) at elevated temperatures and pressures. Detailed comparisons between the model developed in this study and previously published models are provided in section 4.4.

In this paper, an improved $\gamma - \phi$ (activity coefficient - fugacity coefficient) type phase equilibrium model is presented for the CO₂-NaCl-H₂O system. There are three major improvements in the model relative to the previous models of Spycher *et al.* (2003) and Spycher and Pruess (2010). First, the binary interaction parameter ($k_{\text{CO}_2\text{-H}_2\text{O}}$) of the mixing rule was considered to be dependent on temperature and pressure. The parameter $k_{\text{CO}_2\text{-H}_2\text{O}}$ in the mixing rule was carefully tuned against the experimental H₂O solubility in the CO₂-rich phase (Tödheide and Franck, 1963) at temperatures of 273.15-573.15 K and pressures up to 2000 bar. This adjustment significantly improved the calculated water solubility in the CO₂-rich phase, as well as estimates of the CO₂ solubility in the aqueous phase at high temperatures and pressures. Second, in Eq. (1), the partial molar volume of CO₂ at infinite dilution in water ($\bar{v}_{\text{CO}_2}$) was treated as an adjustable parameter to fit the experimental CO₂ solubility in the aqueous phase by Tödheide and Franck (1963). Third, the Pitzer activity model was used to calculate the activity coefficient of the dissolved CO₂ and osmotic coefficient of water. The triple-ion interaction parameter (ξ_{nca} , see section 4.2 Eq.(10)) in the Pitzer model was considered to be dependent on temperature and NaCl concentration. ξ_{nca} values were determined using new experimental CO₂ solubility data presented herein, assuming that the pressure effect on this parameter can be neglected. These improvements allow the model to return more accurate estimates of the activity

of dissolved CO₂ and the water osmotic coefficients for concentrated NaCl(aq) as compared to the previous models of Spycher and Pruess (2010) and Duan *et al.* (2006).

The improved CO₂ solubility model can reproduce literature data for the CO₂-NaCl-H₂O and CO₂-H₂O systems with an overall average absolute deviation (AAD) of less than 3.9% over temperatures from 273.15 to 573.15 K and pressures up to 2000 bar. In Section 4.4, we compare our model with the models of Mao *et al.* (2013), Akinfiyev and Diamond (2010), Spycher and Pruess (2010), Duan *et al.* (2006) and OLI Studio 9.0. This comparison shows that the model developed here provides reliable estimates of both the solubility of CO₂ in the aqueous phase and the solubility of H₂O in the CO₂-rich phase.

2. Review of experimental approaches

In this and many previous studies, a high pressure/temperature-controlled stainless steel autoclave with agitation was used to investigate the gas-liquid phase equilibria. The typical apparatus for such measurements is described in Prutton and Savage (1945), Takenouchi and Kennedy (1964), Malinin and Savelyeva (1972). The experimental systems used by Wiebe and Gaddy (1939), Nighswander *et al.* (1989), and Stewart and Munjal (1970) are more complicated, but, in general, operate in a similar manner. For a phase equilibrium experimental study, the autoclave is loaded with a CO₂-brine mixture and the solution is stirred for 6 to 24 hours until equilibrium is reached. The autoclave temperature is measured by a thermocouple, while the pressure is measured using a pressure gauge or transducer. Generally, the aqueous phase sample is taken from the autoclave to perform the CO₂ solubility measurement. During the sampling

process, the pressure in the system should remain constant. Alternatively, static view-cell 'synthetic' methods without sampling are employed to determine the CO₂ solubility (Rumpf and Maurer, 1993; Pérez-Salado Kamps *et al.*, 2007) and the dew-point of H₂O in the CO₂-rich phase (Mather and Franck, 1992).

There are two common methods to measure the CO₂ solubility in a liquid sample. In the first method, dissolved CO₂ in a sample cell is expanded into a temperature-controlled pressure vessel, and the mass of CO₂ is determined volumetrically (Wiebe and Gaddy, 1939; Prutton and Savage, 1945; Nighswander *et al.*, 1989, Liu *et al.*, 2011). In the second method, dissolved CO₂ in a sample cell is released from the aqueous phase and absorbed in a trap with NaOH(aq) or Ba(OH)₂(aq) (Takenouchi and Kennedy, 1964, 1965; Stewart and Munjal, 1970; Malinin and Savelyeva, 1972, Rochelle and Moore, 2002). In Method (1), the amount of CO₂ is determined from the *PVT* changes in the pressure vessel before and after the gas expansion. This method was used by Kim *et al.* (2008) to measure the mass of the injected CO₂ into the autoclave. Liu *et al.* (2010) also demonstrated the effectiveness of this method. The method can precisely sense the mass change within a pressure cell through the variation in pressure and temperature. Therefore, this method was selected for sample analysis in this study. In Method (2), the dissolved CO₂ is converted to CO₃²⁻ in an alkaline absorbent. As long as the base is present in excess, the CO₃²⁻ is stable (Rochelle and Moore, 2002). The amount of trapped CO₂ can be determined by a standard HCl titration of the excess base absorbent.

The main approaches to sample and measure the CO₂ solubility in the aqueous phases are summarized in Figure 1. Other methods such as the solid absorbent system (Ellis and Golding,

1963) and heat flow calorimetry (Koschel *et al.*, 2006) are not widely used to measure the CO₂ solubility in the aqueous phase due to the complexity of the systems and insufficient accuracy of the measurements.

3. Experimentation

3.1 Experimental P - T - x conditions

In this work, data from all available literature for the CO₂-NaCl-H₂O system at temperatures from 273.15 to 573.15 K and pressures up to 1500 bar were reviewed in order to identify possible gaps in the experimental P - T - x matrix. A large amount of CO₂ solubility data compiled by Scharlin (1996) was also included in our data screening. New CO₂ solubility measurements were performed in P - T - x space where little or no data are available.

A simplified approach proposed by Bachu (2003) was employed in this study to estimate a range of temperatures and pressures of interest (Figure 2). With respect to the salt concentration range, the USGS-produced water database¹ served to select the concentration of NaCl solutions. In addition, we took into account the McIntosh *et al.* (2004) study where eighty five formation brine samples from the Michigan Basin were collected and analyzed. The total ionic strength (Eq. (A9)) of formation brines in the Michigan Basin was shown to range from zero to around 8 mol kg⁻¹, with chloride, sodium, and calcium accounting for more than 95 % of the ions in these brines (McIntosh, *et al.*, 2004); the composition of the reservoir brines is dominated by NaCl.

¹ <http://energy.cr.usgs.gov/prov/prodwat/>

Based on the above discussion, the ionic strength of the NaCl(aq) solutions for our CO₂ solubility experiments was set to range from 0 to 6 mol kg⁻¹.

3.2 Chemicals

The carbon dioxide used in all experiments was Coleman Instrument grade with a minimum purity of 99.99 %. The water was purified by a Milli-Q system and degassed by boiling before loading into the autoclave. The NaCl(aq) solutions were prepared using Milli-Q water (with conductivity below 6 10⁻⁶ S m⁻¹) and ACS reagent grade Sodium Chloride (J.T. Baker, 3624-01).

3.3 Apparatus

A schematic of the experimental apparatus is shown in Figure 3. The setup includes a high pressure liquid-CO₂ pump (SFT-10), a vacuum pump (LEYBOLD TRIVAC D2A), a 600-ml stainless steel Parr Instrument Co. autoclave with a Teflon liner, and a 40-ml stainless steel liquid sample cell attached to the autoclave. The autoclave was enclosed in a heating mantle, and the contained solution was stirred by a four-blade aluminum impeller with a Parr magnetic drive. Temperature and the impeller rotation speed were controlled by the Parr 4842 controller. The autoclave was equipped with ports for both supercritical CO₂ and aqueous phase sampling from the top of the vessel.

An Omega PX602 pressure transducer with an accuracy of 0.45 % ranging from 0 to 345 bar was used to monitor the system pressure. A J-type thermocouple was introduced from the top of the autoclave into the aqueous phase to measure the temperature of the solution. Calibration of the

thermocouple was performed in both boiling DI water and an ice-water mixture prior to use. The uncertainty of the temperature measurements was less than ± 1.0 K over the temperature range of interest (323.15 to 423.15 K).

3.4 Procedure

Degassed Milli-Q water was used in all experiments. Sodium chloride was placed into the autoclave before loading the water. The autoclave was thoroughly evacuated using a vacuum pump and water was loaded into the autoclave under vacuum. The autoclave was then heated to the desired temperature. Once the experimental temperature was achieved, the liquid CO₂ was pumped into the autoclave to the desired pressure. Subsequently, the contents of the autoclave were agitated by the impeller at a speed of about 60 RPM (revolutions per minute). Initial equilibrium was assumed to be reached when no cell pressure variation was observed over a 12-hour period. Before taking the first sample, a small amount of liquid sample was drawn and discarded to purge the sample line.

Whereas either a water-rich or a CO₂-rich sample can be taken using the developed system, this study focused on the aqueous phase. The sample cell was first evacuated to a vacuum pressure of about 0.02 bar. At high pressures, withdrawing fluid from the autoclave can result in a significant reduction of the total pressure of the system. Hence, the pressure drop during the sampling process was compensated for by pumping additional liquid CO₂ into the CO₂-rich phase at a flow rate of about 20 ml min⁻¹. Pressure fluctuations inside the autoclave were kept to within ± 2 bar of the set experimental pressure, and the pumped liquid CO₂ is assumed not to have disrupted the

aqueous phase equilibrium due to the following reasons. First, the liquid CO₂ was injected in the upper layer of the CO₂-rich phase, whereas the aqueous sample was taken from the bottom of the autoclave (Figure 3), so the pumped CO₂ does not directly contact the aqueous sample in the bottom of the autoclave. Second, the sampling time was very short (less than 60 seconds) so there was no, or negligible, disturbance on the aqueous phase equilibrium.

After sample withdrawal was complete, the sample cell was disconnected and weighed on an electronic balance (Veritas L403i) with an accuracy of $\pm 0.001\text{g}$. The mass of the sample was defined by weighing the sample cell before and after sampling. The sample cell was then connected to a 300-ml pressure cell, which was used to determine the amount of dissolved CO₂. The pressure cell volume was calibrated by filling the cell with distilled water and measuring the mass when it was full and empty at a well-defined temperature. The water density was calculated using IAPWS-95 EoS (Wagner and Pr, 2002).

The pressure cell was first evacuated by a vacuum pump and the dissolved CO₂ was slowly released into the pressure cell from the sample cell. The mass of the dissolved CO₂ was determined by the pressure and temperature change before and after CO₂ expansion. Three consecutive expansions were sufficient to determine the total amount of CO₂ dissolved in the sample cell. The remaining CO₂ in the sample cell after three expansions was estimated by Henry's law (see section 4.1, Eq. (3)) and was less than $0.0007\text{ mol kg}^{-1}$, which is negligible compared to the experimental error. The EoS for pure CO₂ developed by Span and Wagner (1996) was used to calculate the mass of CO₂ in the pressure cell after each expansion. Finally, the CO₂ solubility in the aqueous phase was obtained by relating the mass of the total released CO₂ to the total mass of the aqueous sample.

A small amount of water vapor might be transferred to the pressure cell during the CO₂ expansion, which could introduce a small error (approximately 0.0009 mol kg⁻¹ CO₂) in the CO₂ solubility measurement. To eliminate the error caused by water vapor during the sample analysis, the partial pressure of water vapor in the CO₂-H₂O gas mixture was estimated by the model of Spycher and Pruess (2003) and subtracted from the total pressure of the pressure cell. The error analysis based on the error propagation theory showed that the instrumental error of the measurement of CO₂ solubility was around 0.7 % and the random error was from 0.5 to 4.5 %. The detailed error analysis procedure is described in the Supplemental Information.

3.5 Validation of the obtained data

A temperature and pressure of 323.15 K and 100 bar were selected for the CO₂-H₂O system, and several *P-T-x* conditions for the CO₂-NaCl-H₂O system, to validate the reliability of our apparatus and procedures. In Tables 1 and 2, the comparisons show that the experimental CO₂ solubility at these *P-T-x* conditions was in close agreement with the experimental solubility values found in the literature, and was also consistent with CO₂ solubility models (Mao *et al.*, 2013; Akinfiev and Diamond, 2010; Spycher and Pruess, 2010; Duan *et al.*, 2006; OLI Studio 9.0). Subsequently, the names of the models are abbreviated as MZLL2013 for Mao *et al.* (2013), AD2010 for Akinfiev and Diamond's (2010), SP2010 for Spycher and Pruess (2010), DS2006 for Duan *et al.* (2006) model, and OLI for the model adopted in OLI Studio 9.0 software.

From Tables 1 and 2, one can see that the measured CO₂ solubilities are in good agreement with both published experimental and model data. Thus, the reliability of the experimental technique was confirmed before further measurements were performed at the target P - T - x conditions in the CO₂-NaCl-H₂O system.

3.6 Measured CO₂ solubilities

The measured CO₂ solubilities (m_{CO_2}) at 150 bar and 323.15-423.15 K for the CO₂-NaCl-H₂O system at NaCl(aq) concentrations between 0 and 6 mol kg⁻¹ are listed in Table 3. Figure 4 shows that the measured CO₂ solubility data fall closely in line with the data from Koschel *et al.* (2006), with the model calculations of SP2010, and the model developed herein. In Figure 5, the models AD2010, SP2010, DS2006 and OLI were verified against new experimental data reported herein. The experimental CO₂ solubility data obtained in this study are in excellent agreement with both the MZLL2013 and AD2010 models at 150 bar and temperatures from 323.15 to 423.15 K. Given that the accuracy of the AD2010 model is claimed to be 1.6 % at temperatures from 251.15 to 373.15 K and pressures up to 1000 bar, it is striking that deviations of the AD2010 model from experimental data at 423.15 K are still within its computation error. The SP2010 model results also agree well with the measured CO₂ solubility data obtained in this study. The deviation of the DS2006 model results from our experimental data increases with increasing NaCl molality because the model is limited to a NaCl concentration of 4.5 mol kg⁻¹. The OLI studio 9.0 model also performs well in predicting CO₂ solubility in aqueous NaCl solutions. In general, the models developed thus far agree well with the experimental CO₂ solubility obtained

in this work. The average absolute deviations of the calculated values from our CO₂ solubility data (given in Table 3) confirm this conclusion.

4. Thermodynamic model of the CO₂-NaCl-H₂O system

4.1 Thermodynamic framework for vapor-liquid phase equilibrium

The thermodynamic equilibrium for the CO₂-NaCl-H₂O system can be described in terms of the extended Henry's law for CO₂ dissolved in aqueous solutions with NaCl(aq) (Rumpf *et al.*, 1993) or KCl(aq) (Pérez-Salado Kamps *et al.*, 2007):

$$\varphi_{\text{CO}_2} y_{\text{CO}_2} P = k_{\text{H,CO}_2}^o \exp \left(\frac{\bar{v}_{\text{CO}_2} (P - P_{\text{w}}^s)}{RT} \right) a_{\text{CO}_2} \quad (1)$$

and by the extended Raoult's law for water:

$$\varphi_{\text{H}_2\text{O}} y_{\text{H}_2\text{O}} P = P_{\text{w}}^s \varphi_{\text{w}}^s \exp \left(\frac{\bar{v}_{\text{w}} (P - P_{\text{w}}^s)}{RT} \right) a_{\text{H}_2\text{O}} \quad (2)$$

where y_{CO_2} and $y_{\text{H}_2\text{O}}$ are, respectively, the mole fraction of CO₂ and H₂O in the CO₂-rich phase.

In Eqs. (1) and (2), the reference state for the chemical potential of water is chosen to be the pure liquid at the system temperature and pressure, whereas the chemical potential of dissolved CO₂ (or other ionic species) is a hypothetical, ideal Henryan (infinitely diluted) 1 mol kg⁻¹ solution of the solute in pure water at the temperature and pressure of the system (Pérez-Salado Kamps *et al.*, 2007). The pure water vapor pressure (P_{w}^s) and the fugacity coefficient of pure vapor water

(φ_w^s) were calculated using the IAPWS-95 equation of state (EoS) given by Wagner and Pruß (2002). The parameter $\bar{v}_{\text{CO}_2}$ in Eq. (1) was determined by fitting model calculated results to reliable experimental data. The values of $\bar{v}_{\text{CO}_2}$ are presented in Table 4. The partial molar volume of water $\bar{v}_w$, was approximated by the molar volume of saturated liquid water, v_w^s , which was also calculated using the IAPWS-95 EoS. In Eq. (1), $k_{\text{H},\text{CO}_2}^o$ is Henry's constant (molality scale) of carbon dioxide in pure water determined from the experimental CO_2 solubility data in pure water at temperatures up to 573.15 K. In order to achieve the best possible results over a wide range of pressures (from 1 to 2000 bar) and temperatures (from 273.15 to 573.15 K), Henry's constant was fitted separately for two distinct regions (Figures 6 and 8, and Table 5): (1) below 2 bar and temperatures between 273.16 and 363.15 K, and (2) the remaining region of temperatures up to 573.15 K and pressures up to 2000 bar. The expression for $k_{\text{H},\text{CO}_2}^o$ is as follows:

$$\ln(k_{\text{H},\text{CO}_2}^o) = a + b \left(\frac{T}{T_c} \right) + c \left(\frac{T_c}{T} \right) + d \ln(T/T_c) \quad (3)$$

where $T_c = 647.096$ K is the critical temperature of water; a , b , c , and d are empirical parameters given in Table 5.

The fugacity coefficients of CO_2 and H_2O in the gas mixture were computed by a modified Redlich-Kwong EoS given by Spycher *et al.* (2003). The activity coefficient of $\text{CO}_2(\text{aq})$ and ionic species on the molal concentration scale were calculated using Pitzer equations for aqueous electrolyte solutions (Pitzer, 1991). By rearranging Eqs. (1) and (2), the mole fractions of CO_2 and H_2O in the CO_2 -rich phase can be presented as:

$$y_{\text{CO}_2} = Aa_{\text{CO}_2(\text{aq})} \quad (4)$$

$$y_{\text{H}_2\text{O}} = Ba_{\text{H}_2\text{O}(\text{l})} \quad (5)$$

where $A = k_{\text{H},\text{CO}_2}^0 \exp\left(\frac{\bar{v}_{\text{CO}_2}(P - P_{\text{W}}^s)}{RT}\right) / (\varphi_{\text{CO}_2}P)$, $B = P_{\text{W}}^s \varphi_{\text{W}}^s \exp\left(\frac{\bar{v}_{\text{W}}(P - P_{\text{W}}^s)}{RT}\right) / (\varphi_{\text{H}_2\text{O}}P)$. A and B are constants at a specific system temperature and pressure. Since $y_{\text{H}_2\text{O}} + y_{\text{CO}_2} = 1$, Eqs. (4) and (5) can be combined as:

$$Aa_{\text{CO}_2(\text{aq})} + Ba_{\text{H}_2\text{O}(\text{l})} - 1 = 0 \quad (6)$$

At a given salt molality, the Newton-Raphson method was used to solve Eq. (6) with respect to m_{CO_2} .

4.2 Incorporating Pitzer's activity model

The activity of dissolved CO_2 and the activity of water in the aqueous phase can be calculated as follows:

$$a_{\text{CO}_2} = \gamma_{\text{CO}_2} m_{\text{CO}_2} \quad (7)$$

$$\ln a_{\text{H}_2\text{O}} = -\frac{\phi^{MW_{\text{H}_2\text{O}}}}{1000} (2m_{\text{NaCl}} + m_{\text{CO}_2}) \quad (8)$$

The derivatives of Eq. (7) and Eq. (8) with respect to m_{CO_2} are,

$$\frac{\partial a_{\text{CO}_2}}{\partial m_{\text{CO}_2}} = \gamma_{\text{CO}_2} + \gamma_{\text{CO}_2} m_{\text{CO}_2} (2\lambda_{nn} + 6m_{\text{CO}_2} \mu_{nnn} + 6m_{\text{NaCl}} C_{\text{CO}_2-\text{CO}_2-\text{NaCl}}) \quad (9)$$

$$\begin{aligned} \frac{\partial a_{\text{H}_2\text{O}}}{\partial m_{\text{CO}_2}} = & \\ & - \frac{a_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}}{1000} \left(1 + 2(m_{\text{CO}_2} \lambda_{nn} + 3m_{\text{CO}_2}^2 \mu_{nnn} + m_{\text{NaCl}} B_{\text{CO}_2-\text{NaCl}} + 6m_{\text{CO}_2} m_{\text{NaCl}} C_{\text{CO}_2-\text{CO}_2-\text{NaCl}} + \right. \\ & \left. m_{\text{NaCl}}^2 \xi_{nca}) \right) \end{aligned} \quad (10)$$

The Pitzer's expressions for the activity coefficient of CO_2 and the osmotic coefficient of H_2O are given in Appendix A by Eqs. (A6) and (A7), respectively. By substituting Eq. (A6) into Eq. (7), the partial derivative of a_{CO_2} with respect to m_{CO_2} can be obtained resulting in Eq. (9). The partial derivative of $a_{\text{H}_2\text{O}}$ with respect to m_{CO_2} resulting in Eq. (10) is obtained in the same manner by substituting Eq. (A7) into Eq. (8). Thus, the m_{CO_2} can be computed by substituting Eqs. (7)-(10) into Eq. (6). The overall flow chart for calculating CO_2 solubility, including the solution to Eq. (6), is shown in Figure 7. In this calculation, the initial guess of water content in the CO_2 -rich phase was made by using the ideal water content, *i.e.*, $y_{\text{H}_2\text{O}} = P_w^s/P$. One of the main differences between our model and the SP2010 model is the computation of the water activity. In this study, we used the Pitzer model with an iterative Newton-Raphson procedure, whereas Spycher and Pruess (2010) assumed that the water activity equals the mole fraction of water in the aqueous phase, which is a rough assumption for highly concentrated aqueous solutions but allowed a non-iterative solution for Eq. (6).

The Pitzer equations for the activity coefficient of CO₂ and the osmotic coefficient of water are listed in Appendix A (Pitzer, 1991). In order to simplify the notation of Eq. (A6) and Eq. (A7), we defined two parameters, $B_{\text{CO}_2-\text{NaCl}}$ and $C_{\text{CO}_2-\text{CO}_2-\text{NaCl}}$ according to Akinfiev and Diamond (2010) as follows:

$$B_{\text{CO}_2-\text{NaCl}} = \lambda_{nc} + \lambda_{na} \quad (11)$$

$$C_{\text{CO}_2-\text{CO}_2-\text{NaCl}} = \mu_{nnc} + \mu_{nna} \quad (12)$$

These two parameters are taken from Akinfiev and Diamond (2010). The neutral component interaction parameters λ_{nn} and μ_{nnn} of the Pitzer's model in Eqs. (9) and (10) were determined using experimental CO₂ solubility data for the CO₂-H₂O system (data sources are listed in Table 13). The quadratic form of parameters λ_{nn} and μ_{nnn} suggested by Akinfiev and Diamond (2010) was used during the data fitting process, and the results were expressed using Eq. (13). The detailed data fitting procedure used to obtain λ_{nn} and μ_{nnn} are illustrated in Figure 8.

$$\lambda_{nn} \text{ (or } \mu_{nnn}) = a_1 + a_2 T + a_3 T^2 \quad (13)$$

The parameters in Eq. (13) are given in Table 6. The Pitzer binary ion–ion interaction parameters $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and C_{ca} for the CO₂-NaCl system were taken from Pitzer *et al.* (1984).

The Pitzer triple-ion interaction parameter ξ_{nca} in Eqs. (10), (A6) and (A7) was determined by using the bisection search algorithm to find the exact values of ξ_{nca} against the experimental CO₂ solubility data collected in this study over a concentration range of 0-6 mol kg⁻¹ NaCl and temperatures of 323.15-423.15 K. In this study, the parameter ξ_{nca} was found to be insensitive to the pressure, but it is a function of temperature and NaCl molal concentration. Using ξ_{nca} given in Table 7, the cubic spline interpolation was used to characterize the relationship between ξ_{nca} and NaCl molal concentration, the linear interpolation for the temperature was used to determine values of ξ_{nca} at any temperatures between 273.15 and 573.15 K.

4.3. Improved mixing rule parameter ($k_{\text{CO}_2-\text{H}_2\text{O}}$) for the CO₂-rich phase

The Spycher and Pruess (2010) modified Redlich-Kwong equation of state (RK EoS) (see Appendix A) was used in this study to calculate the fugacities of H₂O and CO₂ for the CO₂-rich phase. A combined rule for polar systems (*e.g.* CO₂-H₂O) proposed by Panagiotopoulos and Reid (1986) has been proven successful when describing the gas mixture in the CO₂-H₂O system (Panagiotopoulos and Reid, 1986; Spycher and Pruess, 2010). In this approach, the binary interaction parameter, a_{ij} , takes the following form:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij} + (k_{ij} - k_{ji}) y_i) \quad (14)$$

where y_i is the mole fraction of component i in the gas mixture, and k_{ij} and k_{ji} are the binary interaction parameters (in this study, i and j denote CO₂ and H₂O, respectively). The binary interaction parameters play a critical role in describing the CO₂-rich phase diagram. The

parameters $k_{\text{H}_2\text{O}-\text{CO}_2}$ and $k_{\text{CO}_2-\text{H}_2\text{O}}$ evaluated by Spycher and Pruess (2010) were found to work fine at low to moderate pressures, but with these parameters unchanged, the model cannot accurately predict the mutual solubilities of CO_2 and H_2O at pressures above 800 bar. Therefore, a modification of the parameters should be made to allow the model to apply over a wider pressure range. It was decided to modify one of the parameters, and $k_{\text{CO}_2-\text{H}_2\text{O}}$ was chosen because this parameter has the most pronounced influence on calculating the H_2O solubility in the CO_2 -rich phase. In such an approach, $k_{\text{H}_2\text{O}-\text{CO}_2}$ was treated in the same manner as Spycher and Pruess (2010) did. The fitting results of the parameter $k_{\text{CO}_2-\text{H}_2\text{O}}$ are shown in Table 8.

Determination of the binary interaction parameter $k_{\text{CO}_2-\text{H}_2\text{O}}$ was made using the experimental H_2O solubility data collected in the CO_2 -rich phases. The approach selected to obtain the $k_{\text{CO}_2-\text{H}_2\text{O}}$ was purely empirical. At a given temperature and pressure, the experimental H_2O solubility data in the CO_2 -rich phase was entered into the model, and the parameter $k_{\text{CO}_2-\text{H}_2\text{O}}$ was then manually adjusted until consistency was reached between calculated and experimental values. At temperatures below 473.15 K, the experimental data used to determine the $k_{\text{CO}_2-\text{H}_2\text{O}}$ parameter were taken from Wiebe and Gaddy (1941), Tödheide and Franck (1963), Müller *et al.* (1988), and King *et al.* (1992). By fitting the experimental H_2O solubility data in the CO_2 -rich phase, we found that assuming a temperature dependence and pressure independence of $k_{\text{CO}_2-\text{H}_2\text{O}}$ is suitable when the temperature is below 473.15 K.

The pressure influence on $k_{\text{CO}_2-\text{H}_2\text{O}}$, however, becomes more important as the temperature increases, especially above 473.15 K. Reliable experimental data are desirable to evaluate the parameter $k_{\text{CO}_2-\text{H}_2\text{O}}$ at high P - T conditions. Both Takenouchi and Kennedy (1964) and Tödheide

and Franck (1963) reported experimental data for the CO₂-H₂O system at high temperatures and pressures using the sampling method for both the CO₂-rich and the aqueous phases (Mather and Franck, 1992). Whereas the aqueous phase compositions obtained by Takenouchi and Kennedy (1964) and Tödheide and Franck (1963) are in fairly good agreement, the compositions of the CO₂-rich phase are significantly different. In order to resolve this discrepancy, Mather and Franck (1992) used the so-called 'synthetic' experimental method to study the phase equilibria of the CO₂-H₂O system. Initially, known amounts of CO₂ and H₂O are loaded into an autoclave (with a sapphire window). By heating the components in the autoclave at constant volume, homogeneous single-phase conditions can be observed through the window. By this means, Mather and Franck (1992) measured the dew points (at 498.15-546.15 K and 1100-2640 bar) of H₂O in the CO₂-rich phase to support the experimental data reported by Tödheide and Franck (1963). The experimental data of Tödheide and Franck (1963) are also validated by the theoretical calculations of Gallagher *et al.* (1993) and Shyu *et al.* (1997). Based on the above reasons, the data from Tödheide and Franck (1963) were selected for the determination of the binary interaction parameter $k_{\text{CO}_2\text{-H}_2\text{O}}$ at temperatures above 473.15 K.

In order to correlate Tödheide and Franck's (1963) data, $k_{\text{CO}_2\text{-H}_2\text{O}}$ were considered as a function of both temperature and pressure. However, introducing a pressure-dependent binary interaction parameter in the mixing rule will disrupt the cubic form of the original RK EoS, thus the expressions for the fugacity coefficients of CO₂ and H₂O in Eq. (A5) may not hold true at temperatures higher than 473.15 K. In addition, although $k_{\text{CO}_2\text{-H}_2\text{O}}$ was considered a function of pressure and temperature, the analytical relationships between $k_{\text{CO}_2\text{-H}_2\text{O}}$ and (P , T) are still unknown; thus, it is impossible to derive a new fugacity coefficient expression. By using the

original fugacity coefficient expressions (Eq. (A5)), we compared our calculated $\varphi_{\text{H}_2\text{O}}$ and φ_{CO_2} for the CO_2 -rich phase with the SP2010 model at elevated temperatures; the AAD(%) of calculated φ_{CO_2} and $\varphi_{\text{H}_2\text{O}}$ from 473.15 to 573.15 K and up to 600 bar between the two models are approximately 4.8% and 6.0%, respectively. Thus, the tuning of the parameter $k_{\text{CO}_2-\text{H}_2\text{O}}$ caused a small change in the fugacity coefficient calculations, but these changes were shown to improve the overall performance of the model for the calculation of the mutual solubilities in the CO_2 - H_2O system at elevated temperatures and pressures (Figure 9). The detailed descriptions of this new CO_2 solubility model can be found in Table 9.

4.4 Results and discussion

The calculated phase diagrams of the CO_2 - H_2O and CO_2 - NaCl - H_2O systems for both the aqueous and CO_2 -rich phases are shown in Figures 9 and 10, respectively. In Figures 9 and 10, at temperatures higher than 538.15 K, the modeling results begin to deviate from the experimental values at pressures near the critical region, and finally the calculation does not converge when the pressure increases further. The model is incapable of predicting the CO_2 solubility around critical points, most likely because the $\gamma - \varphi$ approach uses different models for the CO_2 -rich and aqueous phases (*e.g.* RK EoS for the CO_2 -rich phase, Pitzer activity model for the aqueous phase).

As shown in Figures 9 and 10, convergence problems in the vicinity of critical region are also due to relatively high temperatures and pressures where the cubic EoS has a single root (Veeranna and Rihani, 1984), and the VLE calculation in the presence of H_2O could be more

complex around the critical point due to the strong non-ideality of the polar molecules. Gallagher *et al.* (1993) used a Helmholtz free energy model to calculate thermodynamic properties of the CO₂-H₂O binary system up to 623.15 K and observed a numerical instability near the critical region. Shyu *et al.* (1997) presented a calculated CO₂-H₂O phase diagram at 623.15 K by using an EoS and the Wong-Sandler mixing rule. Their phase diagram has a smooth transition through the no-convergence regions encountered by Gallagher *et al.* (1993) (as well as by us), but no details on the calculation procedure are provided by Shyu *et al.* (1997).

The CO₂ solubility model developed in this study for the CO₂-NaCl-H₂O system can be used to predict CO₂ solubility in the aqueous phase, as well as H₂O solubility in the CO₂-rich phase, at a P - T - x range of 1-2000 bar, 273.15-573.15 K and 0-6 mol kg⁻¹ NaCl. In Table 10, the calculated CO₂ solubilities in the aqueous phase are compared with selected reliable experimental data (Wiebe and Gaddy, 1939; Malinin and Savelyeva, 1972; Malinin and Kurovskaya, 1975; Rumpf *et al.* 1994; Yasunishi and Yoshida, 1979; Tödheide and Franck, 1963) and the published CO₂ solubility models (MZLL2013, AD2010, SP2010, DS2006, and OLI). The average absolute deviation (AAD = $\frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{m_{\text{CO}_2,i}^{\text{calc}} - m_{\text{CO}_2,i}^{\text{exp}}}{m_{\text{CO}_2,i}^{\text{exp}}} \right| \%$) of the CO₂ solubility in the aqueous phase between the model calculations and the experimental data shows that our model provides the most reliable performance among the aforementioned models (Table 10).

The model also predicts the H₂O solubility in the CO₂-rich phase over a wide P - T range (1-2000 bar, 273.15-573.15 K) with a very good degree of accuracy (Table 11, Figures 9, 11, 12, and 13). A comparison of the literature models reveals that the AD2010 model only provides a rough estimate of the H₂O solubility in the CO₂-rich phase and the DS2006 and MZLL2013 models do

not provide the H₂O solubility in the CO₂-rich phase. Therefore, thus far, the most reliable models to estimate the H₂O solubility in the CO₂-rich phase are the SP2010 model and the commercial software package OLI Studio 9.0. Table 11 shows a comparison between the calculated results of three models (SP2010, OLI, and our model) and the reliable experimental H₂O solubility data in the CO₂-rich phase (Wiebe and Gaddy, 1941; Tödheide and Franck, 1963; Müller *et al.*, 1988; Valtz *et al.*, 2004). One can see that these three models (our model, OLI, SP2010) predict very similar H₂O solubility in the CO₂-rich phase in low to moderate *P-T* regions, but the model developed herein covers the largest *P-T* range (Table 11).

Figure 11 shows the phase diagram of the CO₂-H₂O system at low temperatures (less than 373.15 K). The model accurately predicts the phase behavior of both the CO₂-rich and aqueous phases. In addition, the three-phase (H₂O(l)+CO₂(g)+CO₂(l)) coexistence pressure at temperatures below the CO₂ critical temperature (304.19 K) can be obtained by the model (Figure 11). For example, the calculated three-phase coexistence pressure at 298.15 K is 65.89 bar, and this result is supported by the experimental result (64.08 bar) of Wendland *et al.* (1999) at 298.15 K.

Figure 12 shows the comparison of the model calculation with the experimental H₂O solubility in the CO₂-rich phase (Müller *et al.*, 1988) at the moderate temperatures of 373.15-473.15 K. There is very good agreement between experimental and calculated values at the highest and lowest temperatures in this interval, but deviations appear at temperatures between 433.15 and 453.15 K.

Figure 13 shows a comparison of three models (this model, SP2010, and DS2006) with the experimental data of Tödheide and Franck (1963) for both phases at temperatures of 523.15-

573.15 K. Our model and SP2010 capture the phase behavior of the CO₂-H₂O system very well at pressures up to 500 bar at 523.15 K, whereas our model provides more accurate results of H₂O solubility in the CO₂-rich phase than the SP2010 model at higher temperatures (*e.g.* 548.15 and 573.15 K).

Figure 14(a,b) shows a comparison between the calculated values of this model and the experimental CO₂ solubility data from various sources (including 4 data points of this study) at 323.15, 373.15, 423.15 K and 1-1000 bar for the CO₂-H₂O system. Our measured CO₂ solubility data in water fall closely in line with the data from the literature, and the model developed in this study describes the phase behavior of the CO₂-H₂O system with good accuracy. In Region I ($P < P_A$, Figure 14a), the CO₂ solubility in the aqueous phase decreases as the temperature increases, until at point A (at pressure $P_A=163.1$ bar, calculated by this model), the CO₂ solubility in the aqueous phase at two different temperatures (373.15 and 423.15 K) reached the same value ($m_{CO_2|A}=1.051$ mol/kg). As pressure increases to $P_B=256.9$ bar (Region II, $P_A < P < P_C$), although no experimental data are available to validate this observation, the CO₂ solubility in the aqueous phase at two different temperatures (323.15 and 423.15 K) is the same ($m_{CO_2|B}=1.370$ mol/kg) as shown by the calculated results of this model (Figure 14b). A similar observation can be found at the pressure $P_C = 466.2$ bar, where the CO₂ solubility again is identical at 323.15 and 373.15 K ($m_{CO_2|C}=1.569$ mol/kg). When the pressure is larger than P_C , the solubility of CO₂ increases, as shown by the ascending trend in Figure 14a (Region III, $P > P_C$), as the temperature increases. The behavior of the CO₂ solubility in response to temperature increase in Region III is the opposite of that in Region I (Figure 14a).

While in region I (or III) the CO₂ solubility in the aqueous phase is decrease (or increase) monotonically in response to increased temperature, at a given pressure in region II, the CO₂ solubility is not a monotonic function of temperature. In fact, region II serves as a transition zone for the temperature-dependent behavior of CO₂ solubility in the aqueous phase between regions I and III. Therefore, we define the pressure-bounded region II in the P - x phase diagram as the CO₂ solubility “transition zone” at given temperatures. The lower- and upper-boundary pressures of the CO₂ solubility transition zone (*i.e.*, Region II) can be founded by the intersection points of the CO₂ solubility curves at given temperatures in the P - x phase diagram (Figure 14b). For example, there are three temperature pairs (a) 373.15 and 423.15 K, (b) 323.15 and 423.15 K, and (c) 323.15 and 373.15 K corresponding to the intersection points A, B and C as shown in Figure 14b. It is implied that the CO₂ solubility curves (bubble point curves of the CO₂-saturated water) with the highest temperature combination (*e.g.* pair (a)) tend to intersect at the lower pressure boundary (P_A) of the transition zone; whereas the CO₂ solubility curves with the lowest temperature combination (*e.g.* pair (c)) tend to intersect at the upper pressure boundary (P_C) of the transition zone.

Figure 15 shows a comparison between this model and the MZLL2013 model. The calculated results of those two models are compared with the reliable literature data (In Table 12: Ref. No. 3, 5, 6, and 7 for Figure 15a; In Table 13: Ref. No. 2, 3, 5, 7, 10, 12 for Figure 15b, Ref. No. 15 for Figures 15c and 15d, Ref. No. 8, 9 for Figure 15e, and Ref. No. 19 for Figure 15f). Both models are in excellent agreement with the experimental data. Figure 15 also illustrates that the performance between the two models are close to each other in the 1-1500 bar, 298.15-573.15 K and 0-4.5 mol/kg NaCl region, but the model developed in this study has a wider pressure and

salt concentration coverage, whereas the MZLL2013 model covers a wider temperature range. In addition to Figure 15, we presented the detailed comparison results between the two models in Tables 12 and 13 for the systems of CO₂-H₂O and CO₂-NaCl-H₂O, respectively.

In Table 12 and 13, the calculated results of the two models (This model and MZLL2013) are compared with available experimental CO₂ solubility data for the CO₂-H₂O and CO₂-NaCl-H₂O systems at elevated temperatures and pressures. The average absolute deviation (AAD%) of the calculated CO₂ solubility values of this model from the experimental data is 3.82 % and 3.83% for the CO₂- H₂O (Table 12) and CO₂-NaCl-H₂O (Table 13) systems, whereas the results from the MZLL2013 model (AAD%) are 4.18% and 4.11%, respectively. Therefore, the model developed in this work provides reliable estimates of the CO₂ solubility in NaCl(aq) solutions as well as the H₂O solubility in the CO₂-rich phase of the CO₂-NaCl-H₂O system over a wide *P-T-x* range (273.15-573.15 K, 1-2000 bar, 0-6 mol/kg NaCl(aq)).

5. Conclusions

A new *PVT* apparatus to measure the CO₂ solubility in aqueous solutions at temperatures and pressures corresponding to CO₂ storage conditions has been constructed and shown to provide accurate and reproducible CO₂ solubility measurements at temperatures up to 423.15 K and pressures up to 150 bar. At 150 bar, new CO₂ solubility data in the aqueous phase were obtained for the CO₂-NaCl-H₂O system at temperatures of 323.15, 373.15, and 423.15 K and from 0 to 6 mol kg⁻¹ NaCl(aq). Error analysis showed that the instrumental error of the observed CO₂

solubility is around 0.7 % and the random error is from 0.5 to 4.5 % based on the molal concentration scale.

In this study, we improved upon the previously published model of Spycher and Pruess (2003, 2010) by including Pitzer's model to calculate the activity coefficient of the dissolved CO₂ and the osmotic coefficient of water in the CO₂-NaCl-H₂O system. The new model can accurately predict the CO₂ solubility in the aqueous phase for both the CO₂-H₂O and CO₂-NaCl-H₂O systems with an overall accuracy better than 3.9 % at temperatures from 273.15 to 573.15 K and pressures up to 2000 bar. A comparison between our model and four widely accepted models (AD2010, SP2010, DS2006, and OLI), as well as a recent published model MZLL2013, showed that our model provides accurate predictions of CO₂-H₂O mutual solubilities for the CO₂-H₂O and CO₂-NaCl-H₂O systems.

A comparison of our model results at three different temperatures (323.15, 373.15 and 423.15 K) with a large number of experimental data reveals a CO₂ solubility transition zone, which is bounded by a low and a high pressure boundary (P_{low} and P_{High} , respectively). In the transition zone ($P_{\text{low}} < P < P_{\text{High}}$), the CO₂ solubility decreases to a minimum before increasing as the temperature increases. The CO₂ solubility is not a monotonic function of temperature in the transition zone. Conversely, outside of that transition zone, the CO₂ solubility decreases ($P < P_{\text{low}}$) or increases ($P > P_{\text{High}}$) in response to increased temperature. This phenomenon is clearly observed and validated by both experimental data and modeling results for the CO₂-H₂O systems.

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Appendix A. Additional model equations

The fugacity coefficients for both CO₂ and H₂O in the CO₂-rich phase were calculated using the Redlich-Kwong equation of state (RK EoS) (Redlich and Kwong, 1949):

$$P = \left(\frac{RT}{v-b} \right) - \left(\frac{a}{T^{0.5}v(v+b)} \right) \quad (\text{A1})$$

where v is the molar volume (cm³/mol) and parameters a and b account for the attraction and repulsion interactions between molecules. By tuning the EoS against the pure CO₂ properties, Spycher and Pruess (2010) set the pure component parameter a as a function of temperature:

$$a = k_o + k_1 T \quad (\text{A2})$$

The parameters k_o , k_1 , and b for pure components (CO₂ and H₂O) can be found in Spycher and Pruess (2010). The standard mixing rules were applied for the CO₂-H₂O gas mixture as

$$a_{mix} = \sum_i^n \sum_j^n y_i y_j a_{ij} \quad (\text{A3})$$

$$b_{mix} = \sum_i^n y_i b_i \quad (\text{A4})$$

The cross parameters a_{ij} (see Eq. (14)) in Eq. (A3) are a measure of the strength of attraction between the molecules of the components i and j . The fugacity coefficient of the k -th component

in the CO₂-H₂O gas mixture can be obtained using the equations given in Panagiotopoulos and Reid (1986) and Spycher and Pruess (2010):

$$\begin{aligned} \ln \varphi_k = & \frac{b_k}{b_{mix}} \left(\frac{Pv}{RT} - 1 \right) - \ln \left(P \frac{(v-b_{mix})}{RT} \right) \\ & + \left(\frac{\sum_{i=1}^n y_i (a_{ik} + a_{ki}) - \sum_{i=1}^n \sum_{j=1}^n y_i^2 y_j (k_{ij} - k_{ji}) \sqrt{a_i a_j} + x_k \sum_{i=1}^n x_i (k_{ki} - k_{ik}) \sqrt{a_i a_k}}{a_{mix}} - \frac{b_k}{b_{mix}} \right) \\ & \times \left(\frac{a_{mix}}{b_{mix} RT^{1.5}} \right) \ln \left(\frac{v}{v+b_{mix}} \right) \end{aligned} \quad (A5)$$

The Pitzer equations for calculating the activity coefficient of dissolved CO₂, γ_{CO_2} , and the osmotic coefficient of H₂O, ϕ , are given in Pitzer (1991):

$$\begin{aligned} \ln \gamma_{CO_2} = & 2m_{CO_2} \lambda_{nn} + 3m_{CO_2}^2 \mu_{nnn} + 2m_{NaCl} (\lambda_{nc} + \lambda_{na}) + 6m_{CO_2} m_{NaCl} (\mu_{nnc} + \mu_{nna}) + \\ & m_{NaCl}^2 \xi_{nca} \end{aligned} \quad (A6)$$

$$\begin{aligned} \phi - 1 = & \frac{2}{2m_{NaCl} + m_{CO_2}} \left\{ -A^\phi \frac{I^{1.5}}{I + bI^{0.5}} + m_{NaCl}^2 \left[\beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp(-\alpha_1 I^{0.5}) + 2m_{NaCl} C_{ca} \right] + \right. \\ & \frac{1}{2} m_{CO_2}^2 \lambda_{nn} + m_{CO_2}^3 \mu_{nnn} + m_{CO_2} m_{NaCl} (\lambda_{nc} + \lambda_{na}) + 3m_{CO_2}^2 m_{NaCl} (\mu_{nnc} + \mu_{nna}) + \\ & \left. m_{CO_2} m_{NaCl}^2 \xi_{nca} \right\} \end{aligned} \quad (A7)$$

In Eq. (A6) and (A7), the Pitzer ion-ion interaction parameters $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and C_{ca}^ϕ for NaCl-H₂O system are taken from Pitzer *et al.* (1984). The molality of CO₂ and NaCl in the aqueous phase are m_{CO_2} and m_{NaCl} , respectively; A^ϕ is the Debye-Hückel slope for the osmotic coefficient,

$b = 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, and $\alpha_1 = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$; and I is the ionic strength based on the molality scale. The Debye-Hückel slope and the ionic strength are defined as follows:

$$A_\phi = \frac{1}{3} (2\pi N_A \rho_{H_2O})^{1/2} \left(\frac{e^2}{4\pi \epsilon_0 \epsilon_r kT} \right)^{3/2} \quad (\text{A8})$$

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (\text{A9})$$

where ρ_{H_2O} is the density of water (g/L) calculated by the IAPWS-95 formulation (Wagner and Pruß, 2002); ϵ_r is the relative permittivity of pure water calculated from the equation of Fernández *et al.* (1997), which is adopted as the IAPWS standard for ϵ_r ; $\epsilon_0 = 8.85419 \cdot 10^{-12}$ (F/m) is the vacuum permittivity; $e = 1.60218 \cdot 10^{-19}$ (C) is the elementary charge; $k = 1.38065 \cdot 10^{-23}$ (J K⁻¹) is the Boltzmann constant; and T is temperature in K.

The combined Pitzer interaction parameters B_{CO_2-NaCl} and $C_{CO_2-CO_2-NaCl}$ are adopted from Akinfiev and Diamond (2010),

$$B_{CO_2-NaCl} = a_1 + a_2 \frac{100}{T-\theta} + \frac{a_3}{2I} [1 - (1 + 2\sqrt{I})\exp(-2\sqrt{I})] \quad (\text{A10})$$

$$C_{CO_2-CO_2-NaCl} = a_4 \quad (\text{A11})$$

where $\theta = 228$ K and a constant, I is molality based ionic strength defined by Eq. (A9). The parameters in Eqs. (A10) and (A11) are given in Table A1 (Akinfiev and Diamond, 2010).

Symbols and Units

Uppercase

$AAD \%$	average absolute deviation
A^ϕ	Debye-Hückel slope for osmotic coefficient
B_{CO_2-NaCl}	combined Pitzer interaction parameter for the CO_2 -NaCl- H_2O system
$C_{CO_2-CO_2-NaCl}$	combined Pitzer triple interaction parameter for the CO_2 -NaCl- H_2O system
I	molality scale ionic strength, $mol\ kg^{-1}(H_2O)$
N_A	Avogadro constant
N_p	number of measured point
P	pressure, bar
P_w^s	vapor pressure of water, bar
P_{low}	lower pressure boundary of the defined CO_2 solubility transition zone
P_{High}	upper pressure boundary of the defined CO_2 solubility transition zone
T	temperature, K

Lowercase

a_{CO_2}, a_{H_2O}	activity of dissolved CO_2 in the aqueous phase and H_2O in CO_2 -rich phase, respectively
a_{mix}, b_{mix}	EoS parameter for CO_2 - H_2O gas mixture
f_{CO_2}, f_{H_2O}	fugacity of CO_2 and H_2O , respectively, bar
e	elementary charge, $1.60218 \cdot 10^{-19}\ C$

k	Boltzmann constant, $1.38065 \cdot 10^{-23} \text{ J K}^{-1}$
k_{H,CO_2}^o	Henry's constant, $\text{bar mol}^{-1} \text{ kg}$
k_{ij}, k_{ji}	binary interaction parameters of combining rule
m_{CO_2}	molality of CO_2 in the aqueous phase, $\text{mol kg}^{-1}(\text{H}_2\text{O})$
m_{NaCl}	molality of $NaCl$ in the aqueous solution
ν_a, ν_c	stoichiometric numbers of anions and cations of dissolved salt
$\bar{v}_{CO_2}$	partial molar volume of CO_2 at infinite dilution in water, an empirical determined parameter in the proposed CO_2 solubility model, $\text{cm}^3 \text{ mol}^{-1}$
$\bar{v}_w$	partial molar volume of water, $\text{cm}^3 \text{ mol}^{-1}$
x_{CO_2}	mole fraction of CO_2 in the aqueous phase

Greek letters

$\beta_{ca}^{(0)}, \beta_{ca}^{(1)}$	Pitzer ion-ion binary interaction parameters for $NaCl\text{-}H_2O$ system
γ_{CO_2}	activity coefficient of dissolved CO_2
δm	CO_2 solubility error based on molality scale
δx	CO_2 solubility error based on mole fraction scale
ε_o	vacuum permittivity, $8.85419 \cdot 10^{-12} \text{ F m}^{-1}$
ε_r	relative permittivity of water
$\xi_{nca}, \mu_{nna}, \mu_{nnc}$	Pitzer triple interaction parameters between neutral species and ions
ρ_{H_2O}	density of water, g cm^{-3}
$\lambda_{nc}, \lambda_{na}$	Pitzer interaction parameters between neutral species and ions
λ_{nn}, μ_{nnn}	Pitzer interaction parameters for neutral species
ϕ	osmotic coefficient

$\varphi_{CO_2}, \varphi_{H_2O}$ fugacity coefficient of CO₂ and H₂O, computed by the modified RK EoS

φ_w^S fugacity coefficient of pure H₂O, computed by IAPWS-95 EoS

Supplemental Information: The Description of Error Propagation

1. 2-D interpolation of scatter experimental data

Multiple measurements (usually 3 to 6 measurements) were made at each target experimental P - T - x point. The inverse distance weighted 2-D interpolation method (Shepard, 1968) was used to get an approximation of the real value based on scattered data generated by measurements at each interpolation point. Based on this approach, the value of the interpolation point in a set, $f(x, y)$, is defined as:

$$f(x, y) = \sum_{i=1}^n f_i(x_i, y_i) W_i(x_i, y_i) \quad (\text{S1})$$

where n is the number of scatter (experimental) points in the set, $f_i(x_i, y_i)$ is the value of the i -th scatter point, and $W_i(x_i, y_i)$ is the weight function assigned to the i -th scatter point.

The weight function is defined as,

$$W_i(x_i, y_i) = \frac{h_i^{-2}}{\sum_{j=1}^n h_j^{-2}} \quad (\text{S2})$$

where h_i is the distance from the interpolation point to the i -th scatter point and is defined as:

$$h_i = \sqrt{(x - x_i)^2 + (y - y_i)^2} \quad (\text{S3})$$

2. Error estimation

The CO₂ solubility in the aqueous phase is commonly expressed by either molality (m_{CO_2}) or mole fraction (x_{CO_2}). The error estimation is performed on the mole fraction scale, but the obtained results can be converted to the molality scale. The mole fraction of CO₂ in an aqueous sample is defined as,

$$x_{\text{CO}_2} = \frac{\frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}}}{\frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}} + \frac{M_{\text{sample}} - M_{\text{CO}_2} - M_{\text{salt}}}{MW_{\text{H}_2\text{O}}} + \frac{M_{\text{salt}}}{MW_{\text{salt}}}(\nu_a + \nu_c)} \quad (\text{S4})$$

where M_{CO_2} is the mass of CO₂ in the sample, M_{sample} is the total mass of sample, M_{salt} is the mass of salt in the sample; MW_{CO_2} , $MW_{\text{H}_2\text{O}}$ and MW_{salt} are the molar masses of CO₂, H₂O and NaCl, respectively; ν_a and ν_c are, respectively, the stoichiometric numbers of the anion and cation of the dissolved salt.

The error propagation theory described by Taylor (1997) is used to determine the instrumental error of each measured point. From Eq. (S4), the error in x_{CO_2} due to the pressure variation in the pressure cell is:

$$\delta x_{\text{err}}^P = \left| \frac{\partial x_{\text{CO}_2}}{\partial P_{\text{pressure cell}}} \right| \delta P = \left| \frac{\partial x_{\text{CO}_2}}{\partial M_{\text{CO}_2}} \frac{\partial M_{\text{CO}_2}}{\partial P_{\text{pressure cell}}} \right| \delta P \quad (\text{S5})$$

The error in x_{CO_2} due to the temperature variation of pressure cell is:

$$\delta x_{\text{err}}^T = \left| \frac{\partial x_{\text{CO}_2}}{\partial T_{\text{pressure cell}}} \right| \delta T = \left| \frac{\partial x_{\text{CO}_2}}{\partial M_{\text{CO}_2}} \frac{\partial M_{\text{CO}_2}}{\partial T_{\text{pressure cell}}} \right| \delta T \quad (\text{S6})$$

The error in x_{CO_2} due to the volume variation is:

$$\delta x_{\text{err}}^V = \left| \frac{\partial x_{\text{CO}_2}}{\partial V_{\text{pressure cell}}} \right| \delta V = \left| \frac{\partial x_{\text{CO}_2}}{\partial M_{\text{CO}_2}} \frac{\partial M_{\text{CO}_2}}{\partial V_{\text{pressure cell}}} \right| \delta V \quad (\text{S7})$$

The error in x_{CO_2} due to the sample mass variation is:

$$\delta x_{\text{err}}^{\text{sample}} = \left| \frac{\partial x_{\text{CO}_2}}{\partial M_{\text{sample}}} \right| \delta M_{\text{sample}} \quad (\text{S8})$$

The error in x_{CO_2} due to the salt mass variation is:

$$\delta x_{\text{err}}^{\text{salt}} = \left| \frac{\partial x_{\text{CO}_2}}{\partial M_{\text{salt}}} \right| \delta M_{\text{salt}} \quad (\text{S9})$$

From Eq. (S4), the derivative of x_{CO_2} with respect to M_{CO_2} is,

$$\frac{\partial x_{\text{CO}_2}}{\partial M_{\text{CO}_2}} = \frac{\frac{1}{MW_{\text{CO}_2}} \left(\frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}} + \frac{M_{\text{sample}} - M_{\text{CO}_2} - M_{\text{salt}}}{MW_{\text{H}_2\text{O}}} + \frac{M_{\text{salt}}}{MW_{\text{salt}}} (v_a + v_c) \right) - \frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}} \left(\frac{1}{MW_{\text{CO}_2}} - \frac{1}{MW_{\text{H}_2\text{O}}} \right)}{\left(\frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}} + \frac{M_{\text{sample}} - M_{\text{CO}_2} - M_{\text{salt}}}{MW_{\text{H}_2\text{O}}} + \frac{M_{\text{salt}}}{MW_{\text{salt}}} (v_a + v_c) \right)^2} \quad (\text{S10})$$

$$M_{\text{CO}_2} = M_{\text{CO}_2}^1 + M_{\text{CO}_2}^2 + M_{\text{CO}_2}^3 = (\rho_{\text{CO}_2}^1 + \rho_{\text{CO}_2}^2 + \rho_{\text{CO}_2}^3) V_{\text{pressure cell}} \quad (\text{S11})$$

In Eq. (S11) $M_{\text{CO}_2}^1$, $M_{\text{CO}_2}^2$ and $M_{\text{CO}_2}^3$ represent the CO₂ amount by mass, as well as $\rho_{\text{CO}_2}^1$, $\rho_{\text{CO}_2}^2$, and $\rho_{\text{CO}_2}^3$ represent the CO₂ density in the pressure cell, due to the 1st, 2nd and 3rd expansion during sample analysis process, respectively. Also, the $P_{\text{pressure cell}}$, $T_{\text{pressure cell}}$, and $V_{\text{pressure_cell}}$ in Eqs. (S5-S11) denote the pressure (bar), temperature (K) and volume (cm³) of the pressure cell.

Other partial derivatives are obtained as follows:

$$\left(\frac{\partial M_{\text{CO}_2}}{\partial P}\right)_{V,T} \delta P = \sqrt{\left(\left(\frac{\partial M_{\text{CO}_2}^1}{\partial P}\right)_{V,T_1} \delta P_1\right)^2 + \left(\left(\frac{\partial M_{\text{CO}_2}^2}{\partial P}\right)_{V,T_2} \delta P_2\right)^2 + \left(\left(\frac{\partial M_{\text{CO}_2}^3}{\partial P}\right)_{V,T_3} \delta P_3\right)^2} \quad (\text{S12})$$

$$\left(\frac{\partial M_{\text{CO}_2}}{\partial T}\right)_{V,P} \delta T = \sqrt{\left(\left(\frac{\partial M_{\text{CO}_2}^1}{\partial T}\right)_{V,P_1} \delta T_1\right)^2 + \left(\left(\frac{\partial M_{\text{CO}_2}^2}{\partial T}\right)_{V,P_2} \delta T_2\right)^2 + \left(\left(\frac{\partial M_{\text{CO}_2}^3}{\partial T}\right)_{V,P_3} \delta T_3\right)^2} \quad (\text{S13})$$

where T_1, T_2, T_3 and P_1, P_2, P_3 are the equilibrium temperatures and pressures of the pressure cell during 1st, 2nd and 3rd expansion; $\delta T_1, \delta T_2, \delta T_3$ and $\delta P_1, \delta P_2, \delta P_3$ are the temperature and pressure changes of the pressure cell during 1st, 2nd and 3rd expansion, respectively. The terms

$\left(\frac{\partial M_{\text{CO}_2}^1}{\partial P}\right)_{V,T_1}$, $\left(\frac{\partial M_{\text{CO}_2}^2}{\partial P}\right)_{V,T_2}$, $\left(\frac{\partial M_{\text{CO}_2}^3}{\partial P}\right)_{V,T_3}$ are determined by the slope of the isothermal curve

generated by the EoS of Span and Wagner (1996). Similarly, the terms $\left(\frac{\partial M_{\text{CO}_2}^1}{\partial T}\right)_{V,P_1}$, $\left(\frac{\partial M_{\text{CO}_2}^2}{\partial T}\right)_{V,P_2}$,

$\left(\frac{\partial M_{\text{CO}_2}^3}{\partial T}\right)_{V,P_3}$ are determined by the slope of isobaric curve generated by the same EoS.

Substituting (S10) and (S12) into (S5), (S10) and (S13) into (S6), (S10) and (S11) into (S7), respectively, the δx_{err}^P , δx_{err}^T , δx_{err}^V can be calculated. By differentiation of Eq. (S4) with respect to M_{sample} and M_{salt} , the Eqs. (S14) and (S15) can be obtained as:

$$\frac{\partial x_{\text{CO}_2}}{\partial M_{\text{sample}}} = - \frac{\frac{1}{MW_{\text{H}_2\text{O}}} \frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}}}{\left(\frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}} + \frac{M_{\text{sample}} - M_{\text{CO}_2} - M_{\text{salt}}}{MW_{\text{H}_2\text{O}}} + \frac{M_{\text{salt}}}{MW_{\text{salt}}} (v_a + v_c) \right)^2} \quad (\text{S14})$$

$$\frac{\partial x_{\text{CO}_2}}{\partial M_{\text{salt}}} = \frac{\left(\frac{1}{MW_{\text{H}_2\text{O}}} \frac{v_a + v_c}{MW_{\text{salt}}} \right) \frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}}}{\left(\frac{M_{\text{CO}_2}}{MW_{\text{CO}_2}} + \frac{M_{\text{sample}} - M_{\text{CO}_2} - M_{\text{salt}}}{MW_{\text{H}_2\text{O}}} + \frac{M_{\text{salt}}}{MW_{\text{salt}}} (v_a + v_c) \right)^2} \quad (\text{S15})$$

Substituting (S14) into (S8), and (S15) into (S9), respectively, the $\delta x_{\text{err}}^{\text{sample}}$ and $\delta x_{\text{err}}^{\text{salt}}$ can be calculated. Thus, the calculated instrumental error of the sample analysis can be estimated by the error propagation as follows:

$$\delta x_{\text{instr}} = \sqrt{(\delta x_{\text{err}}^P)^2 + (\delta x_{\text{err}}^T)^2 + (\delta x_{\text{err}}^V)^2 + (\delta x_{\text{err}}^{\text{sample}})^2 + (\delta x_{\text{err}}^{\text{salt}})^2} \quad (\text{S16})$$

In this study, the calculated instrumental error (δx_{instr}) is found to be below 0.7 % of the mole fraction of CO_2 in the aqueous phase. The instrumental error on the molality scale (δm_{instr}) can be converted from the mole fraction scale as below:

$$\delta m_{\text{instr}} = \frac{55.509 \delta x_{\text{instr}} + (v_a + v_c) m_{\text{salt}} \delta x_{\text{instr}}}{1 - \delta x_{\text{instr}}} \quad (\text{S17})$$

and $\frac{\delta m_{\text{instr}}}{m_{\text{CO}_2}} < 0.77\%$ for all experimental CO₂ solubility.

The random errors were estimated from direct repetitions of the measurement results. The standard deviation between 2-D interpolation point and measured experimental value represents the random error of the value during the experiment:

$$\delta x_{\text{random}} = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - x_{2-D})^2} \quad (\text{S18})$$

where x_{2-D} is 2-D interpolation value of the measured solubility data. In this study, the instrumental and random error are both given in Table 3. The random error based on molality scale (δm_{random}) can also be converted from δx_{random} in the same manner as Eq. (S17) does.

Symbols

h_i	distance between scattered (experimental) and interpolation points
x_{2-D}	2-D interpolation value of scattered measured CO ₂ solubility, mole fraction
M_{CO_2}	mass of CO ₂ in the sample cell, g
M_{salt}	mass of dissolved salt in the sample
M_{sample}	mass of sample, g
$M_{\text{CO}_2}^1, M_{\text{CO}_2}^2, M_{\text{CO}_2}^3$	mass of CO ₂ of 1 st , 2 nd , and 3 rd CO ₂ expansion
MW_i	molecular weight of a component, g mol ⁻¹
$P_{\text{pressure cell}}$	pressure of the pressure cell during sample analysis process, bar

P_1, P_2, P_3	equilibrium pressure of pressure cell during 1 st , 2 nd , and 3 rd CO ₂ expansion
T_1, T_2, T_3	equilibrium temperature of pressure cell during 1 st , 2 nd , and 3 rd CO ₂ expansion, K
$T_{\text{pressure cell}}$	temperature of the pressure cell, K
$V_{\text{pressure cell}}$	volume of the stainless steel vessel for measuring the CO ₂ solubility during sample analysis process, 297.27 cm ³
$\delta P_1, \delta P_2, \delta P_3$	pressure difference of pressure cell during 1 st , 2 nd , and 3 rd CO ₂ expansion
$\delta T_1, \delta T_2, \delta T_3$	temperature difference of pressure cell during 1 st , 2 nd , and 3 rd CO ₂ expansion
δV	estimated error for the pressure cell volume

Figures

Figure 1. Main approaches used to measure the CO₂ solubility in an aqueous phase. The shaded boxes represent the method implemented in this study.

Figure 2. The common envelope of CO₂ phase behavior in sedimentary basins along with selected experimental pressure and temperature conditions (150 bar, 323.15, 373.15 and 423.15 K) in this study (shown by solid circles).

Figure 3. Schematic diagram of the experimental apparatus: (1) 0 to 345 bar pressure transducer, (2) CO₂-rich phase sample cell, (3) sample line for the CO₂-rich phase, (4) rupture disc, (5) CO₂-rich phase, (6) thermocouple, (7) aqueous solution, (8) liquid phase sample cell, (9) liquid CO₂ pump, (10) liquid CO₂ cylinder, (11) liquid CO₂ inlet, (12) sample line for the aqueous phase, (13) impeller, (14) heat mantle, (15) Teflon liner.

Figure 4. Comparison of experimental CO₂ solubility in aqueous NaCl solutions (1 and 3 mol kg⁻¹ NaCl) at 323.15 and 373.15 K obtained in this study and values obtained by Koschel *et al.* (2006). m_{CO_2} is the CO₂ molality in the aqueous phase; the solid symbols stand for the experimental data of Koschel *et al.* (2006), whereas the open symbols represent the experimental data obtained in this work at 150 bar. The dash-dot lines are the results from the SP2010 model; the solid lines represent the results of the model developed in this work.

(a)

(b)

(c)

Figure 5. Comparison of measured CO₂ solubility with model calculations at (a) 323.15 K, (b) 373.15 K, and (c) 423.15 K at 150 bar and concentrations of NaCl(aq) up to 6 mol kg⁻¹. AD2010: Akinfiev and Diamond (2010); SP2010: Spycher and Pruess (2010); DS2010: Duan *et al.* (2006); OLI: OLI Studio 9.0. The MZLL2013 model is almost same with this model, so it was not shown in figure for the purpose of clarity. Use of AD2010 at $T > 373.15$ K, as done in Figure 5(c), is outside the nominal validity of the model stated by Akinfiev and Diamond (2010).

Figure 6. Comparison of Henry's constant (k_{H,CO_2}^0 / bar mol⁻¹ Kg) obtained in this study (Eq. (3)) with literature values. The Henry's constant correlation reported by Harvey (1996) and Fernández-Prini (2003) was converted from mole fraction scale to molality scale for comparison.

Figure 7. The flow chart used to calculate the mutual solubilities of CO₂ and H₂O in the CO₂-NaCl-H₂O system. The inner loop solves the CO₂ solubility in aqueous phase; the outer loop solves the H₂O solubility in the CO₂-rich phase. The convergence criteria is set to $\varepsilon = 10^{-5}$ during the calculations.

Figure 8. The data fitting procedure for determining the neutral component parameters λ_{nn} , μ_{nnn} (Eq. (13)) and the Henry's constant k_{H,CO_2}^o (Eq. (3)): 1) Use Henry's constant (Fernández-Prini, 2003) as an initial value, the activity of dissolved CO₂ can be calculated via Eq. (1); 2) Use experimental CO₂ solubility data and the obtained activity of dissolved CO₂, the activity coefficient of dissolved CO₂ can be calculated by a simple relation $\gamma_{CO_2} = a_{CO_2} / m_{CO_2}$; 3) Neutral component parameters λ_{nn} and μ_{nnn} are obtained by least-square fitting of Eq. (A6) using experimental CO₂ solubility data for the CO₂-H₂O system; 4) Activity of dissolved CO₂ is re-calculated using the newly obtained λ_{nn} and μ_{nnn} via Eq. (A6) as well as the experimental CO₂ solubility data; 5) Obtain a new Henry's constant from Eq. (1). Iterations of the steps (2)-(3)-(4)-(5)-(6)-(2) are needed to get a good consistency between the new- and old-Henry's constant. This procedure allows one to obtain k_{H,CO_2}^o , λ_{nn} and μ_{nnn} directly, following iterative solution of Henry's law constant. The experimental data used during the fitting procedure are listed in Table 12 (No. 1, 2, 3, 5, 9, 10, 13, 15, 16, 18, 19, 21, 22, 26, 28, 30, 41).

Figure 9. Pressure-composition phase diagram for the CO₂-H₂O system at temperatures from 423.15 to 573.15 K and pressures up to 2000 bar for both the aqueous and the CO₂-rich phases. The solid lines represent the calculated results from our model and the lines on the left-hand of the dashed critical line stand for the bubble-point curves of CO₂-saturated H₂O(l) whereas the curves on the right-hand of the critical line represent the dew-point curves of H₂O-saturated supercritical CO₂. The open circles and triangles represent the experimental data from Tödheide and Frank (1963), the solid circles and inverted solid triangles show Malinin's (1959) data, the solid triangles correspond to the results of Müller *et al.* (1988). The model has AAD of 1.51% for the aqueous phase and 4.11% for the CO₂-rich phase when compared with the experimental data reported by Tödheide and Frank (1963).

Figure 10. The model-calculated pressure-composition phase diagram of the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system for 4 mol kg^{-1} NaCl at temperatures from 433.15 to 573.15 K, and pressures from 1 to 2000 bar for both the aqueous phase and CO_2 -rich phase. x'_{CO_2} stand for salt-free mole fraction of CO_2 , and it is calculated as $x'_{\text{CO}_2} = m_{\text{CO}_2} / (m_{\text{CO}_2} + 1000 / M_{\text{H}_2\text{O}})$, where 1000 is the amount of water in gram. Open circles are the experimental data for the $\text{CO}_2\text{-H}_2\text{O}$ binary system from Tödheide and Frank (1963), served as the benchmark for the comparisons of the phase behavior when NaCl is introduced into the system.

Figure 11. Pressure-composition phase diagram for the $\text{CO}_2\text{-H}_2\text{O}$ system from 288.15 to 373.15 K, and pressures up to 300 bar for both the aqueous phase and CO_2 -rich phase. The circles stand for the experimental values for the aqueous phase, and the triangles represent the experimental values for the CO_2 -rich phase. For the aqueous phase, the solid circles are the experimental data from Wiebe and Gaddy (1939) at 323.15, 348.15 and 373.15 K. The gray circles are the experimental data from King *et al.* (1992) at 288.15, 293.15 and 298.15 K. The white circles are the experimental data taken from and Tong *et al.* (2013). For the CO_2 -rich phase, the solid triangles are from Wiebe and Gaddy (1941) at 298.15, 304.19, 323.15 and 348.15 K. The gray triangles are the data from King *et al.* (1992) at 288.15, 293.15, 298.15, 308.15, and 313.15 K; the white triangle are the data from Valtz *et al.* (2004) at 288.15, 298.15, 308.15 K. The solid lines are the results of model calculations from this study. The calculations show the well-known three-phase $[\text{H}_2\text{O(l)} + \text{CO}_2\text{(l)} + \text{CO}_2\text{(g)}]$ coexistence lines where the system pressure lies below the CO_2 critical point (73.77 bar, 304.19 K).

Figure 12. Phase diagram of the CO₂-H₂O system at temperatures 373.15-473.15 K and pressures 1-100 bar for the CO₂-rich phase. The solid lines are our model calculations and points are from experimental work of Müller *et al.* (1988) given by Scharlin (1996).

Figure 13. Comparison between calculations using SP2010 and the model of this study at temperatures from 523.15-573.15 K, and pressures up to 600 bar for the CO₂-H₂O system. Solid lines are our calculation results for both the aqueous phase and CO₂-rich phases, dotted-lines are the calculation results from Spycher and Pruess (2010). The circles are experimental data taken from Töðheide and Frank (1963). The solid circles denote the CO₂ solubility in the aqueous phase, whereas the open circles stand for the water solubility in the CO₂-rich phase. The triangles stand for the calculated CO₂ solubility in the aqueous phase at 523.15 K by DS2006.

(a)

(b)

Figure 14. The phase diagram of the CO₂-H₂O binary system at 323.15-423.15 K and 1-1000 bar. Solid lines are bubble-point curves of CO₂-saturated H₂O(l) at different temperatures corresponding to the experimental CO₂ solubility data. Two vertical lines (*i.e.* P_A and P_C) create three distinct regions (I, II and III) in the diagram. In region I ($P < P_A$), the solubility of CO₂ is decreasing as the temperature increases; In region II ($P_A < P < P_C$), the CO₂ solubility decrease to a minimum then start to increase as the temperature increases; In region III ($P > P_C$), the CO₂ solubility in aqueous phase is increasing as the temperature increases. Region II is a transition zone in which at certain pressure (*e.g.* P_B), the bubble-point curves of CO₂-saturated water with different temperatures may have intersections. Point A, B and C in the region II are the intersections between those bubble-point curves at temperatures 323.15, 373.15 and 423.15 K at pressures P_A , P_B and P_C , respectively. The experimental data at 323.15, 373.15 and 423.15 K were taken from the references (No. 1, 2, 5, 6, 7, 9, 10, 11, 13, 15, 16, 18, 21, 22, 26, 28, 32, 33, 35, 36, 37, 38, 39, 40, and 41) listed in Table 12. Figure 14b is an enlarged view of the region II, the values of P_A , P_B and P_C can be determined via model calculations as shown in Figure 14b.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 15. Vapor-liquid equilibrium of the $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-NaCl-H}_2\text{O}$ systems. Comparison of this model and MZLL2013 (Mao *et al.*, 2013) to experimental CO_2 solubility data in aqueous phase. Results are shown in (a) for the $\text{CO}_2\text{-H}_2\text{O}$ system at 423.15-573.15 K, 1-1500 bar; (b) for the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system at ambient conditions, (c) for the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system at 313.15-433.15 K, 1-120 bar and 4 mol kg^{-1} NaCl, (d) for the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system at 313.15-433.15 K, 1-120 bar and 6 mol kg^{-1} NaCl (the MZLL2013 model is not applicable in this case due to the high NaCl molality), (e) for the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system at 298.15-423.15 K, 48 bar, and 0-6 mol kg^{-1} NaCl, and (f) for the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system at 303.15-333.15 K, 80-220 bar, at 0.529 mol kg^{-1} NaCl.

Tables

Table 1. Comparison of measured CO₂ solubility in the binary CO₂-H₂O system at 323.15 K and 100 bar with literature data and model calculations.

T / K	P / bar	References	$m_{\text{CO}_2} / \text{mol kg}^{-1}$
Experimental measurements			
323.15	100	Bando <i>et al.</i> , 2003	1.116 ± 0.033
323.15	101	Liu <i>et al.</i> , 2011	$1.133^{(a)}$
323.15	101	Dohrn <i>et al.</i> , 1993	$1.176^{(a)}$
323.15	101.3	Briones <i>et al.</i> , 1987	$1.180^{(a)}$
323.15	100.9	Bamberger <i>et al.</i> , 2000	1.162 ± 0.017
323.15	101.3	D'Souza <i>et al.</i> , 1988	$1.121^{(a)}$
323.15	101.3	Wiebe and Gaddy, 1939	$1.151^{(a)}$
323.15	100	This study	1.151 ± 0.028
Modeling ^(b)			
323.15	100	DS2006	1.148
323.15	100	AD2010	1.156
323.15	100	SP2010	1.136
323.15	100	OLI Studio 9.0	$1.146^{(c)}$
323.15	100	MZLL2013	1.147
323.15	100	This model	1.151

^(a)The experimental data without ' $\pm$ ' mean that the error was not given in the references.

^(b)DS2006, AD2010, SP2010 and MZLL2013, respectively, stand for the model developed by Duan *et al.* (2006), Akinfiev and Diamond (2010), Spycher and Pruess (2010) and Mao *et al.* (2013)

^(c)Calculations made by OLI are under the following conditions: (1) enable the second liquid phase, (2) use MSE model, (3) stream inflows contains 55.5082 mol water and 5 mol CO₂.

Table 2. Experimental results of CO₂ solubility in NaCl(aq) compared with literature data (collected at the same *P-T-x* conditions) and model calculations.

<i>T / K</i>	<i>P / bar</i>	<i>m_{NaCl} / mol kg⁻¹</i>	This study <i>m_{CO₂} / mol kg⁻¹</i>	Literature <i>m_{CO₂} / mol kg⁻¹</i>	References	Model calculations ^(a) , <i>m_{CO₂} / mol kg⁻¹</i>				
						This study	OLI ^(b)	AD2010	SP2010	DS2006
323.15	150	0.529	1.114±0.017	1.102	Bando <i>et al.</i> (2003)	1.108	1.150	1.117	1.108	1.095
373.15	48	0.998	0.361±0.006	0.361	Malinin and Kurovskaya (1975)	0.377	0.358	0.368	0.369	0.370
413.15	92.01	5.999	0.278±0.014	0.288	Rumpf <i>et al.</i> (1994)	0.276	0.259	0.280	0.292	-
Average absolute deviation (AAD %) of model calculations from the experimental CO ₂ solubility data						1.88	3.63	1.03	2.59	2.05
										2.48

^(a)OLI: OLI Studio 9.0, which is a simulation software for electrolyte chemistry developed by *OLI Systems Inc.* (Springer *et al.*, 2012); AD2010: Akinfiev and Diamond (2010); SP2010: Spycher and Pruess (2010); DS2006: Duan *et al.* (2006).

^(b)Calculations made by OLI are under the following conditions: (1) enable the second liquid phase, (2) use MSE model, (3) stream inflows contains 55.5082 mol water and 5 mol CO₂.

Table 3. Experimental CO₂ solubility measurements in NaCl(aq) at 150 bar and temperatures from 323.15 to 423.15 K. The experimental data are compared with model calculations in terms of the average absolute deviation (AAD %) between calculated and experimental results.

Experimental CO ₂ solubility at 150 bar (This study)				Calculated CO ₂ solubility: m_{CO_2} / mol kg ⁻¹					
T / K	$m_{\text{NaCl}} / \text{mol kg}^{-1}$	$m_{\text{CO}_2} / \text{mol kg}^{-1}$	$\delta m_{\text{random}} / \text{mol kg}^{-1(a)}$	This study	OLI ^(b)	AD2010	SP2010	DS2006	MZLL2013
323.15	0	1.245	0.006	1.244	1.271	1.256	1.233	1.223	1.253
323.15	1	1.016	0.010	1.016	1.055	1.017	1.012	0.995	1.024
323.15	2	0.859	0.007	0.853	0.889	0.849	0.845	0.822	0.853
323.15	3	0.734	0.015	0.727	0.761	0.724	0.716	0.690	0.723
323.15	4	0.623	0.006	0.629	0.661	0.629	0.618	0.587	0.625
323.15	5	0.551	0.005	0.552	0.582	0.553	0.541	-	-
323.15	6	0.498	0.004	0.492	0.520	0.493	0.481	-	-
AAD (%) at 323.15 K				0.59	4.17	0.80	1.66	3.96	0.79
373.15	0	1.020	0.006	1.012	1.020	1.010	1.001	0.984	1.032
373.15	1	0.836	0.008	0.842	0.839	0.827	0.819	0.808	0.843
373.15	2	0.706	0.007	0.714	0.704	0.699	0.686	0.675	0.704
373.15	3	0.618	0.006	0.614	0.600	0.603	0.588	0.575	0.601
373.15	4	0.527	0.005	0.536	0.520	0.529	0.515	0.499	0.526
373.15	5	0.469	0.005	0.474	0.458	0.471	0.463	-	-
373.15	6	0.427	0.009	0.426	0.408	0.425	0.425	-	-
AAD (%) at 373.15 K				0.90	1.67	0.98	2.26	4.75	1.03
423.15	0	1.001	0.007	0.994	0.975	0.969	1.028	0.961	0.992
423.15	1	0.800	0.017	0.794	0.794	0.793	0.824	0.780	0.798
423.15	2	0.647	0.018	0.660	0.659	0.670	0.679	0.647	0.659
423.15	3	0.566	0.025	0.565	0.558	0.578	0.577	0.549	0.560
423.15	4	0.498	0.010	0.494	0.480	0.507	0.503	0.476	0.488
423.15	5	0.440	0.004	0.438	0.419	0.451	0.450	-	-
423.15	6	0.390	0.007	0.391	0.370	0.407	0.414	-	-
AAD (%) at 423.15 K				0.74	2.87	2.62	3.12	2.81	1.26
Overall AAD (%)				0.74	2.91	1.47	2.35	3.84	1.03

^(a) δm_{random} is the random error estimated on molality scale. The instrumental error was determined to be about 0.7 % of the measured values by application of error propagation theory, with the procedure description detailed in the supplemental information; the δm_{random} was determined by repeated measurements at each given P - T - x condition.

^(b) Calculations made by OLI are under the following conditions: (1) enable the second liquid phase, (2) use MSE model, (3) stream inflows contains 55.5082 mol water and 5 mol CO₂.

Table 4. The results of $\bar{v}_{CO_2}$ ($\text{cm}^3 \text{mol}^{-1}$) determined by this model.

T / K	P / bar						
	200	300	400	500	1000	1500	2000
278.15	32.90	32.35*	31.81*	31.26	29.30	30.26	30.26
323.15	32.90	32.35*	31.81*	31.26	29.30	30.26	30.30
373.15	35.42	33.80*	32.19*	29.60	29.67	30.30	30.55
423.15	36.20	34.35*	32.05*	30.65	33.18	32.95	32.87
473.15	37.00	35.08*	33.15*	31.23	33.57	33.11	33.25
523.15	27.80	26.27*	24.73*	23.2	24.66	27.15	28.90
533.15	33.80	16.50*	22.00*	20.75	24.20	24.44	25.44
538.15	43.86	16.50*	22.00*	20.75	22.72	22.08	17.97
540.15	46.71	16.50*	22.00*	20.75	20.29	18.60	
541.15	47.75	16.50	22.00	20.75	18.68		
543.15	49.23	14.40	20.10	18.50	17.49		
548.15	51.40	16.50	17.34	17.36	9.05		
573.15	77.50	15.60	13.40	11.85			

* indicates the data are interpolated by the method described in Table 9. Other data in the table are obtained by using the experimental CO_2 solubility reported by Tödheide and Franck, 1963.

Table 5. Parameter values used in Henry's constant determination (Eq. (3)).

P / bar	T / K	a	b	c	d
1-2	273.15-363.15	$2.77716 \cdot 10^2$	$-3.62801 \cdot 10^2$	$5.77716 \cdot 10^1$	$3.00135 \cdot 10^2$
2-2000	273.15-573.15	7.25021	$1.15385 \cdot 10^1$	$-1.51174 \cdot 10^1$	$-3.05448 \cdot 10^1$

Table 6. Parameter values used in Eq. (13).

Parameters	a_1	a_2	a_3
λ_{nn}	$-1.6662 \cdot 10^{-01}$	$4.9482 \cdot 10^{-04}$	$-5.1643 \cdot 10^{-07}$
μ_{nnn}	$8.9196 \cdot 10^{-02}$	$-2.8829 \cdot 10^{-04}$	$2.3197 \cdot 10^{-07}$

The units of parameters a_1, a_2, a_3 for λ_{nn} are kg mol^{-1} , $\text{kg mol}^{-1} \text{K}^{-1}$, $\text{kg mol}^{-1} \text{K}^{-2}$, respectively and for μ_{nnn} are $\text{kg}^2 \text{mol}^{-2}$, $\text{kg}^2 \text{mol}^{-2} \text{K}^{-1}$, $\text{kg}^2 \text{mol}^{-2} \text{K}^{-2}$, respectively.

Table 7. The Pitzer triple-ion interaction parameter ($\xi_{nca} / \text{kg}^2 \text{mol}^{-2}$) for the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system at temperatures from 323.15 to 423.15 K and molal NaCl(aq) concentrations from 1 to 6 mol kg^{-1} .

T / K	$\text{NaCl molality (mol kg}^{-1}\text{)}$					
	1	2	3	4	5	6
298.15	0.01617*	0.00250*	-0.00111*	-0.00289*	-0.00390*	-0.00450*
323.15	0.01213	0.00218	-0.00079	-0.00238	-0.00334	-0.00395
373.15	0.00420	0.00161	-0.00012	-0.00133	-0.00221	-0.00285
423.15	0.04899	0.02003	0.00950	0.00466	0.00208	0.00062
473.15	0.09379*	0.03845*	0.01921*	0.01065*	0.00638*	0.00409*
523.15	0.13858*	0.05687*	0.02888*	0.01664*	0.01067*	0.00755*
573.15	0.18337*	0.07529*	0.03854*	0.02263*	0.01496*	0.01102*

*Indicates the data interpolated at 150 bar and the corresponding temperatures (T / K) by the method described in Table 9.

Table 8. The mixing rule binary interaction parameter, $k_{\text{CO}_2-\text{H}_2\text{O}}$ (dimensionless), determined from experimental H_2O solubility in the CO_2 -rich phase.

(a) $T < 473.15$ K										
T / K	273.15	288.15	298.15	304.19	313.15	323.15	348.15	373.15	423.15	473.15
$k_{\text{CO}_2\text{--H}_2\text{O}}$	-25	-20.5	-17	-14.3	-11.5	-9	-5.6	2.1	1.9	0.32

(b) $T \geq 473.15$ K												
T / K	473.15	523.15	533.15	538.15	540.15	541.15	543.15	548.15	573.15			
P / bar	$k_{\text{CO}_2\text{--H}_2\text{O}}$											
200	0.436	-0.065	-0.235	-0.247	-0.255	-0.273	-0.291	-0.312	-0.272			
300	0.548*	0.025*	-0.050*	-0.070*	-0.070*	-0.078	-0.085	-0.095	-0.226			
400	0.646*	0.098*	0.037*	-0.012*	-0.009*	-0.008	-0.019	-0.045	-0.215			
500	0.698	0.136	0.056	0.003	0.001	-0.013	-0.032	-0.081	-0.324			
600	0.697*	0.118*	0.036*	-0.020*	-0.031*	-0.058	-0.092	-0.160				
700	0.692*	0.089*	-0.002*	-0.070*	-0.090*	-0.124	-0.164	-0.252				
800	0.685*	0.060*	-0.051*	-0.125*	-0.158*	-0.192	-0.242	-0.366				
900	0.674*	0.034*	-0.098*	-0.172*	-0.218*	-0.251	-0.308	-0.492				
1000	0.660	0.015	-0.138	-0.211	-0.265	-0.307	-0.375	-0.679				
1100	0.644*	0.003*	-0.174*	-0.248*	-0.307*	-0.359	-0.450					
1200	0.627*	-0.004*	-0.207*	-0.284*	-0.349*	-0.413	-0.537					
1300	0.608*	-0.010*	-0.235*	-0.320*	-0.392*	-0.473	-0.674					
1400	0.595*	-0.014*	-0.259*	-0.357*	-0.438*	-0.536						
1500	0.590	-0.019	-0.278	-0.396	-0.491	-0.627						
2000	0.643	-0.042	-0.314	-0.609								

* Indicates the data interpolated by the method described in Table 9. At $T < 473.15 \text{ K}$, the values of $k_{\text{CO}_2-\text{H}_2\text{O}}$ were evaluated using experimental data of Weibe and Gaddy (1941), Malinin (1959), Tödheide and Franck (1963), Müller *et al.* (1988), King *et al.* (1992). At $T > 473.15 \text{ K}$, the values of $k_{\text{CO}_2-\text{H}_2\text{O}}$ were evaluated using experimental data of Tödheide and Franck (1963).

Table 9. The components, key parameters, approaches and limitations of the CO₂ solubility model presented in this study.

No.	Model Components	Description	Sources of Components	Applicable P - T range	Ref.
1	RK EoS	A modified RK EoS was selected to calculate fugacities of CO ₂ and H ₂ O in the CO ₂ -rich phase in the CO ₂ solubility model.	Spycher and Pruess (2003)	273.15-573.15K 1-2000 bar	Eqs. (A1), (A5)
2	Mixing rule	The two-parameter mixing rule for polar molecules was used.		273.15-573.15K 1-2000 bar	Eqs. (14), (A3), A4
3	$k_{H_2O-CO_2}$	Mixing rule binary interaction parameter $k_{H_2O-CO_2}$ for the CO ₂ -H ₂ O system was given by Spycher and Pruess (2003).	Panagiotopoulos and Reid (1986)	273.15-573.15K 1-2000 bar	-
4	$\varphi_{H_2O}, \varphi_{CO_2}$	Fugacity coefficients of H ₂ O and CO ₂ for the CO ₂ -rich phase were calculated using equations provided by Spycher and Pruess (2003) and Panagiotopoulos and Reid (1986).		273.15-573.15K 1-2000 bar	Eq. (A5)
5	$k_{CO_2-H_2O}$	Approach to obtain the $k_{CO_2-H_2O}$ was purely empirical. At $T > 473.15$ K, the $k_{CO_2-H_2O}$ was determined using experimental data of Tödheide and Franck (1963) for the CO ₂ -rich phase. At $273.15 < T < 473.15$ K, $k_{CO_2-H_2O}$ was evaluated using experimental data of Wiebe and Gaddy (1941), Müller <i>et al.</i> (1988), and King <i>et al.</i> (1992).	Fitted in this study	273.15-573.15K 1-2000 bar	Table 8
6	Interpolation methods used to calculate $k_{CO_2-H_2O}$ at any targeted P - T	1. At 273.15 K $< T < 473.15$ K, $k_{CO_2-H_2O}$ was considered as only temperature-dependent. A cubic spline interpolation with a step of 1 K was used to get the relationship between $k_{CO_2-H_2O}$ and temperature (T). 2. At $T > 473.15$ K, $k_{CO_2-H_2O}$ was treated as a function of both T and pressure (P). A cubic spline interpolation with a step of 1 bar was used to get the relationship between $k_{CO_2-H_2O}$ and P at a constant T , then the linear interpolation was applied to calculate $k_{CO_2-H_2O}$ at any targeted P - T point.	Fitted in this study	273.15-573.15K 1-2000 bar	Table 8
7	Henry's law constant	We have fitted Henry's law constant separately for two distinct regions: 1. The Henry's law constant for low pressures ($P < 2$ bar and temperatures of 273.16-363.15 K); 2. The Henry's law constant fitted by this work (the remaining P - T region). By fitting the Henry's constant specific for low P conditions, the model calculated error at low pressures (<i>e.g.</i> 1.013 bar) can be reduced dramatically from ~5% to ~1%. Thus, it is worthwhile to include two distinct Henry's constant for two P regions in the model. The detailed data fitting procedure is provided in Figure 8.	Fitted in this study	273.15-573.15K 1-2000 bar	Eq. (3) Fig. 8 Fig. 6.
8	$\varphi_w^s, P_s, v_s, \epsilon_r, \rho_{H_2O}$	The fugacity coefficient, vapor pressure, molar volume, and density of pure water were computed using IAPWS-95 EoS. The relative permittivity was calculated by equation given by Fernández <i>et al.</i> (1997) in order to compute the Debye-Hückel slope in the Pitzer's activity model.	Wagner and Prüss (2002) Fernández <i>et al.</i> (1997)	238.15-873.15 K, 0.1-12000 bar for ϵ_r , the others 251.15-1273.15 K 0.1-10000 bar	Eqs. (1), (2)
9	$\bar{v}_{CO_2}$	Our approach to obtain $\bar{v}_{CO_2}$ was purely empirical. The experimental CO ₂ solubility data given by Tödheide and Franck (1963) were used to determine the values of $\bar{v}_{CO_2}$. The calculated CO ₂ solubility is not sensitive to $\bar{v}_{CO_2}$ at low pressures (<i>e.g.</i> $P < 300$ bar), but it has a significant influence in predicting CO ₂ solubility in the aqueous phase at high	Fitted in this study	273.15-573.15K 1-2000 bar	Table 4

		pressures (e.g. $P > 1000$ bar).			
10	Interpolation methods used to get $\bar{v}_{\text{CO}_2}$ at targeted P - T	At a given P - T point, the $\bar{v}_{\text{CO}_2}$ can be obtained by: (1) using the cubic spline interpolation to get the relationship between $\bar{v}_{\text{CO}_2}$ and P at a constant T ; (2) and then applying the linear interpolation of T to get the $\bar{v}_{\text{CO}_2}$ at any targeted P - T point.	Fitted in this study	273.15-573.15K 1-2000 bar	Table 4
11 ^(a)	Pitzer activity model	The Pitzer activity model was incorporated into the CO ₂ solubility model. The benefits of incorporating the Pitzer activity model are: 1. Calculate phase equilibria of the CO ₂ -H ₂ O and CO ₂ -NaCl-H ₂ O system in a larger P - T region than previously developed models (Spycher and Pruess, 2010; Akinfiev and Diamond, 2010; Duan <i>et al.</i> , 2006); 2. Provide a higher accuracy than some of previously developed models (Spycher and Pruess, 2010; Duan <i>et al.</i> , 2006); 3. The model can be extended to other aqueous systems such as CaCl ₂ (aq), MgCl ₂ (aq), Na ₂ SO ₄ (aq) and KCl(aq).	Fitted in this study	273.15-573.15K 1-2000 bar	Eqs. (A6)-(A7) Eqs. (7)-(10)
12	λ_{nn}, μ_{nnn}	The Pitzer pure neutral components interaction parameters were determined in this study by using the CO ₂ solubility data in pure water at elevated T s and P s. The detailed data fitting procedure and experimental data references are provide in Figure 8.	Fitted in this study	273.15-573.15K Not sensitive to pressure	Eq. (13) Table 6 Fig. 8
13 [*]	$\beta_{ca}^{(0)}, \beta_{ca}^{(1)}, C_{ca}$	The Pitzer binary ion-ion interaction model were taken from Pitzer <i>et al.</i> (1984).	Pitzer <i>et al.</i> (1984)	273.15-573.15K 1-1000 bar 0-6 mol kg ⁻¹ NaCl	-
14 ^(b)	$B_{\text{CO}_2-\text{NaCl}}, C_{\text{CO}_2-\text{CO}_2-\text{NaCl}}$	The combined Pitzer interaction parameters depend on T and NaCl concentration. They were taken from Akinfiev and Diamond (2010)	Akinfiev and Diamond (2010)	273.15-373.15K Not sensitive to pressure	Eqs. (A10)-(A11) Table A1
15	ξ_{nca}	Pitzer's triple-ion interaction parameter ξ_{nca} was purely determined from our experimental data at 323.15, 373.15, 423.15 K, and can be extrapolated to any temperature from 273.15 to 573.15 K. No other experimental data listed in Table 13 for the CO ₂ -NaCl-H ₂ O system were used to fit this parameter. A cubic spline interpolation with a step of 0.001 mol kg ⁻¹ NaCl was used to get the relationship between ξ_{nca} and NaCl molal concentration at a constant T , then the linear interpolation was applied to calculate ξ_{nca} at any targeted P - T - x point. The model can accurately reproduce experimental data which are not used in the data fitting procedure.	Fitted in this study	273.15-373.15K Not sensitive to pressure	Table 7.
16	Phase equilibria calculations	The phase equilibria equations were solved by using the Netwon-Raphson method. There are two iteration loops: the inner loop solves the CO ₂ solubility in aqueous phase (m_{CO_2}); the outer loop solves the H ₂ O solubility in the CO ₂ -rich phase ($y_{\text{H}_2\text{O}}$) based on the inner loop results m_{CO_2} .	Calculated in this study	273.15-573.15K 1-2000 bar	Eqs. (1-10) Fig. 7

^(a)The Pitzer model for the CO₂-H₂O system was confirmed at pressures up to 2000 bar and temperatures up to 573.15 K using experimental data of Tödheide and Franck (1963)

^(b) $B_{\text{CO}_2-\text{NaCl}}$ and $C_{\text{CO}_2-\text{CO}_2-\text{NaCl}}$ were determined by Akinfiev and Diamond (2010) at the temperatures from 273.15-373.15 K, these parameters were used in Eq. (A6) to calculate the activity coefficient of the dissolved CO₂ in the aqueous phase. In this study, any uncertainties caused by these parameters at the temperature above 373.15 K is absorbed by triple-ion interaction parameter ξ_{nca} during the data fitting process.

Table 10. The average absolute deviation (AAD %) of CO₂ solubility in the aqueous phase between model calculations and the selected reliable experimental data over a wide *P-T-x* range (25-2000 bar, 288.15-573.15 K, and 0-6 mol kg⁻¹ NaCl). The values in parentheses represent the number of experimental data points evaluated by each model.

Ref. No.# ^(a)	$N_p^{(b)}$	P / bar	T / K	m_{NaCl} / mol kg ⁻¹	Model deviation from experimental data, AAD %					
					This study	OLI ^(c)	AD2010	SP2010	DS2006	MZLL2013
1	21	150	323.15-423.15	0-6	0.74(21)	2.91(21)	1.47(15)	2.35(21)	3.84(15)	0.91(21)
2	29	25-709	323.15-373.15	0	1.90(29)	3.05(29)	1.82(29)	1.70(25)	1.66(29)	2.55(29)
3	32	48	298.15-423.15	0-5.91	1.86(32)	4.64(32)	1.48(28)	1.95(32)	1.74(28)	2.04(28)
4	63	1-100	313.15-433.15	4-6	1.62(63)	4.63(63)	1.46(38)	5.53(63)	3.37(35)	2.09(35)
5	27	1.013	288.15-308.15	0.45-5.73	1.83(27)	3.97(27)	2.65(27)	2.59(27)	2.82(23)	2.09(24)
6	78	200-2000	323.15-573.15	0	1.51(78)	9.98(56)	1.07(6)	3.94(35)	6.27(30)	7.03(69)
Overall AAD % (No.1-No.5)					1.59(172)	3.84(172)	1.78(137)	2.82(168)	2.67(130)	1.94(137)
Overall AAD % (No.1-No.6)					1.58(250)	4.86(228)	1.66(143)	3.01(203)	3.28(160)	2.79(206)
Total data coverage rate by each model (N/N_p)					100%	91%	57%	81%	64%	82%

^(a)1. This study; 2. Wiebe and Gaddy (1939); 3. Malinin and Savelyeva (1972), Malinin and Kurovskaya (1975); 4. Rumpf *et al.* (1994); 5. Yasunishi and Yoshida (1979); 6. Tödheide and Franck (1963).

^(b)*N_p* is the total number of experimental data located in the targeted *P-T* range (*P*: 1-2000 bar, *T*: 298.15-573.15 K).

^(c)Calculations made by OLI are under the following conditions: (1) enable the second liquid phase, (2) use MSE model, (3) stream inflows contains 55.5082 mol water and 15 mol CO₂.

Table 11. The average absolute deviation (AAD %) of the H₂O solubility in the CO₂-rich phase between model calculations and the selected reliable experimental data at 1-2000 bar and 278.15-573.15 K. The numbers noted parenthetically represent the number of experimental data points evaluated by the model.

Ref. No.#	References	$N_p^{(a)}$	P / bar	T / K	Model deviations from experimental data, AAD %	
					This study	OLI ^(c) SP2010
1	Valtz <i>et al.</i> (2004)	30	4-80	278.15-318.15	11.88(30)	11.80(30) 12.06(27)
2	Müller <i>et al.</i> (1988)	49	3-80	373.15-473.15	6.88(49)	5.20(49) 4.85(49)
3	Wiebe and Gaddy (1941)	39	1-709	298.15-348.15	7.88(16) ^(b)	5.85(16) ^(b) 5.67(16) ^(b)
4	Tödheide and Franck (1963)	78	200-2000	323.15-573.15	4.11(78)	13.43(12) ^(b) 6.18(31) ^(b)
Overall AAD % (No.1-No.3)					8.88(95)	7.62(95) 7.53(92)
Overall AAD % (No.1-No.4)					7.69 (173)	9.07(107) 7.19(123)
Total data coverage rate by each model (N/N_p)					88%	55% 63%

^(a) N_p is the total number of experimental data located in the targeted P - T range (1-2000 bar and 273.15-573.15 K).

^(b)The data points which AAD is larger than 20 % were not included in the comparison.

^(c)Calculations using made by OLI are under the following conditions: (1) enable the second liquid phase, (2) use MSE model, (3) stream inflows contains 55.5082 mol water and 15 mol CO₂.

Table 12. The average absolute deviation (AAD %) of calculated CO₂ solubility (mol kg⁻¹) in aqueous phase from experimental data for the CO₂-H₂O system at temperatures of 273.15-573.15 K and pressures of 1-2000 bar: Comparison between this model and the MZLL2013 model.

No.	References	P / bar	T / K	N	AAD % (This model)	AAD % ^(e) (MZLL2013)
1	Wiebe and Gaddy, 1939	25-709	323.15-373.15	29	1.82	2.72
2	Prutton and Savage, 1945	23-654	373.15-393.15	26	5.27	6.96 ^(f)
3	Malinin S.D. 1959	98-490	473.15-573.15	16 ^(a)	5.30	2.28
4	Ellis and Golding, 1963	25-200	450.15-538.15	10	9.16	3.50
5	Tödeheide and Franck, 1963	200-2000	323.15-573.15	78	1.51	7.03(4.51) ^(b)
6	Takenouchi and Kennedy, 1964	100-1500	383.15-573.15	96	7.06	5.28 ^(f)
7	Takenouchi and Kennedy, 1965	100-1400	423.15-573.15	35	4.90	5.18
8	Stewart and Munjal, 1970	10.1-45.6	273.15-298.15	12	11.06	10.85
9	Malinin and Savelyeva, 1972	48	298.15-348.15	3 ^(a)	1.51	1.53 ^(f)
10	Malinin and Kurovskaya, 1975	48	298.15-423.15	3 ^(a)	1.60	3.24 ^(f)
11	Drummond S.E., 1981	40-180	303.15-573.15	50	5.00	9.01 ^(f)
12	Cramer, 1982 ^(c)	8-58	306.15-486.25	7	3.89	7.28 ^(c)
13	Briones <i>et al.</i> , 1987	68-177	323.15	7	3.12	2.30
14	Nakayama <i>et al.</i> , 1987	36.3-109.9	298.25	6	4.06	4.11
15	D'Souza <i>et al.</i> , 1988	101-152	323.15-348.15	4	4.73	5.07
16	Müller <i>et al.</i> , 1988 ^(d)	3-81	373.15-473.15	49	3.11	3.27
17	Nighswander <i>et al.</i> , 1989	23-102	353.15-473.15	33	5.40	6.16
18	Sako <i>et al.</i> , 1991	100-200	348.15-423.15	7	6.79	7.31
19	King <i>et al.</i> , 1992	60-243	288.15-298.15	27	1.87	1.40
20	Mather and Franck, 1992	1614-1692	500.15-533.15	6	5.45	-
21	Dohrn <i>et al.</i> , 1993	101-301	323.15	3	1.87	1.16
22	Rumpf <i>et al.</i> , 1994	11-58	323.15	7	0.65	1.64 ^(f)
23	Teng <i>et al.</i> , 1997	64.4-294.9	278.05-293.05	24	4.29	3.85
24	Gu, 1998	17.1-58.3	304.19-313.15	10	2.78	3.20
25	Dhima <i>et al.</i> , 1999	100-1000	344.15	7	5.37	5.03
26	Bamberger <i>et al.</i> , 2000	40-140	323.15-353.15	29	1.61	1.45
27	Teng and Yamasaki, 2002	75-300	298.05	6	0.44	0.89
28	Bando <i>et al.</i> , 2003	100-200	303.15-333.15	12	2.31	2.76
29	Chapoy <i>et al.</i> , 2004	1.9-93.3	273.85-351.35	27	2.76	3.02
30	Valtz <i>et al.</i> , 2004	5-80	278.15-318.15	47	4.19	4.65

31	Li <i>et al.</i> , 2004	33.4-198.9	332.15	6	3.09	7.24
32	Koschel <i>et al.</i> , 2006	20.6-194.7	323.15-373.15	8	2.97	3.72
33	Qin <i>et al.</i> , 2008	106-499	323.65-375.75	7	3.07	3.77
34	Ferrentino <i>et al.</i> , 2010	75-150	313.05	4	2.41	0.87
35	Han <i>et al.</i> , 2011	3.8-20.2	313.05-333.05	15	5.71	5.69 ^(f)
36	Liu <i>et al.</i> , 2011	20-160	308.15-328.15	31	1.70	1.67
37	Yan <i>et al.</i> , 2011	50-400	323.15-413.15	18	2.33	3.39 ^(f)
38	Hou <i>et al.</i> , 2013	25-175	283.15-448.15	42	7.74	7.49 ^(f)
39	Tong <i>et al.</i> , 2013	72-273	374.15	5	2.08	5.06 ^(f)
40	Serpa <i>et al.</i> , 2013	1.3-4.1	298.15-323.15	9	6.04	5.32 ^(f)
41	This work	100-150	323.15-423.15	4	0.39	0.76 ^(f)
Overall				825	3.81	4.18(4.11)

N is the number of data points evaluated by this model.

^(a)The repeated measurements were counted as 1 datum.

^(b)AAD=4.51% is calculated by Mao *et al.* (2013) using 39 experimental data points given by Tödheide and Franck (1963). We report the calculate AAD=7.03 for the MZLL2013 model by using 69 experimental data points from Tödheide and Franck (1963) within the P - T range of 1-1500 bar and 273.15-573.15 K.

^(c)Cramer's (1982) data are compared with our model calculated values using a modified Henry's law constant defined by $k = \varphi_{\text{CO}_2} P_{\text{CO}_2} / x_{\text{CO}_2}$.

^(d)The experimental data were taken from a large data compilation given by Scharlin (1996).

^(e)Taken from Mao *et al.* (2013).

^(f)Calculated by using the MZLL2013 model.

Table 13. The average absolute deviation (AAD %) of the calculated CO₂ solubility (molality) in the aqueous phase from experimental data for the CO₂-NaCl-H₂O system at 273.15-573.15 K, 1-1400 bar and 0-6 mol kg⁻¹ NaCl: Comparison between this model and the MZLL2013 model

No.	References	P / bar	T / K	m _{NaCl} / mol kg ⁻¹	N	AAD % (This model)	AAD % (MZLL2013)
1 ^(a)	Setchenow, 1892	1.013	288.35	0.225-6.088	9	3.47	2.09 ^(e)
2	Markham and Kobe, 1941	1.013	273.35-313.15	0.1-4	15	3.71	3.66 ^(f)
3	Harned and Davis, 1943	1.013	273.15-323.15	0.2-3	55	2.65	3.14 ^(f)
4	Ellis and Golding, 1963	54-210.1	449.15-603.15	0.5-2	29	4.19	4.48 ^(f)
5	Yeh and Peterson, 1964	1.013	298.15-318.15	0.15	4	1.69	5.83 ^(f)
6	Takenouchi and Kennedy, 1965 ^(b)	100-1400	423.15-673.15	1.09-4.28	55	13.81 ^(b)	5.18 ^(f)
7	Onda, <i>et al.</i> , 1970	1.013	298.15	0.51-3.21	8	1.72	2.90 ^(f)
8	Malinin and Savelyeva, 1972 ^(c)	48	298.15-348.15	0.36-4.46	13	1.57	1.19 ^(e) (4.62) ^(f)
9	Malinin and Kurovskaya, 1975 ^(c)	48	298.15-423.15	1-5.91	13	2.18	2.20 ^(e) (7.18) ^(f)
10	Yasunishi and Yoshida, 1979 ^(c)	1.013	288.15-308.15	0.45-5.73	27	1.82	2.09 ^(e) (6.63) ^(f)
11	Drummond, 1981	34-387.6	292.85-673.15	1-6.3	339	5.73	6.62 ^(f)
12 ^(a)	Burmakina, <i>et al.</i> , 1982	1	298.15	0.001-0.2	8	1.34	1.67 ^(g)
13	Cramer, 1982 ^(d)	8-62	296.75-511.75	0.5-1.95	13	9.55	12.74 ^(e)
14	Nighswander <i>et al.</i> , 1989	21-100	353.15-473.65	0.173	34	5.56	6.28 ^(f)
15	Rumpf <i>et al.</i> , 1994	4.67-96.37	313.15-433.15	4-6	63	1.62	2.09 ^(f)
16 ^(a)	Vázquez <i>et al.</i> , 1994	1.013	298.15-308.15	0.69-2.9	20	1.52	2.78 ^(f)
17	Gu, 1998	17.7-59.0	303.15-323.15	0.5-2.0	60	6.55	5.66 ^(f) (4.05) ^(f)
18	Kiepe <i>et al.</i> , 2002	1-100.61	313.15-353.15	0.52-4.34	64	5.15	5.78 ^(f)
19	Bando <i>et al.</i> , 2003	100-200	303.15-333.15	0.17-0.53	36	1.02	2.30 ^(f)
20	Koschel <i>et al.</i> , 2006	51-202.4	323.15-373.15	1-3	14	5.19	4.50 ^(f)
21	Kim <i>et al.</i> , 2008	101-201	278.9-280.4	1	6	4.87	7.09 ^(e)
22	Ferrentino <i>et al.</i> , 2010	100-150	313	0.17	2	2.57	2.89 ^(f)
23	Liu <i>et al.</i> , 2011	21-158.3	318.15	1.9	8	3.62	4.84 ^(f)
24	Yan <i>et al.</i> , 2011	50-400	323.15-413.15	1-5	36	3.80	3.73 ^(f)
25	This study	150	323.15-423.15	1-6	18	0.78 ^(d)	1.06 ^(e)
Overall					949	3.83	4.11(4.62)

N is the number of evaluated data points for each experimental work.

^(a)Experimental data taken from a large data compilation given by Scharlin (1996)

^(b)The experimental data reported by Takenouchi and Kennedy (1965) has a large uncertainty when compared with our model.

^(c)Cramer's (1982) experimental CO₂ solubility is expressed in terms of a modified Henry's constant therefore the value computed from Mao *et al.*'s (2013) model could not be used for a direct comparison to the experimental data given by Cramer's (1982). We have converted Cramer's data to molality using our model and then make comparison with the calculated results of Mao *et al.*'s (2013) results.

^(d)The number differs from Table 7 due to the removal of the computed results for the CO₂-H₂O system.

^(e)Calculated by using the MZLL2013 model.

^(f)Taken from Mao *et al.* (2013).

Table A1. Parameter values used in Eq. (A10-A11)

Eqs.	a_1	a_2	a_3	a_4
A10	$5.7123 \cdot 10^{-2}$	$2.6994 \cdot 10^{-02}$	$4.5635 \cdot 10^{-02}$	-
A11	-	-	-	$-5.76 \cdot 10^{-04}$