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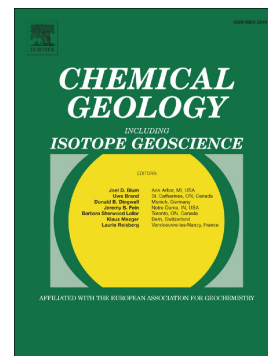
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An improved model for CO₂ solubility in aqueous Na⁺–Cl[–]–SO₄^{2–} systems up to 473.15 K and 40 MPa

Pedro F. dos Santos[†], Laurent Andre^{§,‡}, Marion Ducouso^{†,*}, Arnault Lassin[§], François Contamine[†],
Adeline Lach[§], Marc Parmentier[¶] and Pierre Cézac[†]

[†] Université de Pau et des Pays de l'Adour, E2S UPPA, LaTEP, Pau, France.

[§] BRGM, Water, Environment, Process Development and Analysis Division, 3 avenue Claude Guillemin, 45060 Orléans Cedex, France.

[‡] ISTO, UMR7327, Université d'Orléans, CNRS, BRGM, 45071 Orléans, France.

[¶] BRGM Haut-de-France, Arteparc Bâtiment A, 2 rue des Peupliers, 59810 Lesquin, France.

ABSTRACT

This article contributes to the development of a thermodynamic model for simulating CO₂ solubility in pure water and aqueous brines under different conditions of temperature, pressure and ionic strength. The modeling activity-fugacity (γ - ϕ) approach allows calculating CO₂ solubility, based on the Pitzer electrolyte theory for activity coefficient and Peng-Robinson's equation of state for fugacity. The present work proposes a new set of Pitzer interaction parameters through the set of CO₂ solubility data in saline systems such as CO₂-H₂O-NaCl and CO₂-H₂O-Na₂SO₄. The determined model is capable of covering a wide $T - P - I$ range (273.15–473.15 K, 0.1–40 MPa and 0–6 meq/kg). Average absolute deviation of CO₂ solubility is about 5% compared to a large number of experimental data available (more than 700 data analyzed). New experimental solubility data for the CO₂-H₂O-NaCl-Na₂SO₄ system were also acquired in this study (303.15–423.15 K, 1.5–20 MPa and 0–6 mol/kg) to test the model's capacity: it is able to describe the CO₂ solubility in aqueous salt mixtures without any further optimizations of interaction parameters.

Keywords: CO₂ solubility – thermodynamic modeling – Pitzer interaction parameters - activity coefficient

1. INTRODUCTION

Studies related to the determination of the aqueous solubility of carbon dioxide for capture and geological storage of CO₂ applications, have been investigated in the last years (Benson and Cole, 2008; Eiken et al., 2011; Farret et al., 2017; TORP and GALE, 2003). This acquisition of solubility data is of immense importance for the characterization and better understanding of the complex chemical behavior of these systems (aquifers with different salt compositions, temperature and pressure). When many published studies have focused on the characterization of the solubility of CO₂ in pure water, only few studies were interested in the CO₂ solubility in aqueous electrolyte solutions

(dos Santos et al., 2020). Most of these studies were carried out on NaCl aqueous solutions and, to a much lesser extent to other salts such as CaCl_2 , Na_2SO_4 , KCl and MgCl_2 . They have contributed to enriching significantly the variety of experimental data (dos Santos et al., 2020; Lara Cruz et al., 2020; Messabeh et al., 2017; Poulain et al., 2019; Tong et al., 2013; Zhao et al., 2015b). These data are extremely important for the improvement of high quality thermodynamic and geochemical models capable of simulating and predicting the CO_2 solubility in pure water or in aqueous brine solutions under different conditions of temperature, pressure and salt concentration (Duan et al., 2006; Duan and Sun, 2003; Li and Duan, 2007, 2011; Shi and Mao, 2017; Springer et al., 2012). The improvement of these models depends directly on the available set of experimental data.

There is a wide range of thermodynamic models for the solubility of CO_2 in pure water and in aqueous brine solutions, but few use the Pitzer semi-empirical model, which was developed to calculate the properties of the electrolyte-rich liquid phases, such as water activity and activity coefficients of aqueous species. The Pitzer model proved to be one of the best for determining the activity coefficients in solutions rich in salts, so much so that it serves as the basis for many thermodynamic models (Duan et al., 2006; Duan and Sun, 2003; Mao et al., 2013; Springer et al., 2012; Zhao et al., 2015a, 2015b, 2015c). Duan and Sun (2003) and Duan et al. (2006) proposed a model that can predict CO_2 solubility in pure water, single-salt solutions and mixed salt-solutions with a concentration of up to 4.3 mol/kg (moles of salt per kilogram of water), for temperatures between 273 and 533 K and for pressures between 0 and 200 MPa. Duan's model is able to predict with great precision the solubility of CO_2 in aqueous solutions of NaCl, MgCl_2 and CaCl_2 . However, large deviations are found (deviations of up to 29 %) in systems containing SO_4^{2-} . Spycher and Pruess (2010) established one similar activity expression as Duan and Sun (2003) did, with simplifications for salts other than NaCl, producing deviations similar to Duan, as pointed out by Zhao et al. (2015b). Based on The Pitzer equation, Alifiev and Diamond (2010) worked only with the CO_2 - H_2O -NaCl system, covering a limited temperature range between 251-373 K, with some high deviations from the literature. Li and Duan (2011) presented a model capable of predicting CO_2 solubility in CO_2 - H_2O -NaCl- CaCO_3 - CaSO_4 systems at temperatures from 273 to 523 K, pressures from 0.1 to 100 MPa and NaCl concentrations until saturation - using the interaction parameter CO_2 - Na^+ proposed by Duan and Sun (2003) as a basis. Springer et al. (2012) proposed a model based on the Mixed-Solvent Electrolyte (MSE) framework that has an extensive validity of temperature and pressure (up to 573 K and 400 MPa). However, it does not applied to systems containing aqueous Na_2SO_4 . Mao et al., 2013 developed a model similar to Duan's for aqueous systems containing NaCl only, but increasing the temperature range by up to 723 K. Zhao et al. (2015b) and Zhao et al. (2015c) proposed a fugacity-activity model for predicting CO_2 solubility in aqueous systems containing NaCl, CaCl_2 , KCl, MgCl_2 and Na_2SO_4 . The model covers a range of $T - P - m_{\text{salt}}$ from 288 to 523 K, from 0.1 to 150 MPa and up to salinities close to saturation, respectively. In summary, despite the high quality of the models

described above, there are still gaps in their ability to cover the wide range of temperatures and chemical compositions of aqueous brines that are encountered in natural deep media targeted for CO₂ geological storage applications. These gaps concern mostly CO₂ solubility in single-salt aqueous systems containing either Na₂SO₄, CaCl₂, or MgCl₂ electrolytes near saturation, and in salt mixtures. This means that new developments are still needed to fill these gaps in order to make the model predictions more reliable and, thus, more useful to industrial operators.

In this study, we report the development of a model to calculate the solubility of CO₂ in pure water and in aqueous NaCl and Na₂SO₄ solutions with temperatures up to 473.15 K, pressures up to 40 MPa and salt concentrations near the saturation. Because of the high salinity of the solutions, the Pitzer formalism is applied. We determined a new set of interaction parameters to address the chemical behavior of CO₂-H₂O-salt systems. All the calculations were performed with the PhreeSCALE geochemical simulation software (Lach et al., 2016). This code is an extension of the well-known PHREEQC code widely used by the geochemist community (Appelo, 2015; Appelo et al., 2014; Parkhurst and Appelo, 2013). Like PHREEQC, PhreeSCALE is capable of calculating water properties of brines like activity coefficients of aqueous species and activity of water according to the Pitzer formalism. The originality of PhreeSCALE is that it was developed to add calculation capabilities regarding the thermal (apparent relative molar enthalpy and heat capacity) and volumetric (density) properties of brines in a consistent theoretical framework based on Pitzer's equations (Lach et al., 2017b). The software also uses the standard properties of solutes computed from the HKF theory (Helgeson et al., 1981; Tanger and Helgeson, 1988), which is widely acknowledged by the geochemists community. The input files are similar for the two codes, only some additional output keywords are declared in PhreeSCALE to write the corresponding properties in the output files (Lach et al., 2016). The thermodynamic database is regularly increasing with new chemical systems and it is available on demand (André et al., 2020).

For the estimation of specific interaction parameters, a selection of experimental data was made first. The PhreeSCALE software allows calculating CO₂ solubility using an activity-fugacity ($\gamma - \phi$) approach. By combining the use of PhreeSCALE with that of the PEST software (Doherty, 2004), a software designed for parameter estimation, the interaction parameters of the Pitzer activity coefficient model can be determined. This method was applied in the present work to determine a new set of binary interaction parameters, capable of accurately simulating the solubility of CO₂ in pure water and in solutions of NaCl and Na₂SO₄, for concentrations close to saturation. More than 1200 experimental data were evaluated and compared in this study, the average absolute deviations (AAD) were calculated, covering a wide range of temperatures (from 273 to 473.15 K) and of pressures (from 0.1 to 40 MPa).

Experimental solubility data for the $\text{CO}_2\text{-H}_2\text{O-NaCl-Na}_2\text{SO}_4$ system were also acquired to test the model's capacity to describe the CO_2 solubility in aqueous salt mixtures. A mixture of 3 mol NaCl/kg and 1 mol Na_2SO_4 /kg was prepared and CO_2 solubility data were acquired for pressures between 1.5 and 20 MPa, and temperatures at 303.15, 323.15, 373.15 and 423.15 K. The experimental methodology used was previously proposed by dos Santos et al. (2020). The model was also tested and the AAD calculated with the acquired experimental data without any further optimization.

2. REVIEW OF EXPERIMENTAL DATA FOR CO_2 SOLUBILITY

2.1. IN PURE WATER

The topic of CO_2 solubility in pure water is widely treated in the literature since more than 100 references were found; representing about 1990 experimental data (Supplementary Data). Some of them concern low CO_2 pressures (≤ 0.1 MPa), and they are not considered in this study. A selection was done to check the consistency of the data, according to temperature and pressure ranges. At last, about 650 data were selected and used to determine the thermodynamic and the Pitzer interaction parameters necessary to model both the solubility of CO_2 in pure water and the chemical properties of dissolved CO_2 .

2.2. $\text{CO}_2\text{-H}_2\text{O-NaCl}$ SYSTEM

The CO_2 solubility in aqueous systems containing NaCl has not been studied as much as in pure water; however, there is already a large number of studies that started to work with this electrolyte. The presence of salts in aqueous systems decreases the solubility of the gas. In this way, the CO_2 solubility is reduced by increasing the temperature and the salt concentration. Several studies covering extensive ranges of $T - P - m_{\text{salt}}$ have been carried out, but many are at low salt concentrations or in pressure ranges not so high. Yet, the number of studies has increased over the years and, today a lot of experimental CO_2 solubility data are available up to salinity values close to NaCl saturation (Table 1).

Table 1

Experimental data for the $\text{CO}_2\text{-H}_2\text{O-NaCl}$, $\text{CO}_2\text{-H}_2\text{O-Na}_2\text{SO}_4$ and $\text{CO}_2\text{-H}_2\text{O-NaCl-Na}_2\text{SO}_4$ systems.

References	T/K	P/MPa	$m_{\text{NaCl}}/$ (mol/kg) ^a	$m_{\text{Na}_2\text{SO}_4}/$ (mol/kg) ^a	Np
Markham and Kobe (1941)	298.15-313.15	0.101	0.1-4.0	0	6
Harned and Davis (1943) ^b	273.15-323.15	0.1	0.2-3	0	92
Ellis and Golding (1963)	445.25-607.15	2.67-9.31	0.5-2	0	39

Takenouchi and Kennedy (1965)	423.15-723.15	10-140	1-3.4	0	86
Malinin and Saveleva (1972) ^b	298.15-358.15	4.8	0.4-5	0	26
Malinin and Kurovskaya (1975) ^b	298.15-423.15	4.8	1-6.8	0	27
Drummond (1981) ^c	295.15-563.15	3.66-19.6	0.99-4	0	126
Cramer (1982)	296.75-511.75	0.8-6.2	0.5-1.95	0	13
Gehrig et al. (1986)	408.15-793.15	3-28.12	1.09-4.28	0	2
Nighswander et al. (1989)	353.15-473.15	2.1-10.03	0.17	0	34
Rumpf et al. (1994)	313.15-433.15	0.15-9.64	4-6	0	69
Zheng et al. (1997)	278.15-338.15	0.05-0.09	0.7-3.3	0	18
Kiepe et al. (2002)	313.15-353.15	0.006-10	0.1-4	0	70
Bando et al. (2003)	303.15-333.15	10-20	0.17-0.51	0	36
Koschel et al. (2006)	323.15-373.15	5.1-20.2	1-3	0	14
Ferrentino et al. (2010b)	313.15	10-15	0.17	0	6
Yan et al. (2011)	323.15-413.15	5-4.1	1-5	0	36
Liu et al. (2011)	318.15	2.1-15.83	1.9	0	8
Savary et al. (2012)	398.15	12.5-34.1	2	0	7
Rosenqvist et al. (2012)	294.15	0.3-3.9	1	0	6
Hou et al. (2013)	323.15-473.15	2.61-18	2.5-4	0	36
Zhao (2014)	323.15-413.15	4.8-12.5	0.5-6	0	3
Carvalho et al. (2015)	292.15-353.15	1.02-14.29	0.25-2	0	44
Zhao et al. (2015b)	323.15-423.15	15	1-6	0	18
Mohammadian et al. (2015)	333.15-353.15	0.1-21.3	0.017-0.25	0	49
Guo et al. (2016)	273.15-473.15	10-50	1-5	0	180
Messabeb et al. (2016)	323.15-423.15	5-20	1-6	0	36
Jacob and Saylor (2016)	297.15	2.62-11.58	1-4	0	27
Gilbert et al. (2016)	308.15-413.15	9.8-35.8	1.88-3.4	0	16
Truche et al. (2016)	473.15-553.15	2.9-13.0	1.4	0	7
Deng et al. (2018)	303.15-363.15	5-25	0.07-0.7	0	40
Wang et al. (2019)	303.15-353.15	3-30	1-3	0	306
Chabab et al. (2019)	323.15-373.15	1.70-22.98	1-3.01	0	21
Lara Cruz et al. (2020)	323.15-333.15	5.07-40.4	1-1.2	0	10
Setschenow (1889)	288.35	0.101	0	0.145-0.521	7
Kobe and Williams (1935)	298.15	0.104	0	1.76	2

Markham and Kobe (1941)	298.15-313.15	0.101	0	0.25-1.5	8
Shchennikova et al. (1957)	298.15-348.15	0.101	0	0.201-1.788	23
Gerecke (1969)	288.15-333.15	0.101	0	0.251-1.045	28
Onda et al. (1970)	298.15	0.101	0	0.548-1.496	3
Yasunishi and Yoshida (1979)	288.15-308.15	0.101	0	0.211-2.367	26
Corti et al. (1990)	323.15-348.15	3.79-14.51	0	0.95-2.72	10
He and Morse (1993)	273.15-363.15	0.098-0.101	0	0.01-3	24
Rumpf and Maurer (1993)	313.12-433.16	0.422-9.713	0	1.01-2.01	102
Bermejo et al. (2005)	286.97-368.81	1.98-13.11	0	0.250-0.996	113
Zhao et al. (2015a)	323-423	15	0	0.333-2	18
Gilbert et al. (2016)	303-334	1.5-14.3	0	0.1-1	23
Liborio (2017)	323.15	4.9	0	0.73	1
dos Santos et al. (2020)	303.15-423.15	1.5-20	0	1-2	48
Yasunishi et al. (1979) ^d	298.15	0.101	0.059-1.63	0.067-1.371	15

^aMolalities are expressed in moles per kilogram of water. Data source: ^bNIST, ^cPortier (2005) and ^dShi and Mao (2017). Np is the number of experimental data.

Despite the various studies have enriched the theme, some of them present problems of precision or of consistency. Thus, for our optimization work, we work with pressure, temperature and NaCl concentration ranges confirmed by studies made at the Laboratory of Thermal Engineering, Energy and Process (LaTEP). Messabeh et al. (2016) conducted a study for a system containing NaCl concentrations of 1, 3 and 6 mol/kg, for various temperatures (323–423 K) and pressures (5–20 MPa). In this way, we reduced the amount of data used for the optimization work to the selection shown in Table 2.

An experimental CO₂ solubility isotherm at 6 mol/kg of NaCl and 303.15 K (as there are no previously published data in these conditions) was additionally acquired in the present work (see Table 7). These new solubility data were not used in the optimization process. They were used only for comparison with the proposed model.

2.3. CO₂-H₂O-Na₂SO₄ SYSTEM

For Na₂SO₄, the amount of data is even less than with NaCl (as shown in Table 1). Studies that investigated the solubility of CO₂ in aqueous Na₂SO₄ solution at pressures other than atmospheric pressure started in the 1990s, however, some with problems of inconsistency or precision problems, such as Corti et al. (1990) and Gilbert et al. (2016), as appointed by Shi and Mao (2017) and dos Santos et al. (2020). Only the data by dos Santos et al. were used for the parameterization process.

2.4. CO₂-H₂O-NaCl-Na₂SO₄ SYSTEM

Experimental studies in mixed-salt solutions containing NaCl and Na₂SO₄ at different concentrations, different temperatures and pressures, are scarce. We can only mention the study made by Yasunishi et al. (1979), at one single temperature (298.15 K) and fixed pressure (0.1 MPa) for different concentrations of NaCl and Na₂SO₄ (Table 1). None of these Yasunishi's data were used in our study in the optimization process, however the AAD were also calculated from the proposed model, posteriorly.

In view of the lack of mixed-salt data on NaCl and Na₂SO₄ mixed-salt solutions experimental CO₂ solubility data were measured in a mixture containing 3 mol/kg NaCl and 1 mol/kg Na₂SO₄, at temperatures of 303.15, 323.15, 373.15 and 423.15 K, in a pressure range between 1.5 and 20 MPa. Twenty-four new CO₂ solubility points were obtained for these mixtures of NaCl and Na₂SO₄ aqueous solutions (see Table 7). By calculating the AAD, these data were used to test the model proposed through the optimization of the single-salt systems presented above.

3. MATERIALS AND METHODS

The carbon dioxide used in all experiments was Analaquide with a purity of 99.7% wt. Water was purified by a Barnstead Smart2Pure system and the resistivity was below 18.2 MΩ.cm. All aqueous salt solutions were prepared using this purified water and sodium sulfate (Na₂SO₄, Merck, > 99% wt) and sodium chloride (Acros Organics, 99.5% wt). The experimental system consisted of a one-liter Hastelloy C276 autoclave (Top Industrie), which can operate at temperatures between 293.15 and 473.15 K with a maximum pressure of 20 MPa. For sampling, a syringe containing a precisely known quantity of sodium hydroxide (Fisher Scientific, 46/51% wt) is connected to the autoclave for recovery the samples. An automatic titrator using a pH electrode makes the measurements of carbon dioxide solubility. The content of the syringe is dosed with 0.1 M hydrochloric acid solution (VWR, 0.1 ± 2% mol/L). Details on the CO₂ solubility measuring technique and the uncertainty analysis approach can be found in dos Santos et al. (2020). The experimental CO₂ solubility results at a pressure range between 1.5-20 MPa and temperatures from 303.15 to 423.15 K in aqueous mixed-salt solutions of Na₂SO₄ and NaCl at the ionic strength up to 6 mol/kg are listed in Table 7.

4. THERMODYNAMIC MODELING

The condition for thermodynamic equilibrium in a CO₂-aqueous solution system implies in the equality of pressure, temperature and fugacity of the constituent both in the aqueous and in the gaseous (or supercritical) phases:

$$f_i^{aq}(T, P, x_i) = f_i^V(T, P, y_i) \quad (1)$$

In this work, the chemical equilibrium is described with PhreeSCALE (Lach et al., 2016). In this software, the solubility of gas CO₂ is calculated using a geochemical model present by Appelo (2015) and Appelo et al. (2014) :

$$m_{\text{CO}_2} = \frac{\varphi_{\text{CO}_2}^{\text{vap}} \times P \times y_{\text{CO}_2}}{\gamma_{\text{CO}_2}^m} \times K_H \times \exp\left(\frac{-V_{m,\text{CO}_2}(P - P_0)}{RT}\right) \frac{m_0}{P_0} \quad (2)$$

Where P is the system pressure (atm) and y_{CO_2} is the molar fraction in the gas phase (-). Like in Appelo (2015) and Appelo et al. (2014), V_{m,CO_2} can be computed using the Helgeson–Kirkham–Flowers models (Johnson et al., 1992). The Henry's constant (K_H) corresponds to the equilibrium constant for the $\text{CO}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{aq})$ reaction and its values are given by Plummer and Busenberg (1982). m is the molality, R is the ideal gas constant, and T is the temperature. The subscript 0 represents the standard state, P_0 is equal to 1 atm, and m_0 to 1 mol/kg. The fugacity coefficient (φ) is computed using the Peng–Robinson equation of state, which involves the acentric factor in addition to Van der Waals' a and b factors:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha(T)}{V_m^2 + 2bV_m - b^2} \quad (3)$$

Where V_m is the molar volume (cm^3/mol), b is the minimal molar volume (cm^3/mol), α is the correction factor that is temperature dependent (-) and a is the Van der Waals' attraction ($\text{Pa cm}^3/\text{mol}$). α , a and b factors can be calculated from the critical temperature (T_c), critical pressure (P_c) and factor acentric (ω) of the gas:

$$a = \frac{0.457245(RT_c)^2}{P_c} \quad (4)$$

$$b = \frac{0.07796RT_c}{P_c} \quad (5)$$

$$\alpha(T) = \left[1 + (0.37464 + 1.54226\omega - 0.2699\omega^2) \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (6)$$

From the Eq. (3), the fugacity coefficient is:

$$\ln(\varphi) = \left(\frac{PV_m}{RT} - 1 \right) - \ln\left(\frac{P(V_m - b)}{RT} \right) + \frac{a\alpha}{2.828bRT} \ln\left(\frac{V_m + 2.414b}{V_m - 0.414b} \right) \quad (7)$$

A virial expansion of excess Gibbs energy proposed by Pitzer (1991) is used to obtain the activity coefficient ($\gamma_{\text{CO}_2}^m$). This model has a dependence on temperature, species molality and their respective molecular interactions.

$$\ln(\gamma_{\text{CO}_2}^m) = 2m_{\text{CO}_2}\lambda_{\text{CO}_2,\text{CO}_2} + \sum_{c=1}^{n_c} 2m_c\lambda_{\text{CO}_2,c} + \sum_{a=1}^{n_a} 2m_a\lambda_{\text{CO}_2,a} + \sum_{c=1}^{n_c} \sum_{a=1}^{n_a} m_c m_a \zeta_{\text{CO}_2,c,a} \quad (8)$$

Where λ and ζ are binary and ternary interaction parameters, respectively. c and a stand for cations and anions, respectively. For the temperature dependence for the interaction parameters, the following expression is assumed (which is the combination of equations of Møller (1988) and Christov and Møller (2004a)) as propose by Lach et al. (2016):

$$Y(T) = A1 + A2T + A3T^2 + A4T^3 + \frac{A5}{T} + A6 \ln T + \frac{A7}{(T - 263)} + \frac{A8}{(680 - T)} + \frac{A9}{(T - 227)} \quad (9)$$

Y can be any of the adjustable specific interaction. Most of the time in practice, only a limited number of the coefficients in Eq. (9) are necessary.

4.1. OPTIMIZATION OF INTERACTION PARAMETERS

The interaction parameters $\lambda_{\text{CO}_2, \text{CO}_2}$, $\lambda_{\text{CO}_2, \text{a}}$, $\lambda_{\text{CO}_2, \text{c}}$ and $\zeta_{\text{CO}_2, \text{c, a}}$ of the Pitzer model in Eq. (8) were determined using experimental CO_2 solubility data. First, the interaction parameters were optimized for a simple CO_2 - H_2O system and then for systems containing salt, NaCl and Na_2SO_4 , respectively. The data set used for the optimization process are presented in Table 1 for the CO_2 - H_2O system and, for the CO_2 - H_2O - NaCl and CO_2 - H_2O - Na_2SO_4 systems, they are listed in Table 2.

Table 2

Experimental data used for the optimization of CO_2 - H_2O - NaCl and CO_2 - H_2O - Na_2SO_4 systems.

Type of data	T/K	P/MPa	$m_{\text{NaCl}}/(\text{mol/kg})^a$	References
CO_2 solubility	303.15	3 - 30	1 and 3	Wang et al. (2019)
	323.15	4 - 35 - 20	1, 3 and 6	Drummond (1981)
				Yan et al. (2011)
				Zhao et al. (2015b)
				Messabeb et al. (2016)
				Wang et al. (2019)
	373.15	4.8 - 20	1, 3 and 6	Yan et al. (2011)
				Zhao (2014)
				Zhao et al. (2015b)
				Messabeb et al. (2016)
CO_2 solubility	423.15	4.89 - 20	1, 3 and 6	Chabab et al. (2019)
				Malinin and Kurovskaya (1975)
				Drummond (1981)
				Zhao et al. (2015b)
	473.15	10 - 40	1 and 3	Messabeb et al. (2016)
				Guo et al. (2016)
Type of data	T/K	P/MPa	$m_{\text{Na}_2\text{SO}_4}/(\text{mol/kg})^a$	References
CO_2 solubility	303.15	1.5 - 20	1 and 2	dos Santos et al. (2020)

323.15

373.15

423.15

^aMolalities are expressed in moles per kilogram of water.

The optimizations were carried out by coupling PhreeSCALE with PEST (Doherty, 2004) according to the following principle (André et al., 2009). PEST calls PhreeSCALE to calculate target properties of the chemical systems of interest (e.g. CO₂ solubility), by using an initial set of values for the parameters to estimate (e.g., specific interaction parameters). The calculation results are then compared to the experimental properties values by calculating the objective function characterizing the deviation from the experimental data. If the convergence criterion is not satisfied, a new series of calculations is launched with a new set of parameters. Optimization is carried out by successive iterations of this procedure until the convergence criterion is satisfied or if there is no more evolution of the results.

4.2. IMPROVEMENTS IN THE RESOLUTION OF THE EOS PENG-ROBINSON

In PHREEQC code, the properties of the gaseous phase is computed by the Peng-Robinson equation of state when all constituents own their critical pressure, critical temperature and acentric factor reported in the thermodynamic database. Thus, the cubic equation of state is solved using the Cardan approach (see e.g. Nickalls (1993)), the equation gives three roots and it is necessary to make a choice.

Cubic equations of state have three roots for molar volume, two of which can be complex numbers depending on the sign of the determinant. The values of V_m with physical significance are always real and positive numbers and greater than those of the constant b since b represents the minimal molar volume of the compound (see Eq. 3). For an isotherm at $T > T_c$ (critical temperature), the solution of V_m , at any positive value of pressure, provides only a positive real root. For the critical isotherm ($T = T_c$), this is also true, except for the critical pressure, in which there are three roots, just like V_m at the critical point. For isotherms $T < T_c$ (i.e. when the discriminant is negative), the equation can display one or three real roots, depending on the pressure. Although these roots are real and positive, they do not represent stable physical states for the part of an isotherm located between the saturated liquid and the saturated vapor. In the original version of PHREEQC, the larger root (i.e. the one corresponding to gas) is chosen. Actually, the code calculate only this root.

Thus, the description of CO₂ behavior for temperatures below 304.15 K with the original PHREEQC code remains limited as explained by Appelo et al. (2014). Aiming the applicability of the model also at lower temperatures, the PhreeSCALE code was modified so that it was possible to go beyond the critical point: we inserted the calculation of all roots of the cubic equation of state and an

equilibrium condition able to choose the relevant root to use in subsequent calculation. The modification of PHREEQC consisted mainly to implement in the source code the Maxwell construction (CLERK-MAXWELL, 1875). Thus, such a change is clear as shown in Figure 1, comparing with experimental data and the PHREEQC code. This will also have a direct impact on the calculation of the gas fugacity, as shown in Figure 2. The comparisons with the experimental data for the molar volume (Michels et al., 1937, 1935; Michels and Michels, 1935) and with the Duan Polynomial for the fugacity coefficient (Duan et al., 2006; Duan and Sun, 2003) were made to show that the results are essentially the same.

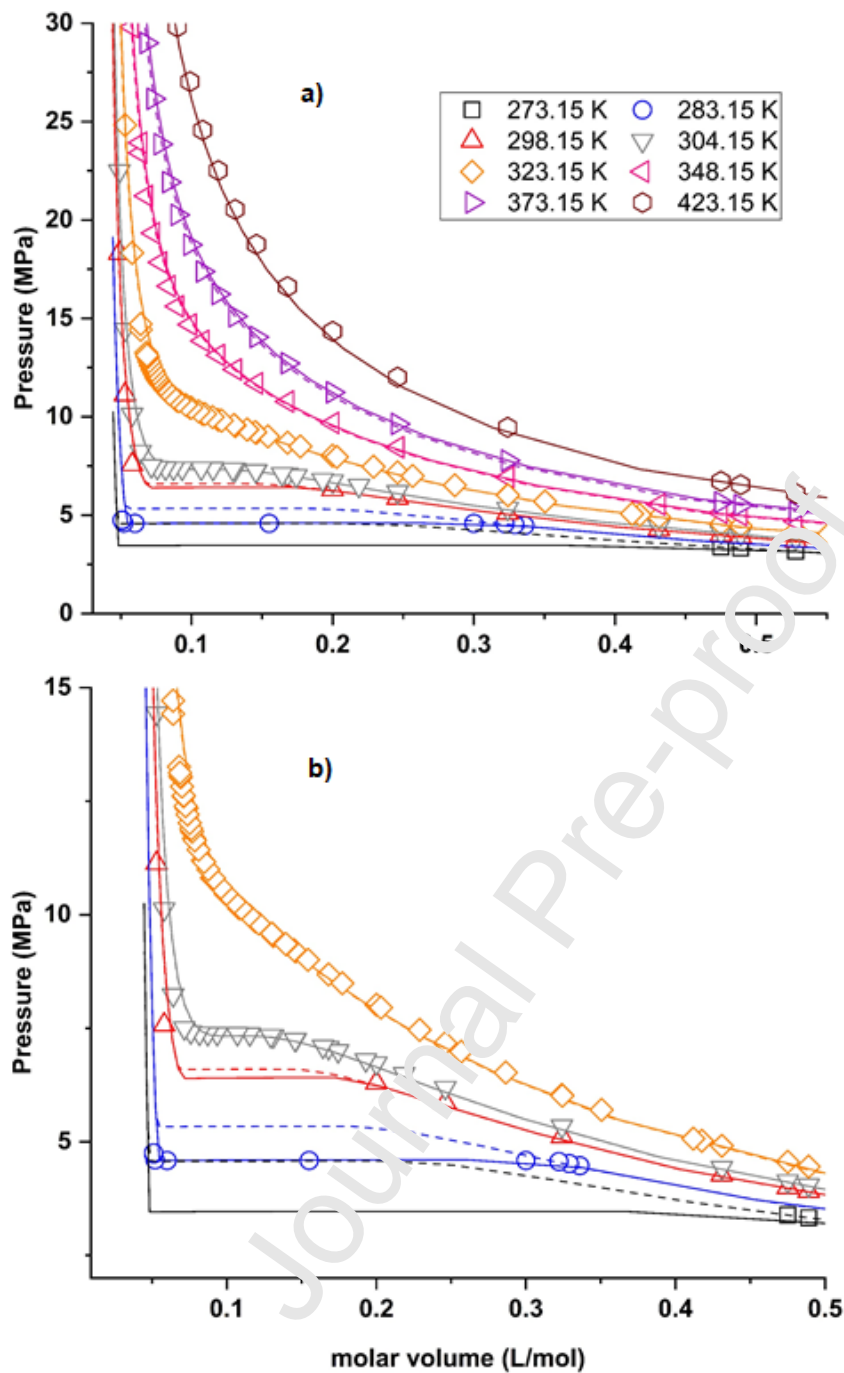


Figure 1 – a) Evolution of CO₂ gas pressure according to molar volume at 273.15, 283.15, 298.15, 304.15, 323.15, 348.15, 373.15 and 423.15 K. Symbols are measured data from Gilgen et al. (1992); Michels et al. (1937, 1935); and Michels and Michels (1935). Solid lines are calculated with PhreeSCALE. Dashed lines are calculated with PHREEQC; b) Graph a) zoom.

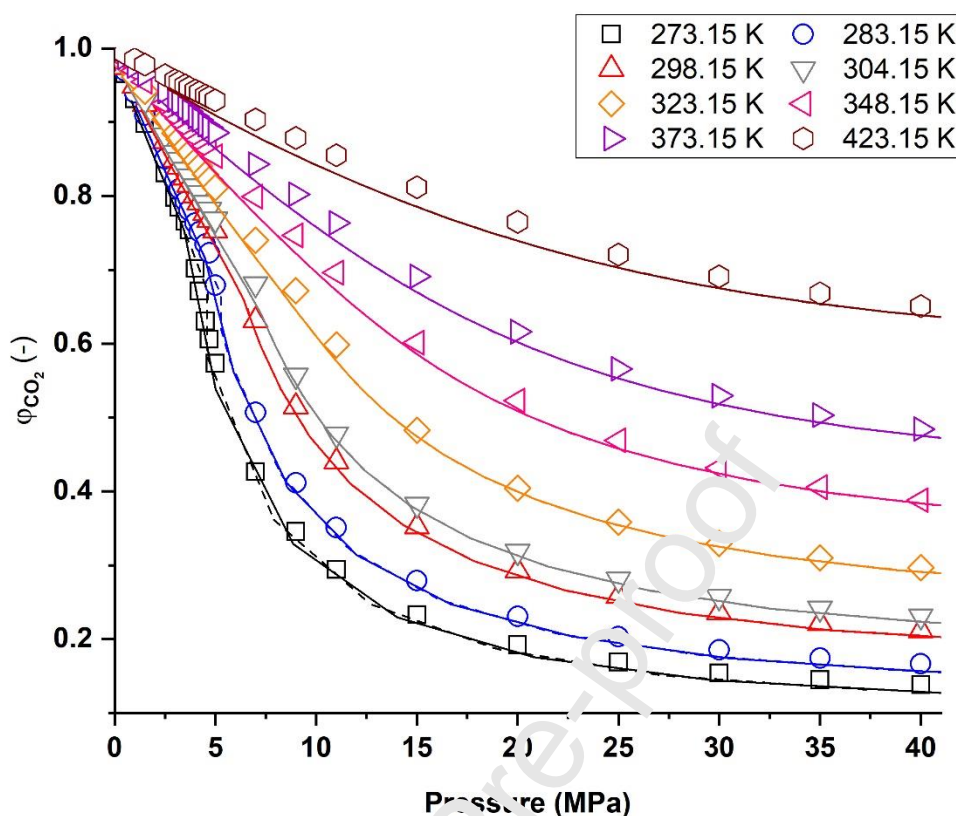


Figure 2 – Fugacity coefficients calculated with Peng-Robinson using PhreeSCALE (solid lines) and PHREEQC (dashed lines) compared to the polynomial of Duan et al. (2006) and Duan and Sun (2003).

Thus, the possible improvement window pointed out by Appelo et al., 2014 could be exploited in this work, and the correction made to the code extends our calculation capacity below the critical temperature of CO₂.

5. RESULTS AND DISCUSSIONS

The characterization of interaction parameters to implement the Pitzer database is always challenging, whatever the studied system, the main issue being the consistency of the database. The success in determining new parameters depends on the methodology applied. Here, we proceed step by step: the solubility of the gas in pure water is considered first, then in NaCl and, finally, in aqueous Na₂SO₄ solutions. At last, the model of gas solubility is applied to more complex systems like the salt mixture NaCl-Na₂SO₄ solutions.

5.1. CO₂-H₂O SYSTEM

Before dealing with CO₂ solubility in brine systems, a focus must be done on the CO₂-H₂O system. Many numerical studies deal with this chemical system among them Shock and Helgeson (1988), Schulte et al. (2001), Plyasunov and Shock (2001), Springer et al. (2012), Appelo et al. (2014). All of these studies revisit the HKF (Helgeson-Kirkham-Flowers) parameters in order to calculate the Log K of the reaction CO₂(g) ↔ CO₂(aq), but also volumic properties of the solution (standard partial molar volume, density, heat capacity...).

To model the CO₂ solubility when the system deviates from ideality, authors determined a lambda Pitzer interaction parameter ($\lambda_{\text{CO}_2, \text{CO}_2}$) to take into account specific interactions between the CO₂ aqueous species. Li and Duan (2007) defined a lambda parameter dependent in temperature and pressure whereas Appelo et al. (2014) considered a parameter that only varies with temperature.

In this study, we tested all these approaches in order to compare the results of the numerical calculations with experimental data for a variety of thermodynamic properties:

- CO₂ solubility measurements listed in Figures 10 and 11 (Supplementary Data);
- Solution density (experimental data from McBride-Wright et al., 2015);
- Standard partial molar volume of CO_{2(aq)} at infinite dilution (McBride-Wright et al., 2015);
- Heat capacity (Barbero et al., 1983; Hnědkovský and Wood, 1997).

It was found that none of the sets of model parameters available in the literature can accurately calculate all the properties of the solution and the dissolved species (Parmentier et al., 2016). The models of Shock and Helgeson (1988) and Schulte et al. (2001) represent the CO₂ solubility data up to high pressure and temperature. However, their HKF parameters don't allow modelling the standard partial molar volume of CO_{2(aq)} and the solution molar volumes published many years later by McBride-Wright et al. (2015) (Data not shown here). The approach of Plyasunov and Shock (2001) are also tested but, as indicated by the authors, their extension of the revisited HKF model to the neutral species does not bring a relevant improvement especially for the volume properties. At last, the model proposed by Appelo et al. (2014) allows determining the solubility of CO₂ up to high temperature and pressure, but no c_1 and c_2 parameters are given, preventing heat capacities calculations of solutions. This led us to revisit some of these thermodynamic parameters.

Concerning the HKF parameters, i.e. a_i ($i = 1$ to 4) and ω_i the values proposed by Appelo et al. (2014) allow calculating the molar volume of dissolved CO₂ with accuracy (Figure 3a). It was decided to keep these parameters (Table 3) and to estimate only c_1 and c_2 parameters, needed for the calculation of the heat capacity, which were not given by the authors. These parameters are estimated using PEST software and the heat capacity data from Hnědkovský et al. (1997). c_1 and c_2 values allow reproducing the heat capacity of dissolved CO₂ up to 450 K (Figure 3d).

Table 3

Values of HKF parameters selected for the calculations of the thermodynamic properties of aqueous CO₂ with PhreeSCALE. a_i and ω are from Appelo et al. (2014) whereas c_1 and c_2 were determined in this work.

$a_1 \times 10$	$a_2 \times 10^{-2}$	a_3	$a_4 \times 10^{-4}$	c_1	$c_2 \times 10^{-4}$	$\omega \times 10^{-5}$
J.mol ⁻¹ .bar ⁻¹	J.mol ⁻¹	J.K.mol ⁻¹ .bar ⁻¹	J.K.mol ⁻¹	J.mol ⁻¹ .K ⁻¹	J.K.mol ⁻¹	J.mol ⁻¹
30.5014	3.84928	8.66088	-5.14632	18.805376	81.817767	-6.69440

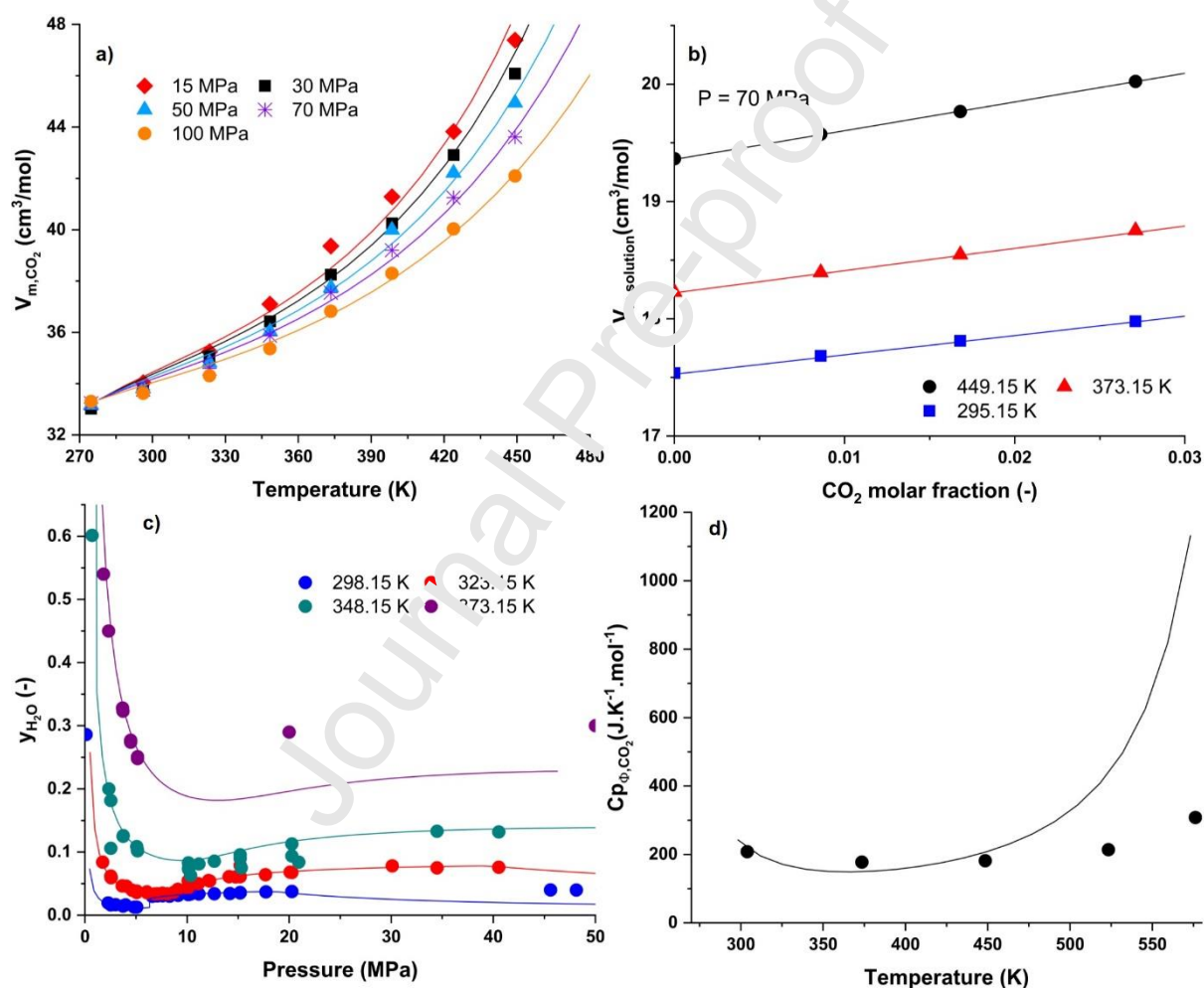


Figure 3 – (a) molar volume of dissolved CO₂ according to temperature and pressure: symbols are experimental data from McBride-Wright et al. (2015); (b) solution molar volume according to temperature and pressure and CO₂ molar fraction: symbols are experimental data from McBride-Wright et al. (2015); (c) water content in the gas phase according to pressure and temperature: symbols are experimental data from Spycher et al. (2003); (d) heat capacity of dissolved CO₂: symbols are experimental data from Hnědkovský and Wood (1997). Lines are calculated values.

Then, from these estimated HKF parameters, the ΔG° of the reaction $\text{CO}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{aq})$ is estimated leading to the determination of Log K at different temperatures. According to the formalism selected in the PhreeSCALE code, the variation of Log K according to temperature is given by the Eq.10:

$$\text{Log K} = A_1 + A_2 T + \frac{A_3}{T} + A_4 \log T + \frac{A_5}{T^2} \quad (10)$$

The estimation of the five parameters is by minimizing the least-square solution leading to the following values: $A_1=109.534$; $A_2 = 0.019913$; $A_3 = -6986.04$; $A_4 = -40.83$; $A_5 = 669370$. These parameters are not new since they were already used in a previous version of the Pitzer.dat database released with PHREEQC code and that uses the same temperature function as Eq.10. They are valid between 273.15 K and 523.15 K.

Finally, we decided to use the temperature variation of the interaction parameter $\lambda_{\text{CO}_2, \text{CO}_2}$ proposed by Appelo et al. (2014). However, since the temperature-function polynomial are different in PHREEQC and PhreeSCALE (see equation 9) the factors of the polynomial function are reinterpreted (Table 4).

Table 4

Pitzer interaction parameters and coefficients for the temperature dependent polynomial of the Eq. (9)

	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	Reference
$\lambda_{\text{CO}_2, \text{CO}_2}$	-1.34E-02	348	0.803	0	0	0	0	0	0	Appelo et al. (2014)
$\lambda_{\text{CO}_2, \text{CO}_2}$	-5.756	0	0	0	348	0.803	0	0	0	This study
$\lambda_{\text{CO}_2, \text{Cl}^-}$	0	0	0	0	0	0	0	0	0	This study
$\lambda_{\text{CO}_2, \text{Na}^+}$	1.694	-2.61E-03	1.824E-05	-1.361E-08	-87.091	0	0	0	0	This study
$\lambda_{\text{CO}_2, \text{SO}_4^{2-}}$	0.916	-5.71E-03	1.351E-05	-1.144E-08	0	0	0	0	0	This study
$\zeta_{\text{CO}_2, \text{Na}^+, \text{Cl}^-}$	-0.002	0	0	0	0	0	0	0	0	This study
$\zeta_{\text{CO}_2, \text{Na}^+, \text{SO}_4^{2-}}$	0	0	0	0	0	0	0	0	0	This study

after the optimization.

Figure 3 shows that all the properties of the solution that can be described correctly with this new parametrization, and that the solubility of CO_2 in pure water is also well reproduced (see Supplementary Data).

In the end, this consistency in the thermodynamic properties of aqueous CO_2 implies a revision of the models describing the solubility of this gas in brines.

5.2. $\text{CO}_2\text{-Na}^+\text{-Cl}^+\text{-H}_2\text{O}$ SYSTEM

Many parameters can be envisaged to fit the experimental data. However, in order to avoid over parameterization, the objective is to reduce as much as possible their number in the modeling. According to previous studies (Duan et al., 2006; Duan and Sun, 2003; Shi and Mao, 2017), it is assumed that $\lambda_{\text{CO}_2,\text{Cl}^-}$ is zero. Two parameters are then investigated: $\lambda_{\text{CO}_2,\text{Na}^+}$ and $\zeta_{\text{CO}_2,\text{Na}^+,\text{Cl}^-}$. A first attempt consisted to consider a constant parameter $\lambda_{\text{CO}_2,\text{Na}^+}$ (independent of temperature) without the ternary parameter ($\zeta_{\text{CO}_2,\text{Na}^+,\text{Cl}^-} = 0$), but we have identified a very strong influence of temperature. We therefore went to look for a temperature dependent parameter $\lambda_{\text{CO}_2,\text{Na}^+}$ (Eq. 9) which was also done by previous authors (Christov and Møller, 2004a; Møller, 1988). Because of the high carbon concentrations in solutions, the pH of the NaCl-bearing solutions is ranging between 2.5 and 3.9 (Li et al., 2018), i.e. far below the pKa of the $\text{CO}_{2(\text{aq})}/\text{HCO}_3^-$ couple. Consequently, $\text{CO}_{2(\text{aq})}$ is the main carbon species in solution and no interaction parameters are fitted for HCO_3^- species. According to this speciation, pH calculations have been done up to 473.15 K and numerical results are consistent with experimental pH measurements (see Supplementary Data). A complete list of aqueous species (and their related thermodynamic properties) considered in this model is found in the Appendix A.

However, the temperature dependence was not sufficient to correctly fit the experimental data and we found an influence of molality rather at 323.15 K and 373.15 K. We added the ternary $\zeta_{\text{CO}_2,\text{Na}^+,\text{Cl}^-}$ (independent of temperature) to reduce the effect of the salt concentration. It is also consistent with the approaches of Duan et al. (2006), Duan and Sun (2003), Mao et al. (2013) and Shi and Mao (2017), who used $\lambda_{\text{CO}_2,\text{Na}^+}$ and $\zeta_{\text{CO}_2,\text{Na}^+,\text{Cl}^-}$ parameters. The parameters are a function of temperature in addition to being a function of pressure too for these authors.

Figures 4-6 show that the measured CO_2 solubilities in aqueous NaCl solutions calculated are in good agreement with the model proposed in this work. Covering a wide range of NaCl temperature, pressure and concentration. The solubility of CO_2 increases with increasing pressure and decreases with increasing temperature, as well as decreasing with increasing salt concentration. The model proposed in this study is capable of covering a wide $T - P - m_{\text{salt}}$ range (273.15-473.15 K, 0.1-40 MPa and 0-6 mol/kg) for $\text{CO}_2\text{-H}_2\text{O-NaCl}$ system.

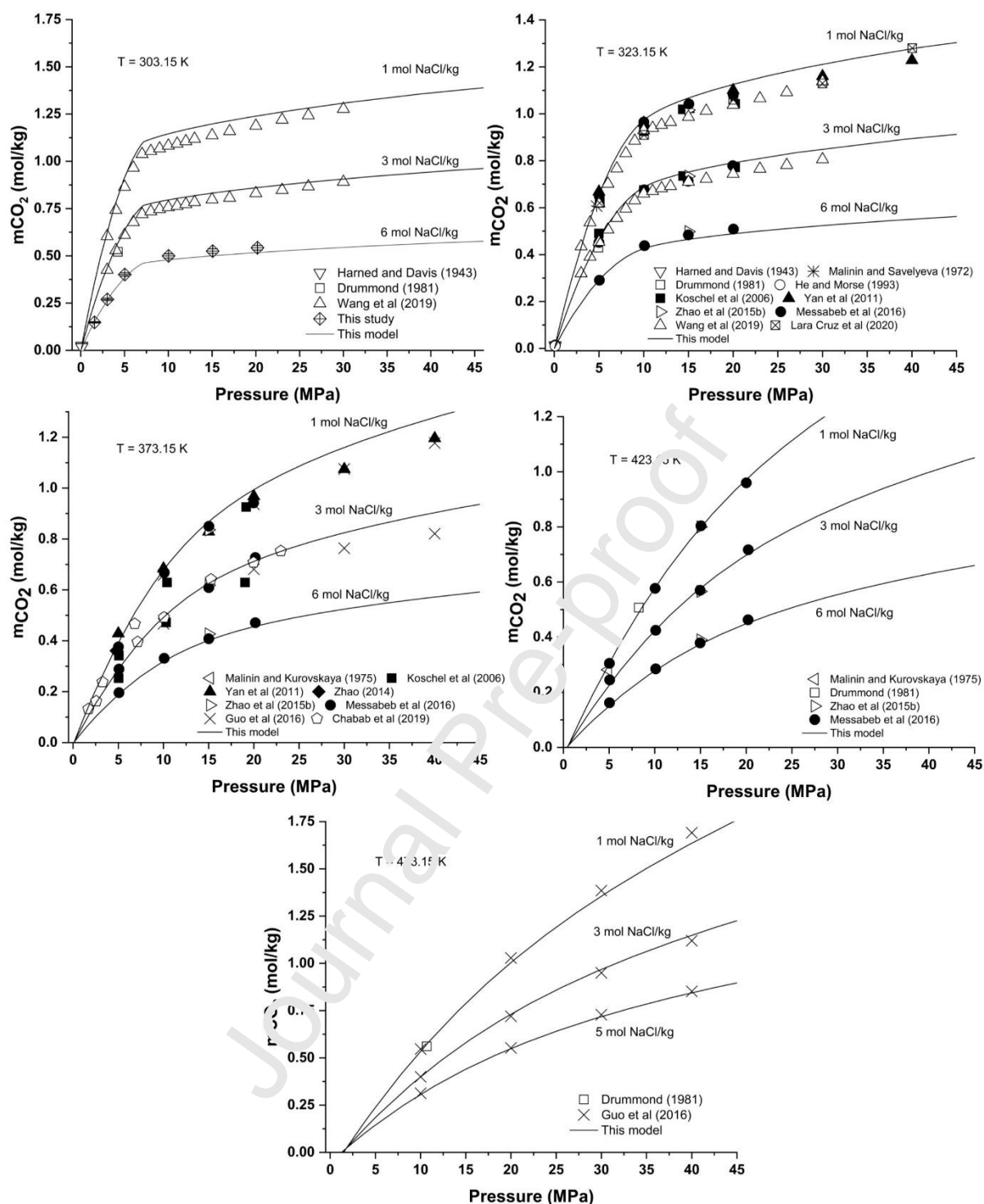


Figure 4 – CO₂ solubilities in aqueous NaCl solution calculated by PhreeSCALE vs. experimental data (Chabab et al., 2019; Drummond, 1981; Guo et al., 2016; Harned and Davis, 1943; He and Morse, 1993; Koschel et al., 2006; Lara Cruz et al., 2020; Malinin and Kurovskaya, 1975; Malinin and Saveleva., 1972; Messabeh et al., 2016; Wang et al., 2019; Yan et al., 2011; Zhao, 2014; Zhao et al., 2015c). Temperatures used in the optimization process (see Table 2).

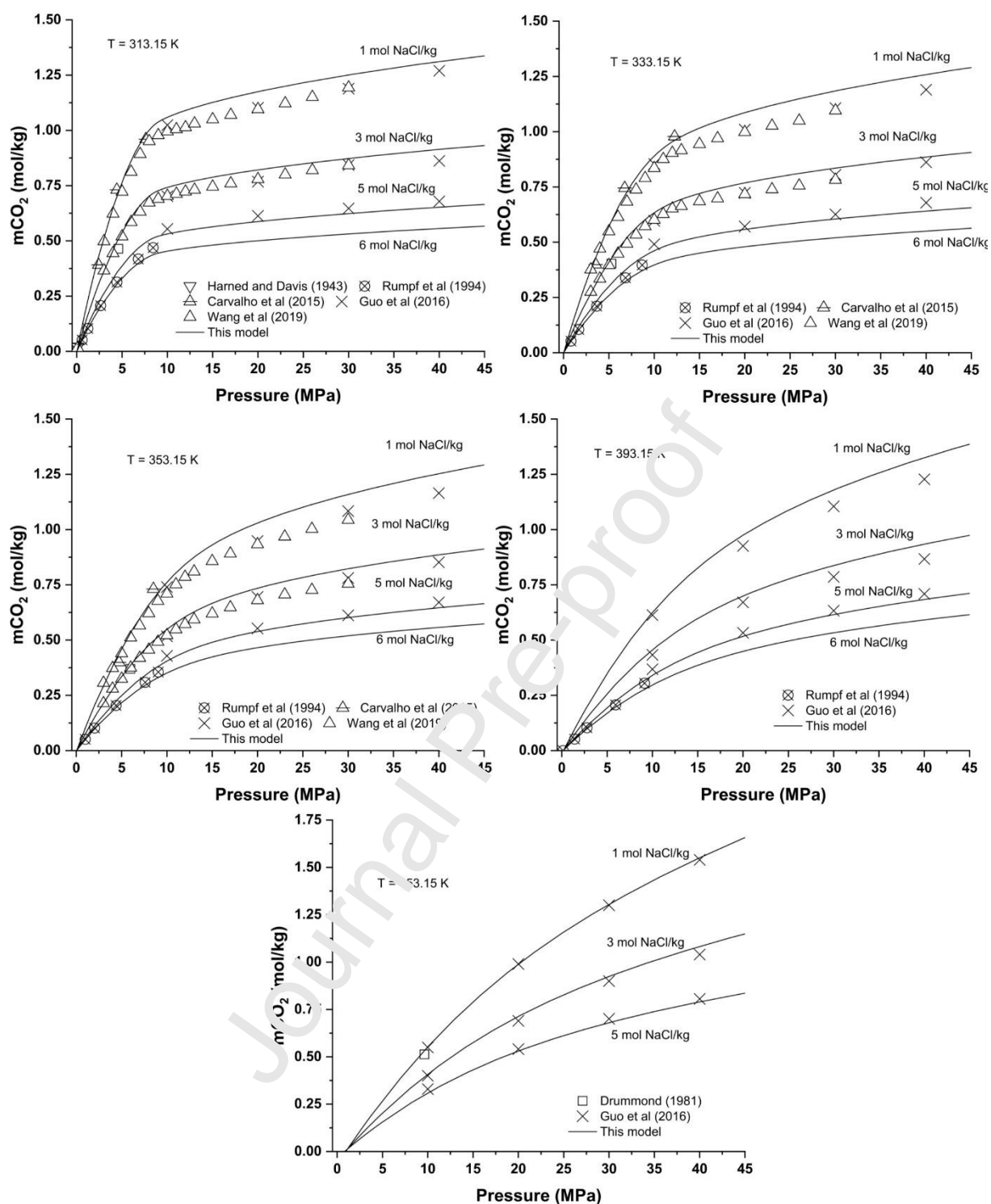


Figure 5 – CO₂ solubilities in aqueous NaCl solution calculated by PhreeSCALE vs. experimental data (Carvalho et al., 2015; Drummond, 1981; Guo et al., 2016; Harned and Davis, 1943; Rumpf et al., 1994; Wang et al., 2019).

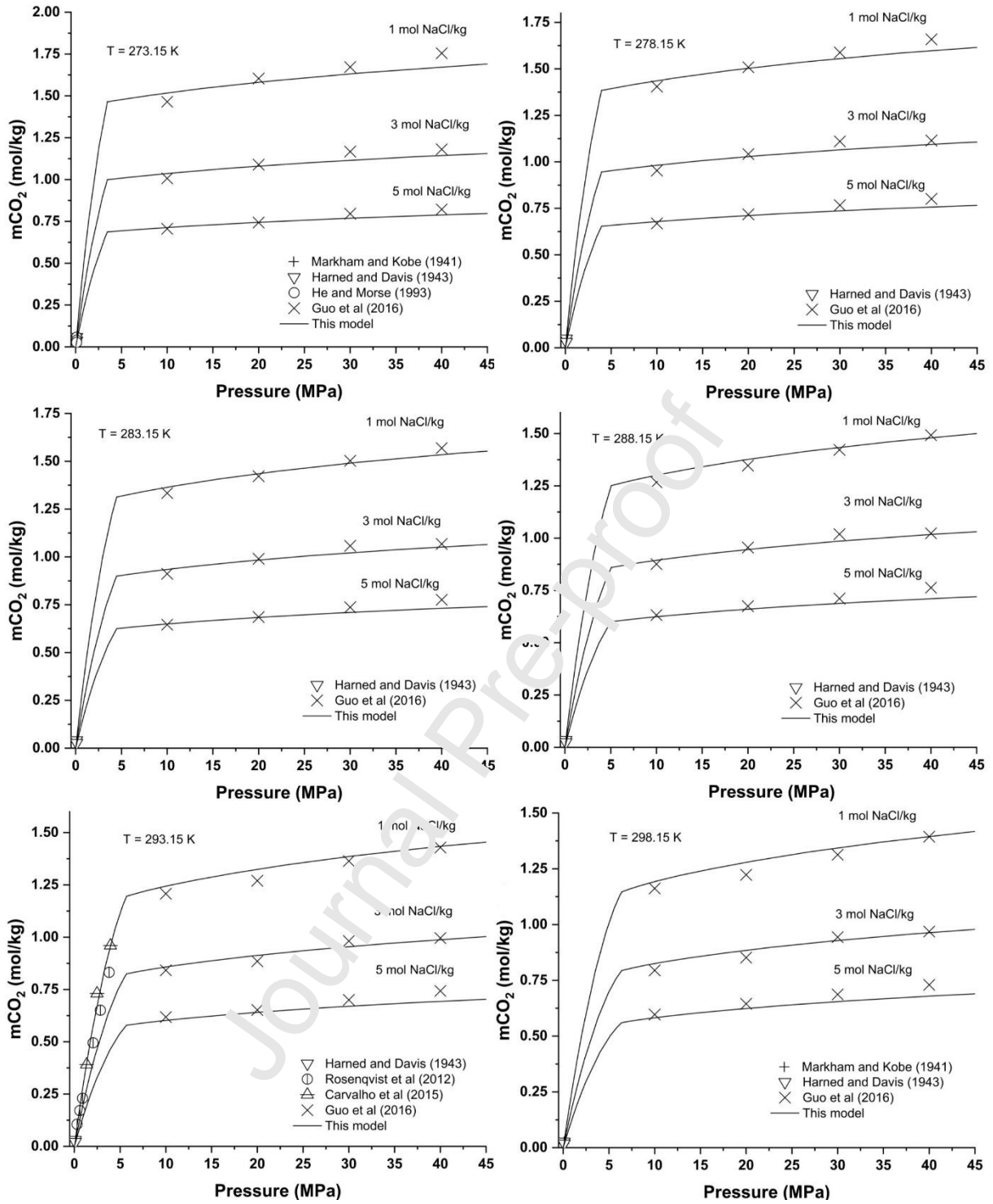


Figure 6 – CO₂ solubilities in aqueous NaCl solution calculated by PhreeSCALE vs. experimental data (Carvalho et al., 2015; Guo et al., 2016; Harned and Davis, 1943; Markham and Kobe, 1941; Rosenqvist et al., 2012; Rumpf et al., 1994; Wang et al., 2019).

5.3. CO₂-Na⁺-SO₄²⁻-H₂O SYSTEM

Finally, the investigations focused on the Na₂SO₄ system. Since the binary $\lambda_{\text{CO}_2, \text{Na}^+}$ is already defined, the $\lambda_{\text{CO}_2, \text{SO}_4^{2-}}$ interaction parameter is to be considered. In a first step, no ternary parameter is

selected. The experimental data used for the parameterization are only issued from dos Santos et al. (2020) (see Table 2). These data covered the temperature range 303.15-423.15 K and the pressure range 1.5-20 MPa whereas the Na_2SO_4 concentration is 1 and 2 mol.kg⁻¹.

For the $\text{CO}_2\text{-H}_2\text{O-Na}_2\text{SO}_4$ system, like for the previous system, the first step consisted in selecting the adequate species in solution. The pH values calculated using different thermodynamic databases are ranging between 3 and 4, i.e. far above the pKa of the $\text{HSO}_4^-/\text{SO}_4^{2-}$ couple and far below the pKa of the $\text{CO}_{2(\text{aq})}/\text{HCO}_3^-$ couple. These calculations are also consistent with data published by Anabaraonye (2017). Consequently, Na^+ , SO_4^{2-} and $\text{CO}_{2(\text{aq})}$ are the main species in solution.

For the $\text{CO}_2\text{-H}_2\text{O-Na}_2\text{SO}_4$ system, the influence of the salt concentration is much less strong than for the NaCl, so it was possible to work without ternary parameter ($\zeta_{\text{CO}_2,\text{Na}^+,\text{SO}_4^{2-}} = 0$), as was it adopted by Shi and Mao (2017). Only a temperature dependence for $\lambda_{\text{CO}_2,\text{SO}_4^{2-}}$ is needed to fit the experimental data. Shi and Mao (2017) comments in their work that the binary parameter $\lambda_{\text{CO}_2,\text{SO}_4^{2-}}$ cannot be seen as a simple constant when they are comparing their model to that of Duan et al. (2006), which treats $\lambda_{\text{CO}_2,\text{SO}_4^{2-}}$ as a constant. Shi and Mao (2017) presents the binary parameter as a function of temperature and pressure, despite the influence of pressure being negligible. Thus, describing $\lambda_{\text{CO}_2,\text{SO}_4^{2-}}$ as an equation is coherent to cover a wide range of temperature, pressure and concentration. The results of the interaction parameters are shown in Table 4. Figures 7 and 8 show that the CO_2 solubilities in aqueous Na_2SO_4 solution from this model are in agreement with the experimental data. The model is capable of covering a wide $T - P - m_{\text{salt}}$ range, 288-433 K, 0.1-20 MPa and 0-2 mol/kg.

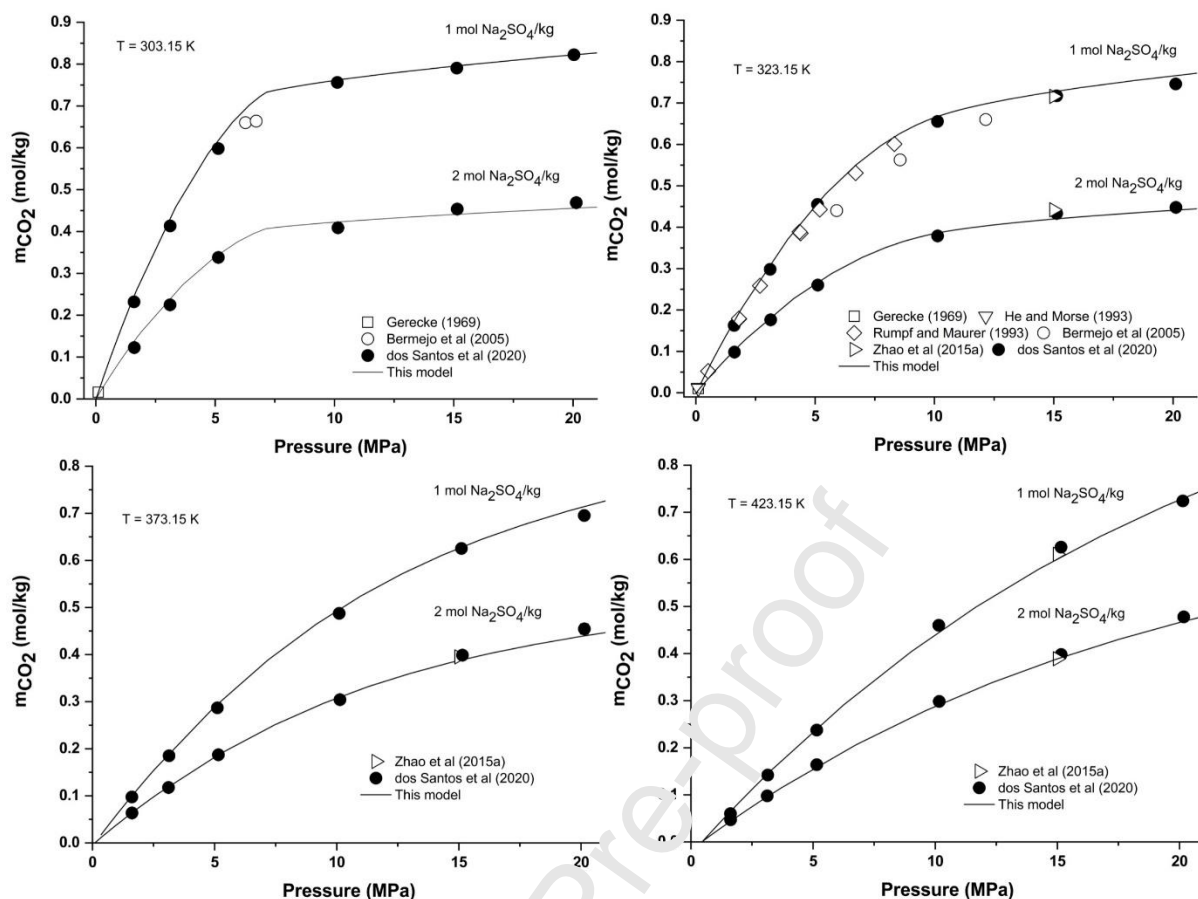


Figure 7 – CO_2 solubilities in aqueous Na_2SO_4 solution calculated by PhreeSCALE vs. experimental data (Bermejo et al., 2005; Corti et al., 1990; dos Santos et al., 2020; Gerecke, 1969; He and Morse, 1993; Rumpf and Maurer, 1993; Zhao et al., 2015b). Temperatures used in the optimization process (see Table 2).

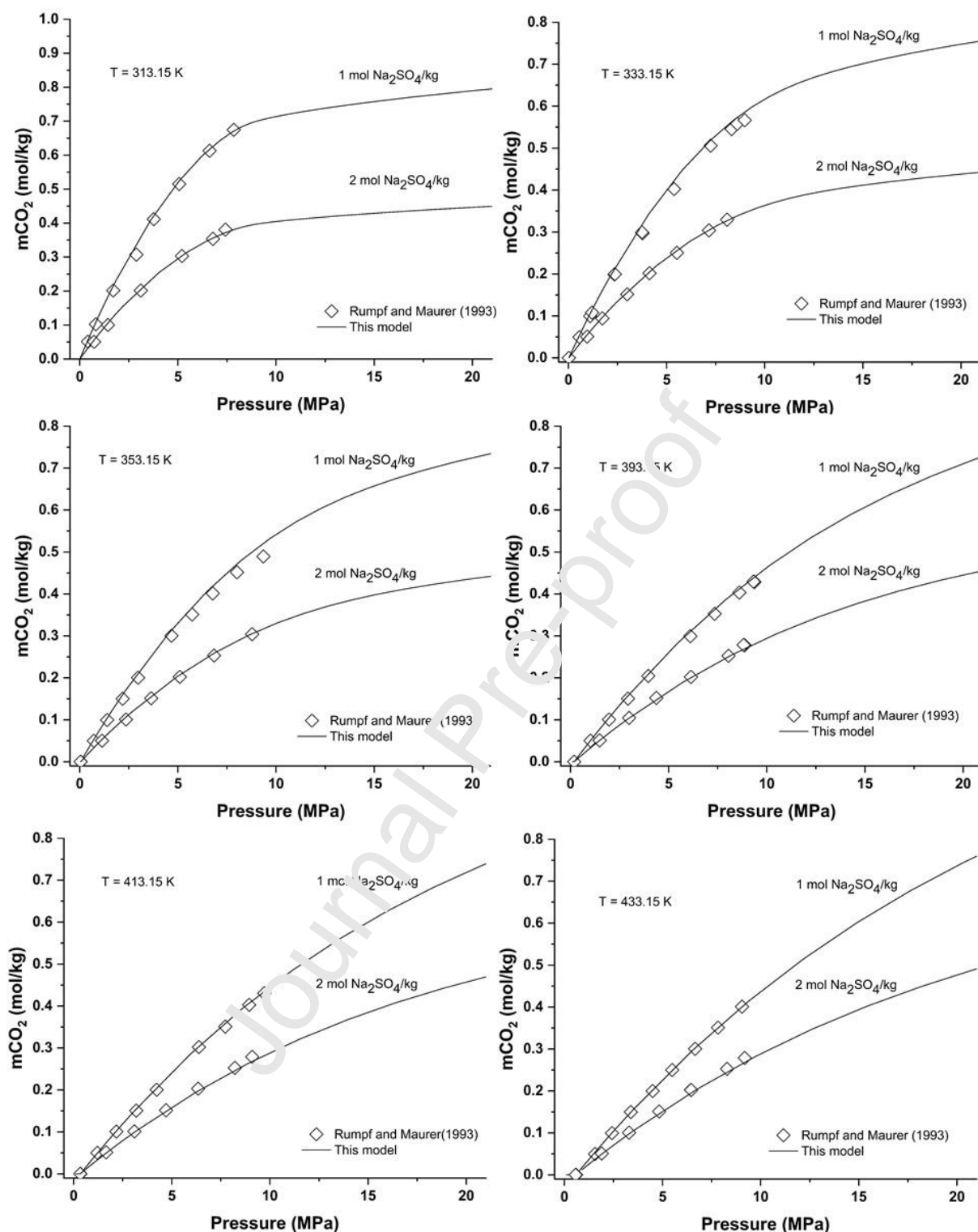


Figure 8 – CO₂ solubilities in aqueous Na₂SO₄ solution calculated by PhreeSCALE vs. experimental data (Rumpf and Maurer, 1993).

5.4. CO₂-H₂O-MIXED SALT SYSTEMS

The results of CO₂ solubility for the CO₂-H₂O-NaCl and CO₂-H₂O-NaCl-Na₂SO₄ system were obtained at an ionic strength of 6 mol/kg and at 4 different temperatures, 303.15 K, 323.15 K, 373.15

K and 423.15 K, at a pressure range between 1.5 MPa and 20 MPa. All experimental data are reported in Table 7, thus the deviations of the model in relation to the experimental data and the AAD values. The Figure 9 compare all experimental solubilities of CO₂ in NaCl-Na₂SO₄ solutions in this study with the model respectively at 303.15 K, 373.15 K and 423.15 K.

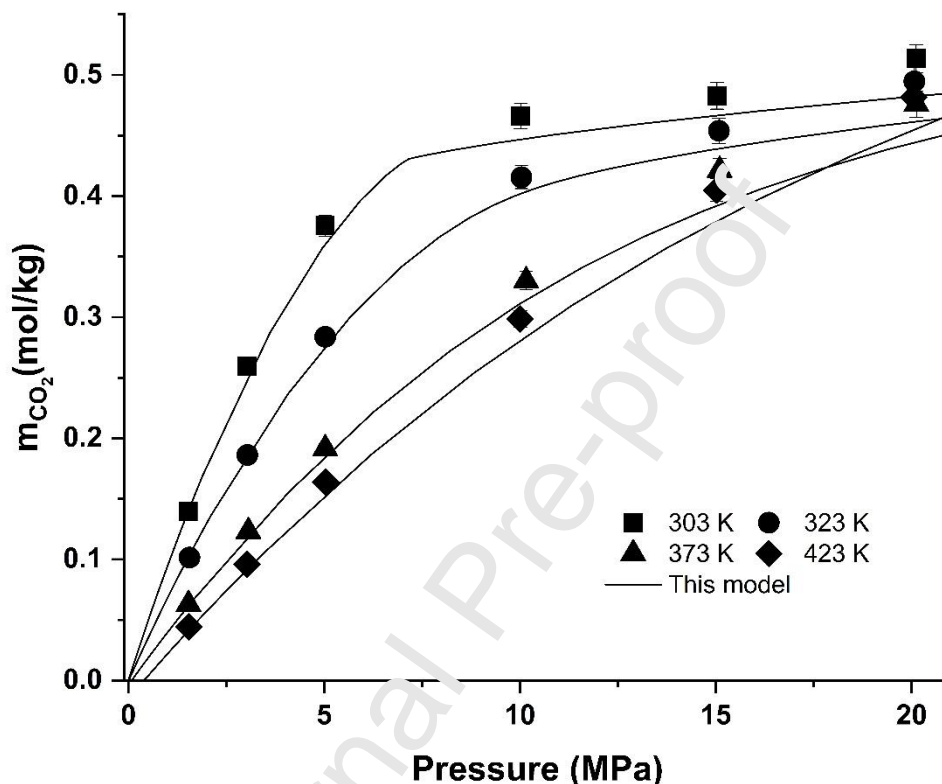


Figure 9 – CO₂ solubilities in aqueous NaCl-Na₂SO₄ solution calculated by PhreeSCALE vs. experimental data at 303.15, 323.15, 373.15 et 423.15 K.

The model proposed through the optimization of single-salt systems, NaCl and then Na₂SO₄, is capable of reproducing the mixed-salt solutions a wide T – P – m_{salt} range, 298.15-423.15 K, 0.1-20 MPa and 0-3 mol/kg.

5.5. AAD'S CALCULATIONS

Tables 5 and 6 show the average absolute deviations (AAD) between the proposed model ($m_{\text{CO}_2,i}^{\text{cal}}$) and the experimental ($m_{\text{CO}_2,i}^{\text{exp}}$) CO₂ solubility data in aqueous systems containing NaCl and Na₂SO₄. As well as Figs. 3-9 show the comparison between the experimental data and our model.

$$AAD_{\%} = \frac{100}{N_p} \sum_{i=1}^{N_p} \left(\left| \frac{m_{CO_2,i}^{cal} - m_{CO_2,i}^{exp}}{m_{CO_2,i}^{exp}} \right| \right) \quad (11)$$

Where N_p is the number of points.

The model was also tested for different temperatures and concentrations on data published in the literature that were not used in the optimization process. Almost 560 data were analyzed for NaCl, with the overall AAD of approximately 5%. As for Na₂SO₄, almost 180 data have been analyzed and the overall AAD is approximately 4%. The AAD calculations were also done by salt concentration to show the model's capacity to reproduce solubility data at high salt concentrations. If we look at the AAD values for concentrations close to the saturation of the salts (6 mol/kg for NaCl and 2 mol/kg for Na₂SO₄), we see that the values are below 4%, more precisely 3.6% for NaCl and 3 % for Na₂SO₄, respectively.

In general, observing the calculated isotherms and experimental data, the model is capable of satisfactorily reproducing pressures up to 20 MPa. Given the temperatures between 273.15-313.15 K and 453.15 and 473.15 K, we see that the model is capable of satisfactorily describing solubility points up to 40 MPa. Notably the data by Guo et al. (2016) that have an AAD below 4% for all molalities. Important fact, if we look at Table 3, we see that Guo's data were used only to optimize the parameters at 473.15 K, showing the extensibility for temperature of our model (temperatures below 303.15 K).

Despite the little data available at concentrations of NaCl close to saturation, we see when analyzing the Figures 4-6 and Table 5, that the model is capable of reproducing such available points. The points of Rumpf et al. (1994), which were also not used in the optimization process, its 69 points were reproduced by the model that obtained an AAD below 3.3%. Showing the extensibility for concentration of salt of our model as well. Also confirming this good extension of the model, with the experimental data acquired in this work at 6 mol/kg of NaCl at 303.15 K, the AAD value was 3.24%.

Analyzing the isotherms between 313-393 K for the CO₂-H₂O-NaCl system, it is possible to notice more notable deviations between the simulations generated by the model and experimental points of Guo et al. (2016) and Wang et al. (2019), which can reach up to 7 % and 7.7% respectively. The deviations are more marked in the isotherms at 1 mol/kg in this temperature range, having a good behavior up to 15 MPa, then the deviations become more marked. Note that when we increase the salt concentration, such deviations decrease. An attempt to satisfy these points was made, significant improvements were obtained in the AAD values at 1 mol/kg and 3 mol/kg, but the results were considerably degraded at 5 and 6 mol/kg globally. Reaching AAD values of up to 11% and 14% for isotherms at 5 and 6 mol/kg, respectively. Thus, as we aim to propose a model that can reproduce CO₂ solubility data in saline systems that can reach saturation, we decided to keep the proposed configuration.

Table 5Calculated deviations of CO₂ solubility in aqueous NaCl solutions.

References	T/K	P/MPa	$m_{\text{NaCl}}/$ (mol/kg) ^a	Np	AAD _%	AAD _% 1 mol/kg ^a	AAD _% 3 mol/kg ^a	AAD _% 5 mol/kg ^a	AAD _% 6 mol/kg ^a
Markham and Kobe (1941)	298.15- 313.15	0.10	1-3	6	4.00	3.11	4.89		
Harned and Davis (1943)	273.15- 323.15	0.10	1-3	33	5.54	3.57	7.52		
Malinin and Saveleva (1972)	323.15	4.8	1	1	4.17	4.17			
Malinin and Kurovskaya (1975)	373.15- 423.15	4.8	1	2	3.80	3.80			
Drummond (1981)	303.15- 473.15	3.66-19.6	0.99-3	8	6.27	4.36	7.41		
He and Morse (1993)	273.15- 323.15	0.10	1	5	3.74	4.14	2.32	5.75	
Rumpf et al. (1994)	313.15- 433.15	0.15-9.64	6	69	3.27				3.27
Koschel et al. (2006)	323.15- 373.15	5.1-20.2	1-3	14	7.49	8.45	6.54		
Yan et al. (2011)	323.15- 373.15	5.40	1	12	3.91	3.91			
Rosenqvist et al. (2012)	293.15	0.3-3.80	0.96	6	12.80	12.80			
Zhao (2014)	373.15	4.8-12.5	1	1	4.58	4.58			
Carvalho et al. (2015)	293.15- 353.15	1.02- 14.29	1	11	5.48	5.48			
Zhao et al. (2015b)	323.15- 423.15	15	1-6	9	3.54	3.19	2.20		5.23
Guo et al. (2016)	273.15- 473.15	10-50	1-5	152	3.48	3.49	3.73	3.21	
Messabeb et al. (2016)	323.15- 423.15	5-20	1-6	36	2.41	2.43	2.16		2.63

Wang et al. (2019)	303.15-353.15	3-30	1-3	170	5.81	6.52	5.11
Chabab et al. (2019)	373.15	1.70-22.98	1-3.01	9	6.23	11.63	0.83
Lara Cruz et al. (2020)	323.15	5.07-40.4	1	5	4.55		
This study	303.15	1.55-20.18	6	6			3.24
Overall				555	4.96	5.30	4.27
						4.48	3.59

^aMolalities are expressed in moles per kilogram of water.

Duan and Sun (2003) proposed a model which is widely used in several studies with regard to the CO₂-H₂O-NaCl system, where the CO₂ solubility can be calculated with an accuracy of 5 % (Li and Duan, 2011). In view of this set of data, Table 5 shows (see also Appendix B) the good coherence of the proposed model (AAD of 5%), not only with the experimental data but with the Duan's models as well (Duan et al., 2006; Duan and Sun, 2003; Li and Duan, 2011).

Distinctly that NaCl, the system containing sodium sulfate presents much less data available in the literature (Table 1). Only dos Santos et al. (2020) dataset was used for $\lambda_{\text{CO}_2, \text{SO}_4^{2-}}$ optimization and analyzing the results of AAD and Figures 7 and 8, we see how the proposed model is able to satisfactorily predict the experimental data (AAD approximately 3 %).

With the exception of Bermejo et al. (2005), all simulation results have AAD lower than 5 %. For Gerecke (1969) points, values below 2 % were obtained and for Zhao et al. (2015a), values below 2.3 %. Despite not being considered for optimization, the model was able to accurately simulate the 102 solubility data generated by Rumpf and Maurer (1993) at different temperatures, concentrations and pressure (AAD < 4 %) as highlighted in Figures 8.

Table 6

Calculated deviations of CO₂ solubility in aqueous Na₂SO₄ solutions.

References	T/K	P/MPa	$m_{\text{Na}_2\text{SO}_4}/$ (mol/kg) ^a	Np	AAD%	AAD% 1 mol/kg	AAD% 2 mol/kg
Markham and Kobe (1941)	298.15-313.15	0.10	1	2	4.65	4.65	
Gerecke (1969)	288.15-333.15	0.10	1	11	1.81	1.81	
Rumpf and Maurer (1993)	313.12-	0.42-9.71	1.011-	102	3.78	4.13	3.38

	433.15		2.01				
Bermejo et al. (2005)	303.15- 323.15	1.98- 13.11	1	5	8.36	8.36	
Zhao et al. (2015a)	323.15- 423.15	15	1-2	6	1.92	1.60	2.24
dos Santos et al. (2020)	303.15- 423.15	1.5-20	1-2	48	3.01	2.67	3.35
Overall				174	3.92	3.87	2.99

^aMolalities are expressed in moles per kilogram of water.

Sun et al. (2021) showed that the AAD calculated for the Duan's model (Duan et al., 2006; Duan and Sun, 2003) for the CO₂-H₂O-Na₂SO₄ system is 27.33 % (over 215 evaluated data) probably because of the absence of the interaction parameters $\lambda_{\text{CO}_2, \text{SO}_4^{2-}}$. Duan and Duan (2011) included this parameter in their model. They considered the experimental data from Bermejo et al. (2005) and Rumpf and Maurer (1993) for the CO₂-H₂O-Na₂SO₄ system and used the $\lambda_{\text{CO}_2, \text{Na}^+}$ parameter of Duan and Sun (2003) to determine the $\lambda_{\text{CO}_2, \text{SO}_4^{2-}}$ parameter. This way, they could reproduce the CO₂ solubility data in the H₂O-NaCl-CaSO₄ system. The model proposed in the present work is also capable of reproducing the experimental data from the literature for the CO₂-H₂O-Na₂SO₄ system with a slight advantage in the CO₂ solubility results, notably at 2 mol/kg solutions (see Appendix B).

Table 7 shows how the new experimental data - remembering that they were not used in the model creation process - are consistent with the model's predictions. In general, the AAD values are less than 4%, only 423 K for the mixture that is less than 4.5%. Observing the values in Table 7 and Figure 9, we can highlight that for the NaCl+Na₂SO₄ isotherm that the biggest differences are between the highest pressure values and that when we increase the temperature, the AAD values increase, however, globally, the model continues to respond well to experimental data. It is also important to note that the model is able to represent Yasunishi et al. (1979) experimental data very well. The average absolute deviations were calculated and it is about 1.65 %. Even if these data are not used at any point in the optimization process, the model is able to represent them perfectly and it is usable from very low to very high ionic strength.

Table 7

Experimental data of CO₂ solubility in mixed-salt Sodium Chloride and Sulfate Solutions at 303.15, 323.15, 373.15, and 423.15 K.

$m_{\text{NaCl}}/$ (mol/kg) ^b	$m_{\text{Na}_2\text{SO}_4}/$ (mol/kg) ^b	T/K ^a	P/MPa ^a	$m_{\text{CO}_2}/$ (mol/kg) ^b	$u(m_{\text{CO}_2})/$ (mol/kg) ^c	AD% ^c	AAD%
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6	0	303.15	1.55	0.148	0.003	1.05	3.24
			3.02	0.270	0.006	1.29	
			5.02	0.401	0.009	3.71	
			10.02	0.500	0.011	4.07	
			15.06	0.525	0.012	4.69	
			20.18	0.543	0.012	4.64	
3	1	303.15	1.53	0.140	0.003	1.31	3.61
			3.04	0.259	0.006	3.39	
			5.03	0.375	0.009	3.65	
			10.02	0.466	0.011	4.04	
			15.03	0.483	0.011	3.24	
			20.12	0.514	0.012	6.02	
3	1	323.15	1.56	0.102	0.002	2.56	3.12
			3.04	0.186	0.004	1.22	
			5.03	0.284	0.006	2.10	
			10.04	0.416	0.009	2.94	
			15.08	0.454	0.010	3.39	
			20.07	0.495	0.011	6.50	
3	1	373.15	1.54	0.063	0.001	1.44	3.89
			3.07	0.123	0.003	2.62	
			5.03	0.191	0.004	2.35	
			10.16	0.330	0.008	4.72	
			15.10	0.421	0.010	6.32	
			20.12	0.476	0.011	5.89	
3	1	423.15	1.54	0.044	0.001	2.19	4.43
			3.03	0.096	0.002	3.80	
			5.04	0.164	0.004	4.30	
			10.01	0.299	0.007	5.39	
			15.02	0.405	0.009	5.63	
			20.05	0.482	0.011	5.31	

^aStandard uncertainties u are $u(T) = 0.06$ K, $u(P) = 0.03$ MPa. ^bRelative uncertainties u_r are $u_r(m_{\text{CO}_2}) = 0.0228$ and $u_r(m_{\text{salt}}) = 0.001$. Molalities are expressed in moles per kilogram of water.

$$^c u(m_{\text{CO}_2}) = 0.0228 \cdot m_{\text{CO}_2} \text{ mol/kg. } ^d \text{The absolute deviation } AD\% = 100 \times \left| \frac{m_{\text{CO}_2,i}^{\text{cal}} - m_{\text{CO}_2,i}^{\text{exp}}}{m_{\text{CO}_2,i}^{\text{exp}}} \right|.$$

In addition to single-salts aqueous systems containing NaCl or Na₂SO₄, the model proposed by Li and Duan (2011) can reproduce the experimental CO₂ solubility data in the CO₂-H₂O-NaCl-Na₂SO₄

system. The superiority of the model developed in the present work for this system is here again demonstrated by the comparison of the global AAD: < 5% for the present model versus < 10% for the Li and Duan's one (see also Appendix B).

6. CONCLUSIONS

An improved $\gamma - \phi$ equilibrium model was presented to calculate the CO_2 solubility in aqueous solutions containing NaCl and Na_2SO_4 covering a wide $P - T - m_{\text{salt}}$ range of 273.15–473.15 K, 0.1–40 MPa and 0–6 mol/kg with great precision to the experimental data available in the literature. The chemical equilibrium was described by PhreeSCALE software (Lach et al., 2016), which is based on the equations of Appelo et al. (2014). Using the available experimental data, it was possible to propose a new set of specific interaction parameters for Pitzer's formulation. The optimizations of the Pitzer interaction parameters occurred at first in the $\text{CO}_2\text{-H}_2\text{O}$ system, then $\text{CO}_2\text{-H}_2\text{O-NaCl}$ and finally, $\text{CO}_2\text{-H}_2\text{O-Na}_2\text{SO}_4$. The average absolute deviations (AAD) were also calculated to compare the results of the simulations and the experimental data, more than 700 points were compared and the AAD values globally were less than 5%.

In addition, new CO_2 solubility data in aqueous NaCl and NaCl- Na_2SO_4 solutions were measured at temperatures from 303 to 423 K, the ionic strengths from 6 mol/kg and a pressure range between 1.5-20 MPa. The comparison with the model was made and it is worth highlighting its capacity to reproduce the experimental data of the system containing salt mix, $\text{CO}_2\text{-H}_2\text{O-NaCl-Na}_2\text{SO}_4$. In this way, the model created from the optimization of the Pitzer parameters in single-salts systems, is capable of reproducing mixed-salt systems for NaCl and Na_2SO_4 equally well. Thus, the proposed model has great value to assist studies and projects in the area of CO_2 injection in deep saline geological formations in CCS, contributing to the mitigation of global warming.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SUPPLEMENTARY DATA

The literature references used by the present work for experimental measurements of phase equilibrium in the CO₂-H₂O system are found in Table 8. Details of the experimental information, including authors, number of measurements, temperature and pressure ranges are shown in Table 8. Measurements of the solubility of CO₂ in the aqueous phase are gathered from 102 available literature studies. Figures 10 and 11 show the reproduction of experimental data for CO₂-H₂O by the present model.

Figures 12, 13 and 14 refer to the model calculations regarding pH in CO₂-H₂O-NaCl systems, compared to experimental data (Li et al., 2018).

Table 8

Experimental data for CO₂-H₂O.

References	T (K)	P (MPa)	Np
Bunsen (1855) ^b	277.55 - 285.55	0.101	6
de Khanikof and Louguinine (1867) ^b	288.15	0.093 - 0.415	10
Bohr and Bock (1891) ^b	310.44-373.15	0.086 - 0.094	2
Setchenow (1892) ^b	238.3	0.075 - 0.117	12
Prytz and Holst (1895) ^b	273.15	0.101	2
Bohr (1899) ^b	273.25-334.55	0.101	15
Hantzsch and Vagt (1901) ^b	273.15-363.15	0.101	8
Geffcken (1904) ^b	288-15-298.15	0.101	2
Findlay and Creighton (1910) ^b	298.15	0.099 - 0.18	10
Findlay and Shen (1912) ^b	298.15	0.10 - 0.18	12
Sander (1912) ^b	293.15-373.15	2.45 - 16.67	55
Findlay and Williams (1913) ^b	298.15	0.035 - 0.102	10
Findlay and Howell (1915) ^b	298.15	0.036 - 0.132	18
Kunerth (1922) ^b	293.15-307.15	0.101	8
Buch (1926) ^b	292.95-293.95	0.101	14
Morgan and Pyne (1930) ^b	298.15	0.101	2
Morgan and Maass (1931)	273.15-298.15	0.008 - 0.114	19
Kobe and Williams (1935) ^b	298.15	0.101	1
Kritschewsky et al. (1935) ^b	293.15-303.15	0.490 - 1.942	9
Shedlovsky and MacInnes (1935) ^b	298.15	0.101	1
Zel'venskii (1937) ^b	273-373	1.084-9.446	60
Curry and Hazelton (1938) ^b	298.15	0.098 - 0.101	4
Wiebe and Gaddy (1939) ^b	323.15-373.15	2.53 - 70.92	29
Van Slyke (1939) ^b	295.95-298.65	0.101	6

Wiebe and Gaddy (1940) ^b	285.15-313.15	2.53 - 50.66	42
Markham and Kobe (1941) ^b	273.15-313.15	0.101	3
Harned and Davis (1943) ^b	273.15-323.15	0.101	18
Prutton and Savage (1945) ^b	374.15-393.15	2.33 - 70.32	26
Koch et al. (1949) ^b	291.45-295.05	0.012 - 0.018	6
Morrison and Billett (1952) ^b	286.45-347.85	0.101	19
Rosenthal (1954) ^b	293.15	0.101	1
Shchennikova et al. (1957) ^b	293.15-348.15	0.101	18
Ellis (1959) ^b	387.15-592.15	0.50 - 16.40	36
Malinin (1959) ^b	473.15-603.15	9.8 - 58.8	116
Bartels and Wrbitzky (1960) ^b	288.15-311.15	0.101	6
Novák et al. (1961) ^b	284.65-350.15	0.013 - 0.095	54
Austin et al. (1963) ^b	393.20-311.15	0.101	5
Ellis and Golding (1963) ^b	450.15-607.15	1.57 - 7.55	15
Takenouchi and Kennedy (1964)	383.15-623.15	10 - 150	116
Yeh and Peterson (1964) ^b	298.15-318.15	0.101	4
Takenouchi and Kennedy (1965)	423.15-623.15	10 - 140	37
Vilcu and Gainar (1967) ^b	293.16-308.16	2.53 - 7.59	20
Gerecke (1969)	288.15-333.15	0.101	10
Matouš et al. (1969)	303.15-353.15	0.99 - 3.90	13
Onda et al. (1970)	298.15	0.101	1
Power and Stegall (1970) ^b	310.15	0.101	1
Stewart and Munjal (1970) ^b	273.15-298.15	1.01 - 4.56	12
Hsu and Barton (1971) ^b	273.35-313.15	0.101	3
Li and Tsui (1971) ^b	273.85-303.15	0.101	5
Murray and Riley (1971) ^b	274.19-308.15	0.101	8
Malinin and Saveleva. (1972) ^b	298.15-358.15	4.795	11
Weiss (1974) ^b	293.75	0.101	5
Malinin and Kurovskaya (1975) ^b	298.15-423.15	4.795	9
Tokunaga (1975) ^b	283.15-313.15	0.101	4
Yasunishi and Yoshida (1979)	288.15-308.15	0.101	3
Drummond (1981) ^c	309.45-591.65	4.083 - 21.174	53
Zawisza and Malesinska (1981) ^b	323.15-273.15	0.154 - 5.389	33
Burmakina et al. (1982) ^b	298.15	0.101	1
Cramer (1982) ^b	306.15-486.15	0.8 - 5.8	7
Gillespie and Wilson (1982) ^b	288.71-533.15	0.69 - 20.28	40

Shagiakhmetov and Tarzimanov (1981) ^b	323.15-423.15	10 - 80	14
Briones et al. (1987) ^b	323.15	6.82 - 17.68	9
Nakayama et al. (1987) ^b	298.20	3.63 - 10.99	6
Postigo and Katz (1987) ^b	288.15-308.15	0.101	5
D'souza et al. (1988) ^b	323.15-348.15	10.1 - 15.2	4
Müller et al. (1988) ^b	373.15-473.15	0.32 - 8.11	49
Eremina et al. (1989) ^b	298.15-313.15	0.101	2
Nighswander et al. (1989) ^b	352.85-471.25	2.11 - 10.21	33
Traub and Stephan (1990) ^b	313.15	4 - 10	2
Sako et al. (1991) ^b	348.20-421.4	10.18 - 20.94	8
King et al. (1992) ^c	288.15-313.15	1.15 - 21.79	68
Dohrn et al., 1993) ^b	323.15	10.1 - 30.1	3
Yuan and Yang (1993)	278.15-318.5	0.101	5
Rumpf et al. (1994)	323.17	1.059 - 5.798	7
Teng et al. (1997)	278.15-293.15	6.44 - 29.49	24
Zheng et al. (1997)	278.15-338.15	0.049 - 0.084	10
Dhima et al. (1999)	343.15	10 - 100	7
Bamberger et al., (2000)	323.15-353.15	4.05 - 14.11	29
Yang et al. (2000)	277.84-280.98	4.99 - 14.2	32
Servio and Englezos (2001)	273.95-283.15	2.0 - 3.7	21
Anderson (2002)	274.15-288.15	0.067 - 2.183	54
Kiepe et al. (2002)	313.2-393.17	0.051 - 9.258	43
Bando et al. (2003)	303.15-333.15	10 - 20	12
Sabirzyanov et al. (2003)	298.15-423.15	10 - 80	17
Chapoy et al. (2004)	274.14-351.31	0.19 - 5.17	27
Li et al. (2004)	332.15	3.34 - 19.89	6
Valtz et al. (2004)	278.22-318.23	0.465 - 7.963	77
Bermejo et al. (2005)	296.73-369.65	1.55 - 8.34	26
Dalmolin et al. (2006)	288-323	0.092 - 0.466	49
Koschel et al. (2006)	323.1-373.1	2.06 - 20.20	8
Qin et al. (2008)	323.6-375.8	20.3 - 49.9	7
Siqueira Campos et al. (2009)	298.2 - 323.2	0.059 - 0.535	50
Han et al. (2009)	313.2 - 343.2	4.33 - 18.34	28
Ferrentino et al. (2010a)	308-15 - 323.15	7.58 - 13.10	18
Ferrentino et al. (2010b)	313.00	7.5 - 15.0	12
Liu et al. (2011)	308-15-328.15	2.08 - 15.99	31

Lucile et al. (2012)	298.15 - 393.15	0.54 - 5.14	30
Rosenqvist et al. (2012)	294.00	0.3 - 3.9	7
Savary et al. (2012)	393.15	11.3 - 33.7	3
Hou et al. (2013)	298.15 - 448.15	1.089 - 17.551	42
Langlais (2013)	298.15 - 423.15	0.72 - 20.07	29

Data source: ^bNIST, ^cPortier (2005). Np is the number of experimental data.

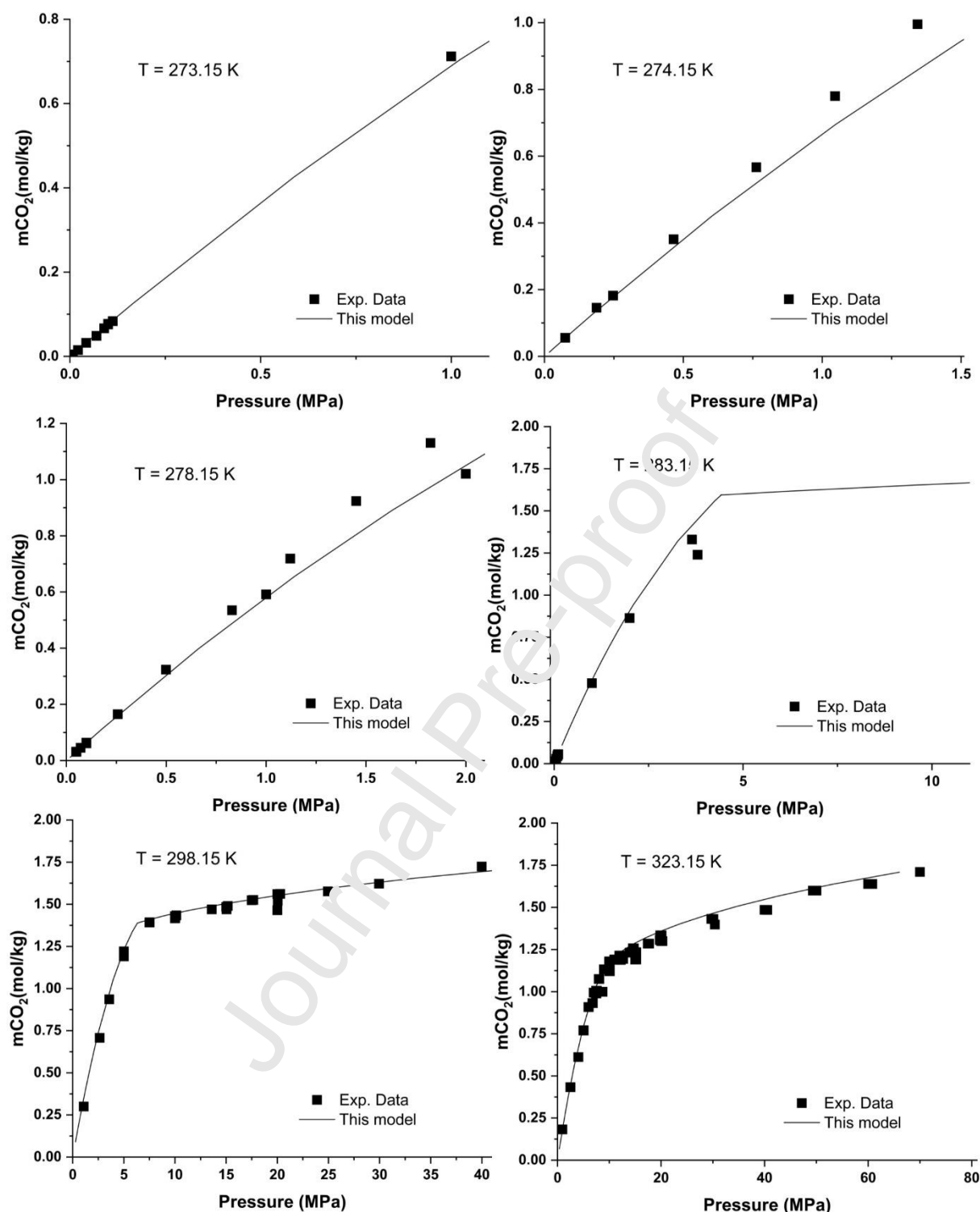


Figure 10 – CO_2 solubility in pure water from 273.15 to 323.15 K: symbols are experimental data (Table 1) whereas lines are calculated data with PhreeSCALE and the interaction parameters of the Pitzer model given in the text (Table 4).

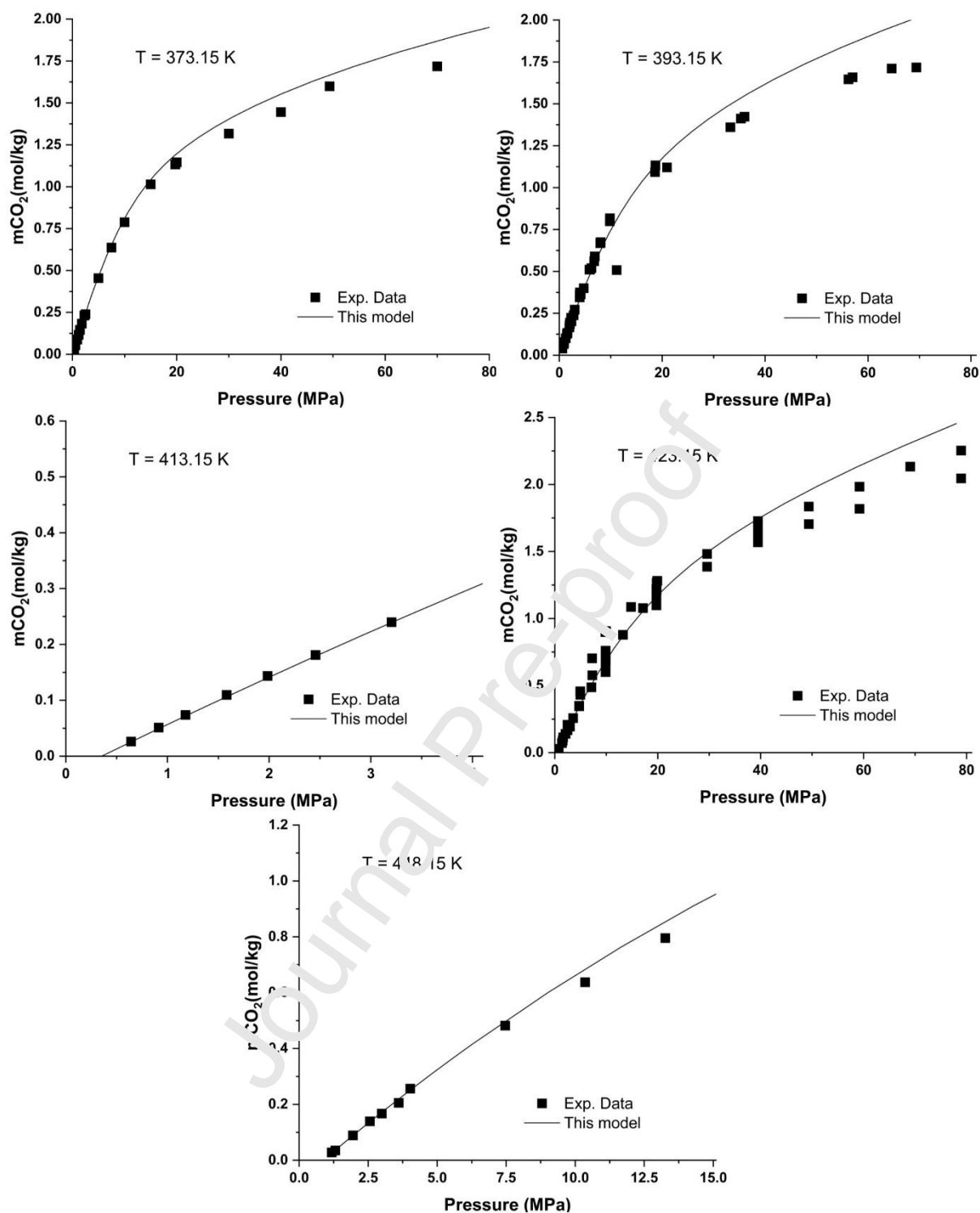


Figure 11 – CO₂ solubility in pure water from 373.15 to 448.15 K: symbols are experimental data (Table 1) whereas lines are calculated data with PhreeSCALE and the interaction parameters of the Pitzer model given in the text (Table 4).

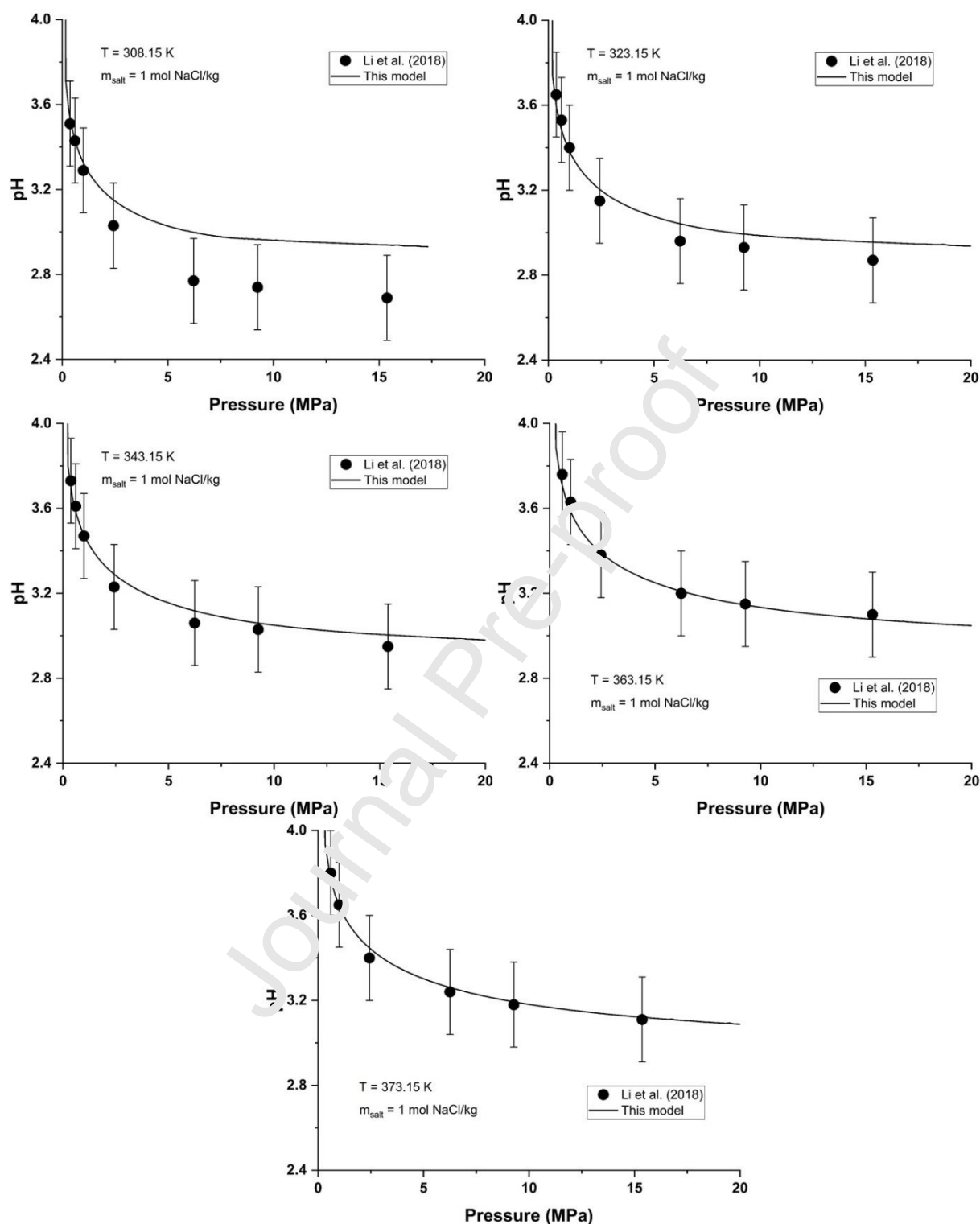


Figure 12 – Experimental pH measurements of CO₂-H₂O-NaCl (1 mol/kg) system as a function of pressure at 308, 323, 343, 363 and 373 K by Li et al. (2018). Solid lines show the pH calculated by PhreeSCALE. The calculations are performed according to the MacInnes assumption to be consistent with the results published by Li et al. (2018). Error bar shows the standard uncertainty of the experimental data ($U(\text{pH}) = 0.2$).

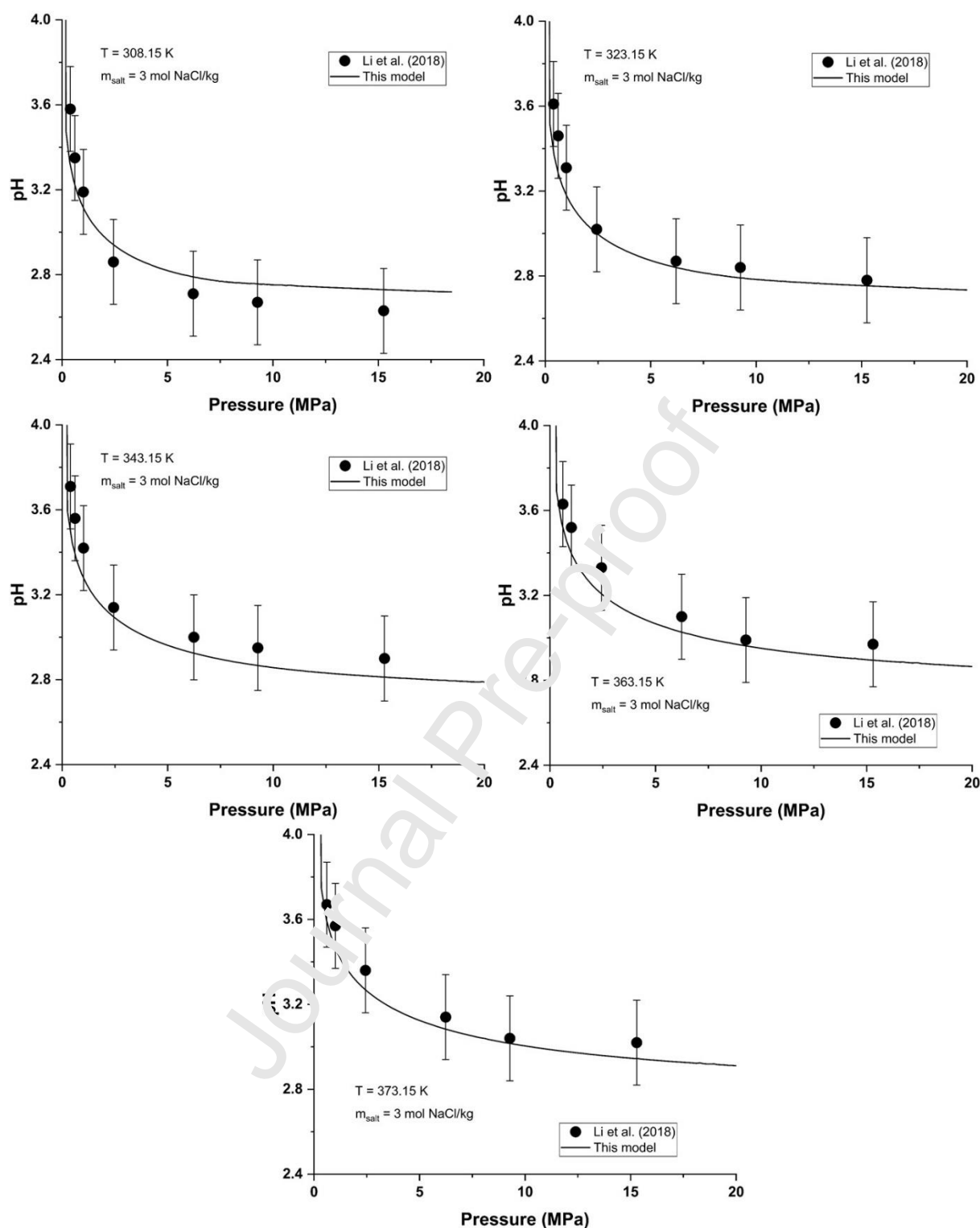


Figure 13 – Experimental pH measurements of $\text{CO}_2\text{-H}_2\text{O-NaCl}$ (3 mol/kg) system as a function of pressure at 308, 323, 343, 363 and 373 K by Li et al. (2018). Solid lines show the pH calculated by PhreeSCALE. The calculations are performed according to the MacInnes assumption to be consistent with the results published by Li et al. (2018). Error bar shows the standard uncertainty of the experimental data ($U(\text{pH}) = 0.2$).

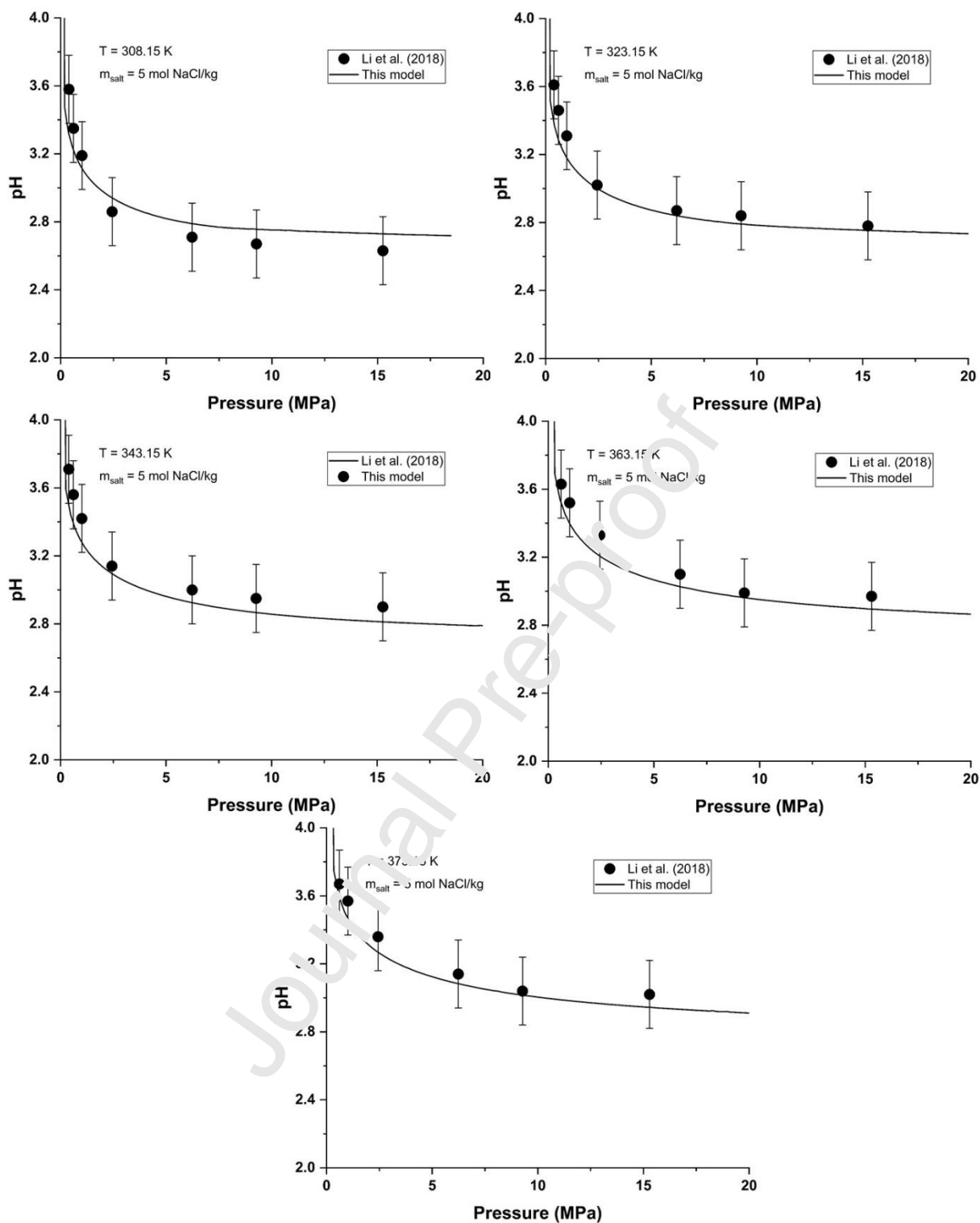


Figure 14 – Experimental pH measurements of $\text{CO}_2\text{-H}_2\text{O-NaCl}$ (5 mol/kg) system as a function of pressure at 308, 323, 343, 363 and 373 K by Li et al. (2018). Solid lines show the pH calculated by PhreeSCALE. The calculations are performed according to the MacInnes assumption to be consistent with the results published by Li et al. (2018). Error bar shows the standard uncertainty of the experimental data ($U(\text{pH}) = 0.2$).