Experimental Studies and Modeling of CO_2 Solubility in High Temperature Aqueous $CaCl_2$, $MgCl_2$, Na_2SO_4, and KCl Solutions

Haining Zhao
John and Willie Leone Family Dept. of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA 16802

Electrochemical Technologies Program, EMS Energy Institute, The Pennsylvania State University, University Park, PA 16802

Petroleum and Natural Gas Engineering Program, EMS Energy Institute, The Pennsylvania State University, University Park, PA 16802

Robert M. Dilmore
U.S. Dept. of Energy, National Energy Technology Laboratory, 626 Cochrans Mill Road, Pittsburgh, PA 15236

Serguei N. Lvov
John and Willie Leone Family Dept. of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA 16802

Electrochemical Technologies Program, EMS Energy Institute, The Pennsylvania State University, University Park, PA 16802

Dept. of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802

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The phase equilibria of CO_2 and aqueous electrolyte solutions are important to various chemical-, petroleum-, and environmental-related technical applications. CO_2 solubility in aqueous $CaCl_2$, $MgCl_2$, Na_2SO_4, and KCl solutions at a pressure of 15 MPa, the temperatures from 323 to 423 K, and the ionic strength from 1 to 6 mol kg^{-1} were measured. Based on the measured experimental CO_2 solubility, the previous developed fugacity-activity thermodynamic model for the CO_2-NaCl-H_2O system was extended to account for the effects of different salt species on CO_2 solubility in aqueous solutions at temperatures up to 523 K, pressures up to 150 MPa, and salt concentrations up to saturation. Comparisons of different models against literature data reveal a clear improvement of the proposed PSUCO2 model in predicting CO_2 solubility in aqueous salt solutions. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2286–2297, 2015

Keywords: CO_2 solubility, aqueous solutions, activity coefficient, setschenow coefficient, PSUCO2

Introduction

The phase equilibria of CO_2 and aqueous electrolyte solutions are important to many chemical-, petroleum-, and environmental-related technical applications, such as multi-stage flash desalination,[1] humidified supercritical CO_2 extraction,[2] geological CO_2 sequestration,[3] CO_2 enhanced geothermal system,[4] CO_2-enhanced oil recovery,[5] and CO_2-induced metal corrosion,[6] and so forth. Study of CO_2 solubility in single-salt aqueous solutions provides essential knowledge in understanding gas-liquid equilibrium concentration and mass-transfer rate between the CO_2-rich and aqueous phases for these industrial applications.

While the solubility of CO_2 in single-salt aqueous NaCl solutions at elevated temperatures and pressures has been widely studied at pressures of 0.1–150 MPa and temperatures from 273 to 673 K,[7–10] the CO_2 solubility in other

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Correspondence concerning this article should be addressed to S. N. Lvov at lvov@psu.edu.

Table 1. Experimental CO_2 Solubility in Aqueous $CaCl_2$, Na_2SO_4, $MgCl_2$, and KCl Solutions at 323–423 K and 15 MPa

(a) The CO_2-$CaCl_2$-H_2O System

T/K	m_{cacl_2}/mol kg^{-1}	m_{co_2}/mol kg^{-1}	δm_{random}/mol kg^{-1}
323	0.333	1.094	0.021
323	0.667	0.965	0.020
323	1.000	0.853	0.011
323	1.333	0.746	0.002
323	1.667	0.663	0.002
323	2.000	0.618	0.009
373	0.333	0.898	0.015
373	0.667	0.777	0.008
373	1.000	0.683	0.011
373	1.333	0.614	0.007
373	1.667	0.544	0.008
373	2.000	0.491	0.006
423	0.333	0.866	0.025
423	0.667	0.723	0.006
423	1.000	0.632	0.003
423	1.333	0.550	0.006
423	1.667	0.490	0.009
423	2.000	0.442	0.004

(b) The CO_2-Na_2SO_4-H_2O system

T/K	$m_{Na_2SO_4}$/mol kg^{-1}	m_{co_2}/mol kg^{-1}	δm_{random}/mol kg^{-1}
323	0.333	1.029	0.015
323	0.667	0.866	0.022
323	1.000	0.716	0.015
323	1.333	0.584	0.016
323	1.667	0.502	0.017
323	2.000	0.442	0.015
373	0.333	0.855	0.012
373	0.667	0.729	0.010
373	1.000	0.617	0.010
373	1.333	0.534	0.013
373	1.667	0.452	0.007
373	2.000	0.395	0.012
423	0.333	0.831	0.025
423	0.667	0.710	0.026
423	1.000	0.611	0.016
423	1.333	0.524	0.019
423	1.667	0.444	0.008
423	2.000	0.389	0.009

(c) The CO_2-$MgCl_2$-H_2O system

T/K	m_{MgCl_2}/mol kg^{-1}	m_{co_2}/mol kg^{-1}	δm_{random}/mol kg^{-1}
323	0.333	1.071	0.007
323	0.667	0.961	0.012
323	1.000	0.834	0.020
323	1.333	0.743	0.006
323	1.667	0.671	0.022
323	2.000	0.609	0.010
373	0.333	0.875	0.009
373	0.667	0.767	0.005
373	1.000	0.664	0.001
373	1.333	0.594	0.012
373	1.667	0.533	0.016
373	2.000	0.483	0.002
423	0.333	0.815	0.012
423	0.667	0.699	0.008
423	1.000	0.618	0.023
423	1.333	0.536	0.020
423	1.667	0.468	0.012
423	2.000	0.430	0.002

(d) The CO_2-KCl-H_2O system

T/K	m_{KCl}/mol kg^{-1}	m_{co_2}/mol kg^{-1}	δm_{random}/mol kg^{-1}
323	0.500	1.174	0.018
323	1.000	1.112	0.007

TABLE 1. *Continued*

(d) The CO_2-KCl-H_2O system

T/K	m_{KCl}/mol kg^{-1}	m_{co_2}/mol kg^{-1}	δm_{random}/mol kg^{-1}
323	2.000	1.005	0.014
323	3.000	0.929	0.003
323	4.000	0.880	0.014
323	4.500	0.855	0.017
373	0.500	0.941	0.011
373	1.000	0.895	0.002
373	2.000	0.805	0.015
373	3.000	0.740	0.030
373	4.000	0.683	0.017
373	4.500	0.657	0.005
423	0.500	0.881	0.008
423	1.000	0.816	0.012
423	2.000	0.724	0.020
423	3.000	0.651	0.004
423	4.000	0.593	0.014
423	4.500	0.565	0.006

Note: The instrument error δm_{instr} was not listed in the table and it was estimated approximately 0.7% of the measured results (detailed error estimation please see Zhao et al.[10]). The range of random errors are: (1) the CO_2-$CaCl_2$-H_2O system, 0.3–2.9%, the average is 1.3%; (2) the CO_2-Na_2SO_4-H_2O system, 0.7–3.6%, the average is 2.4%; (3) the CO_2-$MgCl_2$-H_2O system, 0.2–3.8%, the average is 1.7%; (4) the CO_2-KCl-H_2O system, 0.3–4.0%, the average is 1.5%. m_{co_2} is the molality of CO_2 in aqueous phase, mol/kg; and δm_{random} denotes random error caused by repeated measurements.

single-salt aqueous solutions [e.g., $CaCl_2$(aq), Na_2SO_4(aq), $MgCl_2$(aq), and KCl(aq)], especially for the CO_2-Na_2SO_4-H_2O and CO_2-$MgCl_2$-H_2O systems, have not been fully investigated. Considering NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4, and KCl are the five most frequently encountered salt species in natural water (groundwater, seawater, and natural brines)[11,12] and also common salts in industrial applications, high quality experimental data are still necessary to develop a reliable CO_2 solubility model for these CO_2-salt-H_2O systems. There are some reliable models deal with CO_2 solubility in aqueous solutions with salt species other than NaCl. To the best of our knowledge, one of the best thermodynamic modeling works on CO_2 solubility in aqueous electrolyte solutions of NaCl and Na_2SO_4 is reported by AspenTech.[13] Pérez-Salado Kamps et al.[14] developed a model to calculate CO_2 solubility in aqueous KCl and K_2CO_3 solutions with excellent results. In addition, three previously published models, which are capable of calculating CO_2 solubility in aqueous solutions containing a wide range of different salt species (NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4, and KCl), are considered herein for model comparison: (1) OLI: OLI Studio 9.0.6 (a commercial software developed by OLI Systems);[8] (2) SP2010;[7,15] and (3) DS2006.[16,17]

The objectives of this study are to (1) investigate the behavior of CO_2 solubility in different electrolyte solutions by measuring CO_2 solubility in aqueous $CaCl_2$, Na_2SO_4, $MgCl_2$, and KCl solutions at the same ionic strength (up to $I = 6$ mol kg^{-1}) at the P-T region of 15 MPa and 323–423 K; and (2) apply and extend our previously developed CO_2 solubility model[10] for the CO_2-NaCl-H_2O system to the single-salt aqueous solutions of $CaCl_2$, Na_2SO_4, $MgCl_2$, and KCl within the same thermodynamic framework. This article is organized as follows: we described the experimental materials, apparatus, approaches, and results in the experimentation section. In the modeling section, we presented a general approach to extend Pitzer's activity equations for calculating activity coefficient of dissolved CO_2 in different types of electrolyte solutions. The modeling results are presented through a detailed comparison of different CO_2 solubility models against all experimental data available

Table 2. Coefficients of Eqs. 10 and 11 for Calculating B_{CO_2-salt} and $C_{CO_2-CO_2-salt}$

Salt Species	a_1	a_2	a_3	a_4	a_5
$CaCl_2$[a]	-2.3219×10^{-1}	1.306910^{-1}	8.0693×10^{-1}	4.9642×10^{-2}	7.0156×10^{-3}
Na_2SO_4[b]	1.2396×10^{-1}	1.1765×10^{-1}	2.0199×10^{-1}	1.4198×10^{-3}	-1.7424×10^{-3}
$MgCl_2$[c]	-5.0410×10^{-2}	2.2742×10^{-2}	2.3521×10^{-1}	1.1069×10^{-1}	-2.8093×10^{-4}
KCl[d]	-1.8409×10^{-1}	6.2729×10^{-2}	5.0722×10^{-1}	8.7653×10^{-2}	-2.6025×10^{-3}

[a]For the CO_2-$CaCl_2$-H_2O sytem, the parameters $a_1a_5$were determined from the experimental data of this study and literature.[22,23–27]
[b]For the CO_2-Na_2SO_4-H_2O system, the parameters a_1a_5 were determined from the experimental data of this study and literature.[23,26,28–30]
[c]For the CO_2-$MgCl_2$-H_2O system, the parameters a_1 to a_5 were determined from the experimental data of this work and Yasunishi and Yoshida.[26]
[d]For the CO_2-KCl-H_2O system, the parameters a_1 to a_5 were determined from the experimental data of this and other studies.[14,26,31,32,27,33,34]

to us; finally, we interpreted and discussed the different behaviors of CO_2 solubility in various electrolyte solutions. In the end of this study, we proposed an approach to further extend the CO_2 solubility model for predicting CO_2 solubility in natural or synthetic brines (mixed-salt aqueous system).

Experimentation

The carbon dioxide used in all experiments was Coleman Instrument grade with a purity of 99.99%. Water was purified by a Milli-Q system and was degassed before being loaded into the autoclave. The purified water conductivity was below 6×10^{-6} S m^{-1}. All aqueous salt solutions were prepared using this Milli-Q water and ACS Grade reagents: calcium chloride ($CaCl_2{\cdot}2H_2O$, AlfaAesar, 99%), sodium sulfate (Na_2SO_4, Amresco, 99%), magnesium chloride ($MgCl_2$, Alfa Aesar, 99%), and potassium chloride (Alfa Aesar, 99%).

The experimental system consisted of a 600-mL stainless steel autoclave (Parr Instrument Co.), a 40-mL stainless steel sample cell, a liquid CO_2 pump, and a 300-mL stainless steel pressure cell for sample analysis. Details on the CO_2 solubility measuring technique and the error analysis approach can be found in Zhao et al.[10] The experimental CO_2 solubility results at a pressure of 15 MPa and temperatures from 323 to 423 K in aqueous $CaCl_2$, Na_2SO_4, $MgCl_2$, and KCl solutions at the ionic strength up to 6 mol kg^{-1} are listed in Table 1.

Modeling

We use a fugacity-activity procedure[18] to calculate fluid phase equilibria for CO_2-salt-H_2O systems. The fugacity coefficients (φ_{CO_2} and φ_{H_2O}) of all components in the CO_2-rich phase are calculated by a modified Redlich–Kwong equation of state (EoS),[7,15] and the activity coefficients for all components in the aqueous phase are calculated using the Pitzer activity model. The Pitzer activity model is selected due to its high accuracy among existed activity models for aqueous electrolyte solutions.[19] The Pitzer activity model is incorporated into vapor–liquid equilibrium relationship for water and CO_2 as shown by Eqs. 1–4[7,10,15]

$$\varphi_{CO_2} y_{CO_2} P = k^{o}_{H,CO_2} \exp\left(\frac{\overline{v}_{co_2}(P-P^s_w)}{RT}\right) a_{CO_2} \quad (1)$$

$$\varphi_{H_2O} y_{H_2O} P = P^s_w \varphi^s_w \exp\left(\frac{\overline{v}_w(P-P^s_w)}{RT}\right) a_{H_2O} \quad (2)$$

where y_{CO_2} and y_{H_2O} are, respectively, the mole fraction of CO_2 and H_2O in the CO_2-rich phase. In Eqs. 1 and 2, $k^{o}_{H,\ CO_2}$ is Henry's constant (molality scale) of carbon dioxide in pure water;[10] The vapor pressure (P^s_w) and the fugacity coefficient of water (φ^s_w) were calculated using the IAPWS-95 EoS;[20] $\overline{v}_{co_2}$ is a model parameter determined by fitting model calculated results to reliable experimental data for the binary CO_2-H_2O system;[10] and the partial molar volume of water $\overline{v}_w$, was approximated by the molar volume of saturated liquid water, v^s_w, which was also calculated using the IAPWS-95 EoS. The activity of dissolved CO_2 (a_{CO_2}) and the activity of water (a_{H_2O}) in the aqueous phase can be calculated as follows

$$a_{CO_2} = \gamma_{CO_2} m_{CO_2} \quad (3)$$

$$\ln(a_{H_2O}) = -\frac{\phi}{\Omega}\left[(v^+ + v^-) m_{salt} + m_{CO_2}\right] \quad (4)$$

where v^+ and v^- are stoichiometric coefficient for cation and anion, respectively; m_{CO_2} and m_{salt} are molality of dissolved CO_2 and single-salt species; γ_{CO_2} and ϕ are the activity coefficient of dissolved CO_2 and osmotic coefficient of water, which are both calculated by Pitzer equations [Appendix, Eqs. A1 and A2]; and Ω is the number of moles of solvent in a kilogram (55.51 for water). By substituting Eq. 3 into Eq. 1 and Eq. 4 into Eq. 2, and assuming the salt species is no volatile (means $y_{H_2O} + y_{CO_2} = 1$), Eqs. 1 and 2 can

Table 3. Pitzer Triple-Ion Interaction Parameter (ξ_{nca}) at 15 MPa

		Ionic Strength (mol kg^{-1})							
Salt Species	T/K	0.5	1	2	3	4	4.5	5	6
$CaCl_2$	323	–	0.77073	0.39436	0.26277	0.19510	–	0.15454	0.12769
	373	–	0.92645	0.46400	0.30811	0.22918	–	0.18232	0.15141
	423	–	1.10394	0.55441	0.36504	0.26831	–	0.21085	0.17319
Na_2SO_4	323	–	−0.05670	−0.03783	−0.03180	−0.02852	–	−0.02644	−0.02508
	373	–	−0.10374	−0.05646	−0.04081	−0.03287	–	−0.02802	−0.02489
	423	–	−0.06269	−0.04135	−0.03205	−0.02657	–	−0.02293	−0.02038
$MgCl_2$	323	–	0.63298	0.32062	0.21067	0.15474	–	0.12163	0.09991
	373	–	0.64031	0.32867	0.21797	0.16100	–	0.12696	0.10452
	423	–	0.86806	0.40224	0.25688	0.18685	–	0.14620	0.11964
KCl	323	0.59800	0.32006	0.16333	0.10802	0.07958	0.07004	–	–
	373	0.71435	0.36749	0.18537	0.12400	0.09210	0.08128	–	–
	423	0.95168	0.45440	0.21731	0.14267	0.10498	0.09233	–	–

Table 4. Comparison of the Model Calculations to Experimental CO_2 Solubility in Various CO_2-salt-H_2O Systems

							Model Calculations, AAD %			
Year	References	Systems	*P*/MPa	*T*/K	m_{salt}/mol kg^{-1}	*N*	PSUCO2	OLI[d]	SP2010	DS2006
1892[a]	Setschenow[35]	CO_2-$CaCl_2$-H_2O	0.1	288.4	0.1–5.0	11	4.11(11)	5.58(9)[b]	4.34(9)[b]	7.08(10)[c]
		CO_2-KCl-H_2O			1–4.3	3	1.92(3)	4.60(3)	21.47(3)	15.98(3)
1904[a]	Geffcken[36]	CO_2-KCl-H_2O	0.1	288–298	0.4–1.1	8	0.70(8)	2.29(8)	10.30(8)	6.37(8)
1912	Findley and Shen[37]	CO_2-KCl-H_2O	0.1	298	0.2–1	4	0.56(4)	3.40(4)	8.25(4)	6.18(4)
1935	Kobe and Williams[38]	CO_2-Na_2SO_4-H_2O	0.1	298	1.76	2	1.30(2)	26.82(2)	N/A(0)	N/A(0)
		CO_2-$MgCl_2$-H_2O	0.1	298	4.5	1	5.50(1)	N/A(1)[b]	N/A(0)[b]	N/A(0)[c]
1941	Markham and Kobe[31]	CO_2-Na_2SO_4-H_2O	0.1	298–313	0.2–1.5	8	0.61(8)	7.85(8)	7.03(4)	25.89(8)
		CO_2-KCl-H_2O		273.4–313	0.1–4	16	0.84(16)	4.59(16)	15.65(10)	10.62(16)
1945	Prutton and Savage[22]	CO_2-$CaCl_2$-H_2O	1.5–71.2	348–394	1–3.9	116	5.58(116)	3.86(116)	9.06(104)	9.22(116)
1969[a]	Gerecke[32]	CO_2-KCl-H_2O	1.5–6	274.16	0.5–3.4	40	3.69(40)	7.19(40)	16.73(40)	13.01(40)
1970	Onda et al.[23]	CO_2-$CaCl_2$-H_2O	0.1	298	0.2–2.3	8	0.49(8)	5.94(8)	4.16(8)	1.00(8)
		CO_2-Na_2SO_4-H_2O	0.1	298	0.5–1.5	3	1.77(3)	10.60(3)	26.49(3)	30.33(3)
1972 1975	Malinin and Savelyeva[24] Malinin and Kurovskaya[25]	CO_2-$CaCl_2$-H_2O	4.8	298–423	0.2–6.9	25	4.32(25)	5.74(25)	1.64(25)	3.17(21)[c]
1979	Yasunishi and Yoshida[26]	CO_2-$CaCl_2$-H_2O	0.1	298–308	0.2–5.3	16	3.46(16)	6.14(16)	5.76(14)[b]	3.16(15)[c]
		CO_2-Na_2SO_4-H_2O		288–308	0.2–2.4	26	3.46(26)	11.95(26)	5.35(7)	28.49(25)
		CO_2-$MgCl_2$-H_2O		288–308	0.1–4.4	29	3.66(29)	9.72(29)	7.47(25)	2.63(29)
		CO_2-KCl-H_2O		298–308	0.4–4.8	16	0.95(16)	8.01(16)	22.39(16)	17.05(14)[c]
1982	Burmakina et al.[33]	CO_2-KCl-H_2O	0.1	298	0.001–0.2	8	1.15(8)	4.48(8)	5.90(8)	3.93(8)
1990	Corti et al.[28]	CO_2-Na_2SO_4-H_2O	1.6–20	323–348	1–3.3	24	13.91(24)	20.50(15)[b]	N/A(0)	38.87(8)
1993	Rumpf and Maurer[29]	CO_2-Na_2SO_4-H_2O	0.4–9.7	313–433	1–2	102	2.73(102)	6.91(102)	N/A(0)	27.57(102)
2002	Kiepe et al.[34]	CO_2-KCl-H_2O	0.1–10.5	313–353	0.5–4	88	10.16(88)	9.42(88)	13.58(87)	13.07(88)
2005	Bermejo et al.[30]	CO_2-Na_2SO_4-H_2O	2–13.1	287–369	0.25–1	113	6.70(113)	12.77(113)	12.73(24)	22.72(113)
2007	Pérez-Salado Kamps et al.[14]	CO_2-KCl-H_2O	0.4–9.4	313–433	2–4	98	1.65(98)	2.67(98)	18.35(98)	18.34(98)
2011	Liu et al.[27]	CO_2-$CaCl_2$-H_2O	2–16	318	1	8	8.43(8)	11.26(8)	9.63(8)	11.76(8)
		CO_2-KCl-H_2O	2–16	318	1.5	8	2.93(8)	3.32(8)	13.78(8)	15.39(8)
2013	Tong et al.[39]	CO_2-$CaCl_2$-H_2O	1.5–38	308–424	1–5	36	7.36(36)	6.73(24)[b]	4.85(24)[b]	4.69(24)[c]
		CO_2-$MgCl_2$-H_2O	1.2–35	308–424	1–5	39	5.14(39)	6.14(26)[b]	5.67(26)[b]	5.83(26)[c]
2014	This study	CO_2-$CaCl_2$-H_2O	15	323–423	0.33-2	18	0.88(18)	2.13(18)	3.12(18)	3.61(18)
		CO_2-Na_2SO_4-H_2O		323–423	0.33–2	18	0.75(18)	8.04(18)	7.50(3)	15.90(18)
		CO_2-$MgCl_2$-H_2O		323–423	0.33–2	18	0.83(18)	2.30(18)	3.49(18)	3.20(18)
		CO_2-KCl-H_2O		323–423	0.5–4.5	18	0.33(18)	4.21(18)	14.91(18)	16.71(18)
Overall AAD % for each single-salt system (Including this study)		CO_2-$CaCl_2$-H_2O					4.3(238)	5.9(224)	5.3(210)	5.5(220)
		CO_2-Na_2SO_4-H_2O					3.9(296)	13.2(287)	11.8(41)	27.1(277)
		CO_2-$MgCl_2$-H_2O					3.8(87)	6.1(73)	5.5(69)	3.9(73)
		CO_2-KCl-H_2O					2.3(307)	4.9(307)	14.7(300)	12.4(305)
Overall AAD %							3.6	7.5	9.3	12.2
Experimental data *P-T-x* coverage							100%	96%	67%	94%

The numbers in parentheses stand for the number of experimental data evaluated by each model. "N/A" in the table denotes the *P-T-x* region of the experimental data beyond the capacity of the corresponding model.
[a]Indicates the experimental data taken from large the data compilation by Scharlin.[40]
[b]The experimental *P-T-x* points at $m_{cacl_2} > 3$ mol kg^{-1} were removed from the comparison for both the OLI and SP2010 model due to relatively large AAD % for these models at high $CaCl_2$ concentration.
[c]The experimental *P-T-x* points at $m_{cacl_2} > 4.5$ mol kg^{-1} were removed due to the DS2006 model is limited to 4.5 mol kg^{-1} salt molality.
[d]Calculations made by OLI Studio 9.0.6 are under the following conditions: (1) enable the second liquid phase, (2) use MSE model, (3) stream inflows contains 55.51 mol water and 5 mol CO_2.

be solved simultaneously using the Newton Raphson method with respect to m_{CO_2}. The essential aspects of the phase equilibrium calculation are discussed in detail in Zhao et al.[10] In the following paragraphs, we present a general method to evaluate Pitzer model parameters, which enable the calculation of CO_2 solubility for different CO_2-salt-H_2O systems within the same thermodynamic framework.

The calculation of CO_2 solubility in aqueous salt solutions other than NaCl is achieved by fitting Pitzer model parameters to experimental CO_2 solubility for each CO_2-salt-H_2O system. Three parameters (B_{CO_2-salt}, $C_{CO_2-CO_2-salt}$, and ξ_{nca}) are needed to accurately correlate the experimental CO_2 solubility data for each CO_2-salt-H_2O system. Among these parameters, the combined Pitzer interaction parameters (B_{CO_2-salt} and $C_{CO_2-CO_2-salt}$) can be written for any salt species as[21]

$$B_{CO_2-salt} = v^+ \lambda_{nc} + v^- \lambda_{na} \quad (5)$$

$$C_{CO_2-CO_2-salt} = v^+ \mu_{nnc} + v^- \mu_{nna} \quad (6)$$

where λ_{nc} and λ_{na} are the Pitzer neutral-cation and neutral-anion binary ion interaction parameters, respectively; μ_{nnc} and μ_{nna} are the Pitzer neutral-neutral-cation and neutral-neutral-anion triple ion interaction parameters, respectively. Subsequently, the Pitzer equation for activity coefficient of dissolved CO_2 [Appendix, Eq. A1] can be simplified as

$$\ln\gamma_{CO_2} = 2m_{CO_2}\lambda_{nn} + 3m_{CO_2}^2\mu_{nnn} + 2B_{CO_2-salt}m_{salt} + v^+v^-m_{salt}^2\xi_{nca} + 6m_{CO_2}m_{salt}C_{CO_2-CO_2-salt} \quad (7)$$

where λ_{nn} and μ_{nnn} are the Pitzer pure neutral component interaction parameters;[10] and ξ_{nca} is the Pitzer tripe-ion

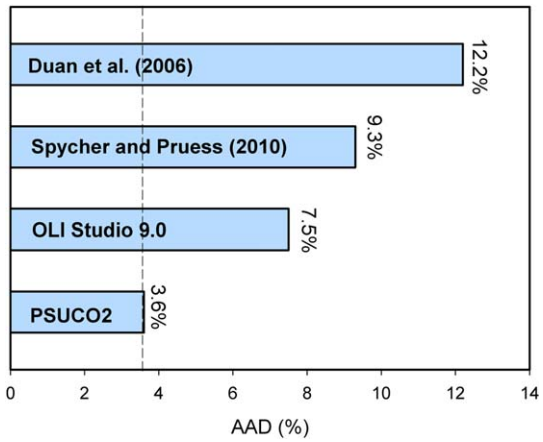

Figure 1. The AAD % of the calculated CO_2 solubility values in aqueous $CaCl_2$, Na_2SO_4, $MgCl_2$, and KCl solutions by different models compared with the experimental data (all available experimental data listed in Table 4.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

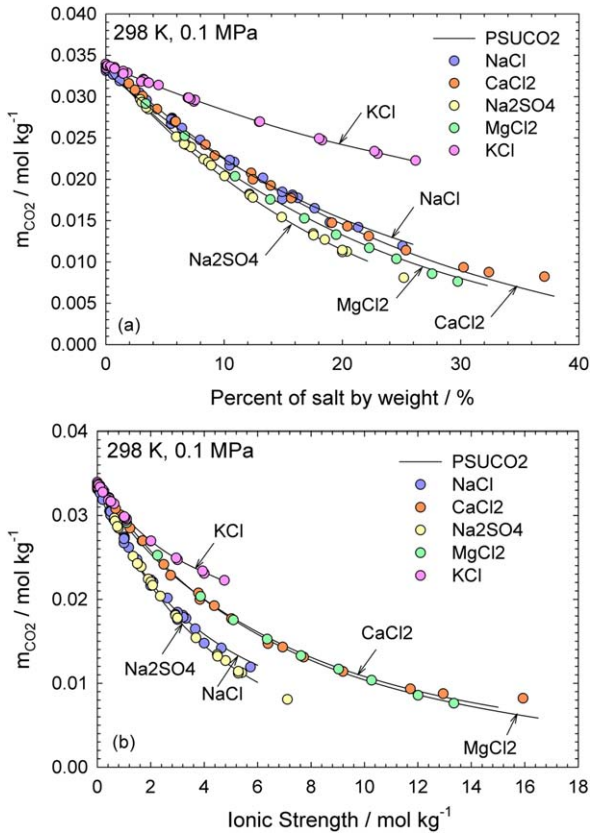

Figure 2. (a,b). Comparison of the experimental CO_2 solubility[23,26,31,35–38,40] in various aqueous salt solutions at 298.15 K and 0.1 MPa based on different concentration scales: (a) percent of salt by weight; (b) ionic strength.

Solid lines represent the calculated values from the PSUCO2 model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interaction parameter. For CO_2-H_2O system, Eq. 7 can be reduced to Eq. 8 by setting the parameters B_{CO_2-salt}, ξ_{nca}, and $C_{CO_2-CO_2-salt}$ equal to zero

$$\ln\gamma^{o}_{CO_2} = 2m^{o}_{CO_2}\lambda_{nn} + 3(m^{o}_{CO_2})^2\mu_{nnn} \quad (8)$$

where $\gamma^{o}_{CO_2}$ and $m^{o}_{CO_2}$ are the activity coefficients of dissolved CO_2 and solubility of CO_2 (CO_2 molality) in the CO_2-H_2O system. The combined Pitzer interaction parameters B_{CO_2-salt} and $C_{CO_2-CO_2-salt}$ in Eq. 7 were determined using experimental CO_2 solubility in both pure water and aqueous single-salt solutions. To evaluate these two parameters, we made an assumption that the chemical potentials of CO_2 in the CO_2-H_2O and CO_2-salt-H_2O systems are the same at a given P-T condition based on the similar approach used by Akinfiev and Diamond.[21] At

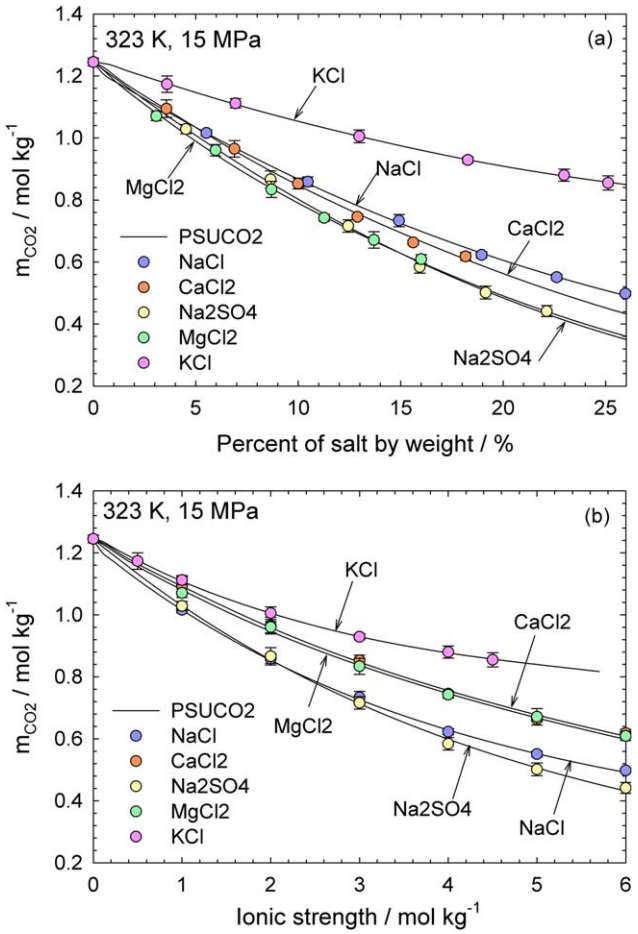

Figure 3. (a,b). Comparison of the experimental CO_2 solubility (this study) in different aqueous salt solutions based on different concentration scales at 323 K and 15 MPa (the comparison at 373 and 423 K were not shown due to the similar pattern as that in 323 K, but the calculated solubility curves at those temperatures become more closer to each other than 323 K): (a) percent of salt by weight (%); (b) ionic strength.

Experimental CO_2 solubility in aqueous NaCl solutions is taken from Zhao et al.[10] Solid lines represent the calculated values from the PSUCO2 model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

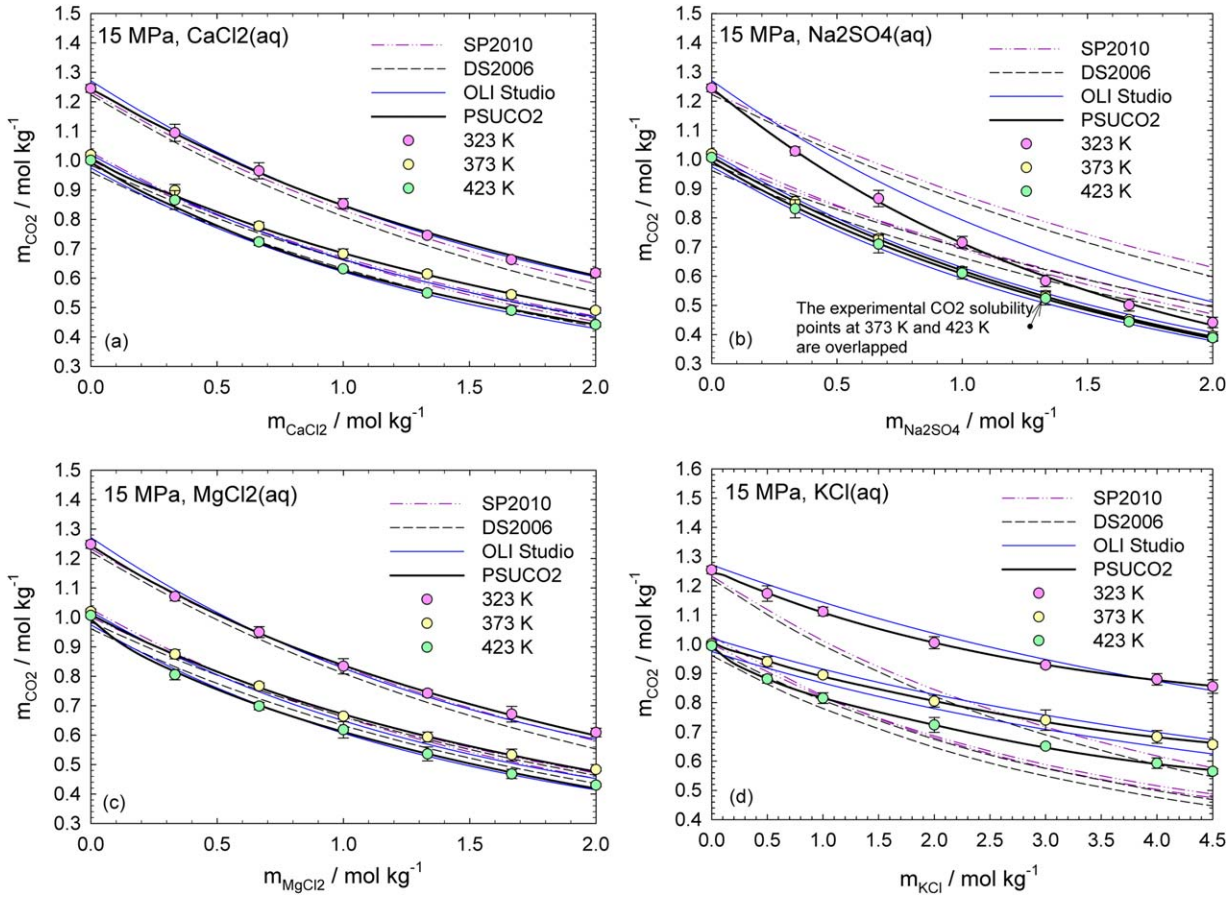

Figure 4. (a–d). Comparison of model calculated values against the experimental CO_2 solubility (this study): (a) CO_2-$CaCl_2$-H_2O system; (b) CO_2-Na_2SO_4-H_2O system; (c) CO_2-$MgCl_2$-H_2O system (d) CO_2-KCl-H_2O system.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

equilibrium, the chemical potential of CO_2 in the CO_2-rich phase is equal to that in the aqueous phase, given by $\mu_{CO_2}^{(g)}=\mu_{CO_2}^{(aq)}$ for the CO_2-H_2O system and $\mu_{CO_2}^{(g)}=\mu_{CO_2}^{(aq)}$ for the CO_2-salt-H_2O system. In fact, the chemical potentials of CO_2 between the salt-bearing and salt-free systems are different. However, assuming that $\mu_{CO_2}^{(g)}=\mu_{CO_2}^{(g)}$ results in a mean error of about 0.3% of calculated CO_2 solubility in the aqueous phase,[21] so this assumption is not significantly impactful to the overall model results. Thus, the equality of CO_2 activity between the CO_2-H_2O and CO_2-salt-H_2O systems ($\mu_{CO_2}^{(g)}=\mu_{CO_2}^{(g)}$) can be represented as follows

$$\ln\left(m_{CO_2}\gamma_{CO_2}\right)=\ln\left(m^{o}_{CO_2}\gamma^{o}_{CO_2}\right) \tag{9}$$

Combining Eqs. 7, 8, and 9, the combined Pitzer interaction parameters $B_{CO_2\text{-salt}}$ and $C_{CO_2\text{-}CO_2\text{-salt}}$ (in Eq. 7) can be determined by fitting of Eq. 9 to the corresponding experimental CO_2 solubility data in both CO_2-H_2O and CO_2-salt-H_2O systems. As a results, the parameters $B_{CO_2\text{-salt}}$ and $C_{CO_2\text{-}CO_2\text{-salt}}$ for each CO_2-salt-H_2O system can be calculated in terms of the temperature, ionic strength, and coefficients a_1 to a_5

$$B_{CO_2\text{-salt}}=a_1+a_2\frac{100}{T-\theta}+a_3\frac{T}{1000}+a_4 g(x) \tag{10}$$

$$C_{CO_2\text{-}CO_2\text{-salt}}=a_5 \tag{11}$$

where $\theta=228$ K, $g(x)=\frac{2}{x^2}\left(1-(1+x)e^{-x}\right)$, $x=\alpha_1 I^{0.5}$, and $\alpha_1=2.0$ kg$^{0.5}$ mol$^{-0.5}$. The detailed data fitting procedure to estimate coefficients a_1 to a_5 is provided in Supporting Information. The data fitting results of coefficients a_1 to a_5 are shown in Table 2.

In addition, through the comparison between model calculated results and the experimental data reported herein, we found that the parameter ξ_{nca} has a strong dependence on temperature and salt concentration, especially at high temperatures and low salt concentrations, but it is insensitive to the system pressure. Therefore, the Pitzer triple-ion interaction parameter ξ_{nca} (in Eq. 7) was calculated by performing a binary search for m_{CO_2} in the PSUCO2 model until consistency between the calculated and experimental values was obtained. The results of ξ_{nca} determined in this manner are listed in Table 3. By assuming independence of pressure, ξ_{nca} at any *P-T-x* conditions can be obtained through an interpolation or extrapolation of the values listed in Table 3 for the corresponding CO_2-salt-H_2O system. The procedure is: (1) a cubic spline interpolation with a step of 0.001 mol kg^{-1} salt molality was used to get the relationship between ξ_{nca} and salt concentration (molality) at a constant temperature; and then (2) the linear interpolation was applied to calculate ξ_{nca} at any targeted *P-T-x* point. Finally, using the calculated results of $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, and C_{ca}^{ϕ} (Supporting Information) along with the parameters B_{CO_2-salt}, $C_{CO_2-CO_2-salt}$, and ξ_{nca}, the previously developed CO_2 solubility model for the aqueous NaCl solution was effectively extended to the aqueous $CaCl_2$, Na_2SO_4, $MgCl_2$, KCl solutions.

In Table 4, the modeling results of CO_2 solubility in the aqueous phase from various models (PSUCO2, SP2010, DS2006, and OLI) were compared to the experimental

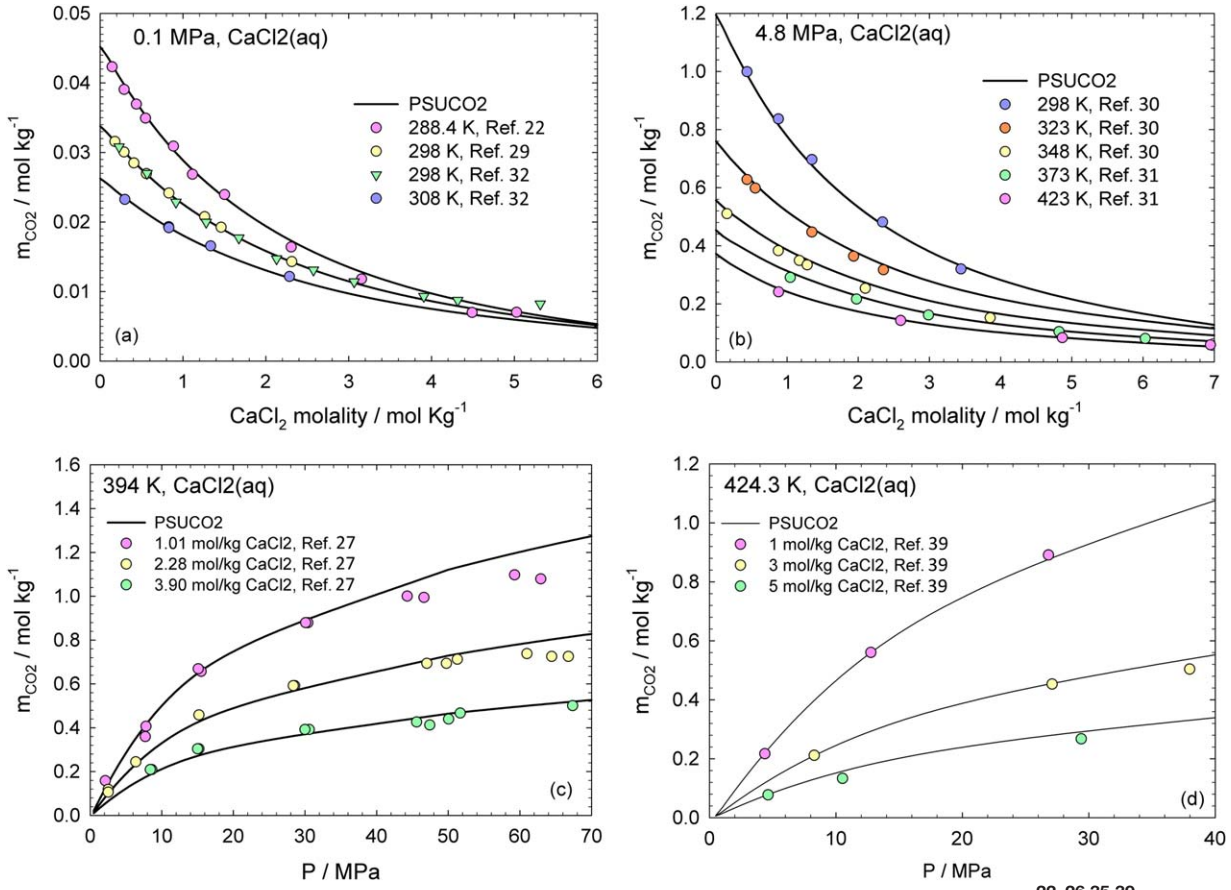

Figure 5. (a–d). Comparison of model calculations against the experimental CO_2 solubility[22–26,35,39] in aqueous $CaCl_2$ solutions.

(a) 0.1 MPa, 288–308 K, and 0.14–5.31 mol kg^{-1} $CaCl_2$; (b) 4.8 MPa, 298–423 K, and 0.16–6.95 mol kg^{-1} $CaCl_2$; (c) 2.1–71.2 MPa, 394 K, and 1.01–3.90 mol kg^{-1} $CaCl_2$; (d) 4.4–38 MPa, 424.4 K, and 1–5 mol kg^{-1} $CaCl_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data[14,22–40] in terms of average absolute deviation (AAD %), which is defined as below

$$\mathrm{AAD}(\%)=\frac{100}{N_\mathrm{p}}\sum_{i=1}^{N}\left|\frac{m_{\mathrm{CO}_2,i}^{\mathrm{calc}}-m_{\mathrm{CO}_2,i}^{\mathrm{exp}}}{m_{\mathrm{CO}_2,i}^{\mathrm{exp}}}\right|\% \qquad (12)$$

where $m_{\mathrm{CO}_2,i}^{\mathrm{calc}}$ represents the calculated CO_2 solubility values from the CO_2 solubility models (PSUCO2, SP2010, DS2006, and OLI); $m_{\mathrm{CO}_2,i}^{\mathrm{exp}}$ denotes the experimental CO_2 solubility taken from literature and obtained in this study; and N means the total number of experimental data in each work. Table 4 demonstrates that the PSUCO2 model predicts the CO_2 solubility in aqueous $CaCl_2$, Na_2SO_4, $MgCl_2$, and KCl solutions with a high degree of accuracy over a wide *P-T-x* range [288–433 K, 1–71 MPa, and ionic strength up to 20.7 mol kg^{-1} for $CaCl_2$(aq), 7.2 mol kg^{-1} for Na_2SO_4(aq), 15 mol kg^{-1} for $MgCl_2$(aq), and 4.8 mol kg^{-1} for KCl(aq)]. Although there is a lack of experimental CO_2 solubility to validate the model performance at the pressures higher than 71 MPa and temperatures above 433 K, the proposed PSUCO2 model can still be safely extended to 150 MPa and 523 K due to the following reasons: (1) the model is based on a sound thermodynamic framework, which is validated by reliable experimental up to 200 MPa and 573 K for the CO_2-H_2O binary system;[10] and (2) the same thermodynamic framework is also validated by reliable experimental CO_2 solubility in the aqueous phase for the CO_2-NaCl-H_2O system up to 150 MPa and 573 K.[10] In addition to Table 4, Figure 1 clearly indicates that the proposed PSUCO2 model provides the best performance in calculating the CO_2 solubility in all CO_2-salt-H_2O systems investigated in this study relative to the published models (SP2010, DS2006, and OLI). The updated model is named as PSUCO2 and is available as an Internet-based computational tool (Supporting Information).

Discussion

At atmospheric pressure, Li and Tsui[41] measured CO_2 solubility in aqueous NaCl solution (0.6413 mol kg^{-1} NaCl) and acidified seawater (with 10, 20, and 29‰ Chlorinity) at the temperature range from 273.85 to 303.15 K. Based on the obtained experimental results, Li and Tsui[41] concluded that the Buch's assumption[42] —the effect of a given weight of sea salts on solubility of CO_2 is the same as that of an identical weight of NaCl—is proved to be valid. A question arises when extending Li and Tsui's conclusion from sea salt to any salt species—is the effect of a given weight of any salt (or mixed-salt) on solubility of CO_2 still the same as that of an identical weight of NaCl? The answer is no. In this study, we have experimentally demonstrated that CO_2 solubility in aqueous solutions with different salt species are significantly different at 15 MPa, whether the solutions have the same percent of salt by weight or have the same ionic strength. This observation is also substantiated by experimental CO_2 solubility data[23,24] at ambient conditions (Figure 2). Figures

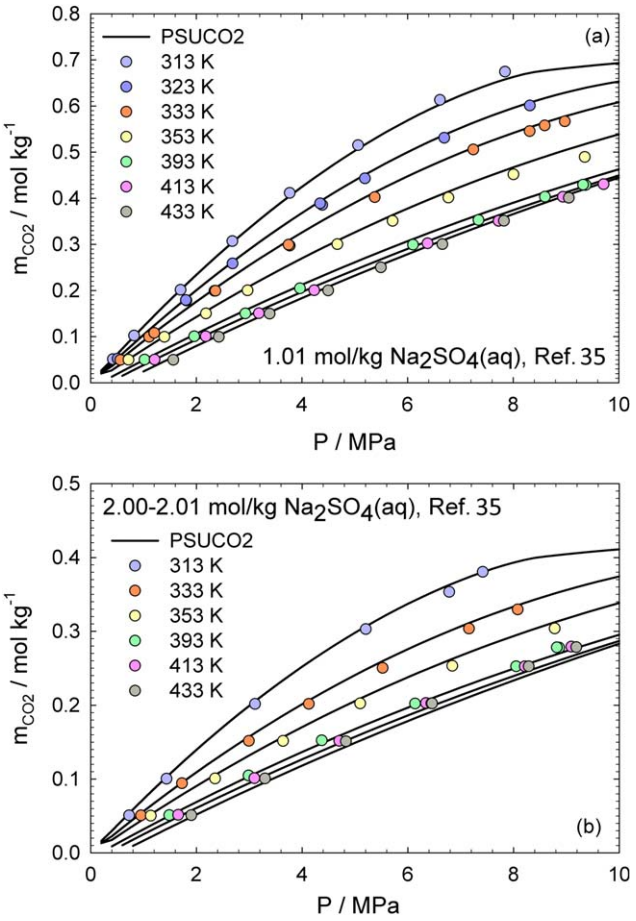

Figure 6. (a,b). Comparison of the model calculations against the experimental CO_2 solubility[29] in aqueous Na_2SO_4 solutions.

(a) 0.4–9.7 MPa, 313–433 K, and 1 mol kg^{-1} Na_2SO_4; (b) 0.7–9.2 MPa, 313–433 K, and 2 mol kg^{-1} Na_2SO_4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2b and 3b show that the magnitude of CO_2 solubility in aqueous salt solutions follows a decreasing sequence of $m_{CO_2}^{KCl} > m_{CO_2}^{CaCl_2} > m_{CO_2}^{MgCl_2} > m_{CO_2}^{NaCl} > m_{CO_2}^{Na_2SO_4}$ based on the same ionic strength.

The ion-water molecule interactions dominate the CO_2 solubility behavior in different aqueous salt solutions. For example, on the basis of the number of ions produced when strong electrolyte dissociates in solution, $MgCl_2$ and $CaCl_2$ are the same type electrolytes (1-2 type). The measured solubility of CO_2 in $CaCl_2$(aq) and in $MgCl_2$(aq) are quite close in a wide *P-T-x* range (Figures 2 and 3), but the measured CO_2 solubility in $CaCl_2$(aq) is always slightly greater than that in $MgCl_2$(aq). Whereas, the solubility of CO_2 in aqueous NaCl solution is considerably smaller than that in aqueous KCl solution given that these two salts share the same electrolyte type (1-1 type; Figures 2 and 3). The studies of the ion hydration and ion-water molecule interactions[43,44] demonstrated that small ions of high charge density bind water molecules strongly, whereas large ions of low charge density bind water molecules weakly. Thus, the high charge density ions have strong influence on water structure, which determines the capacity of the aqueous phase to trap dissolved CO_2. Based on the experimental results, if two single-salt aqueous solutions have the same type of electrolyte (e.g., 2-1 or 1-1 type) and share the same anion (e.g., Cl^-), a cation with greater charge density (a smaller radii and a greater charge number) has more significant salting-out effect on dissolved CO_2 than that with smaller charge density. For example, the charge density of Mg^{2+} is slightly greater than that of Ca^{2+} (same charge number but Mg^{2+} has a smaller radius than Ca^{2+}),[45] as a result, the amount of CO_2 dissolved in aqueous $MgCl_2$ is less than that in aqueous $CaCl_2$ solution at the same ionic strength. The similar situation occurs for the CO_2 solubility in aqueous NaCl and KCl solutions. Na^+ has a significantly greater charge density than K^+, thus the CO_2 solubility in aqueous NaCl solution is considerably less than that in aqueous KCl solutions.

Figure 4 and Table 4 (row 19) show that SP2010 and DS2006 models predict the experimental data obtained herein quite well for the CO_2-$CaCl_2$-H_2O (Figure 4a) and CO_2-$MgCl_2$-H_2O (Figure 4c) systems, however, these models (SP2010 and DS2006) predict the measured CO_2 solubility in aqueous Na_2SO_4 and KCl solutions with a large error (Figures 4b, d). The SP2010 and DS2010 models use the same type of simplified Pitzer equation to calculate aqueous phase activity coefficients.[7] Because the similar activity equation is used in both DS2006 and SP2010 models, the

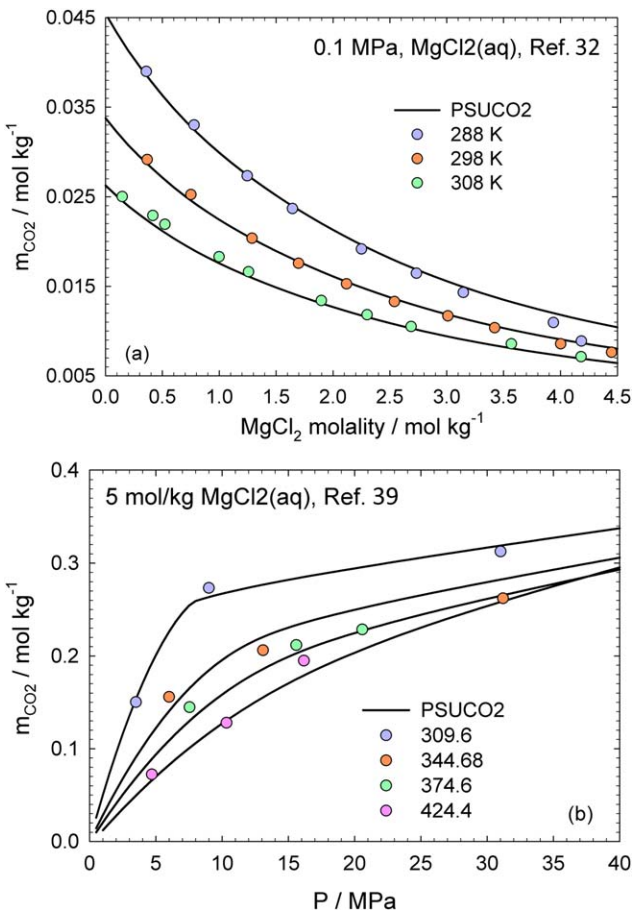

Figure 7. (a,b). Comparison of the model calculations against the experimental CO_2 solubility[26,39] in aqueous $MgCl_2$ solutions.

(a) 0.1 MPa, 288–303 K, and 0.15–4.45 mol kg^{-1} $MgCl_2$; (b) 3.5–31.2 MPa, 309.6–424.4 mol kg^{-1} $MgCl_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

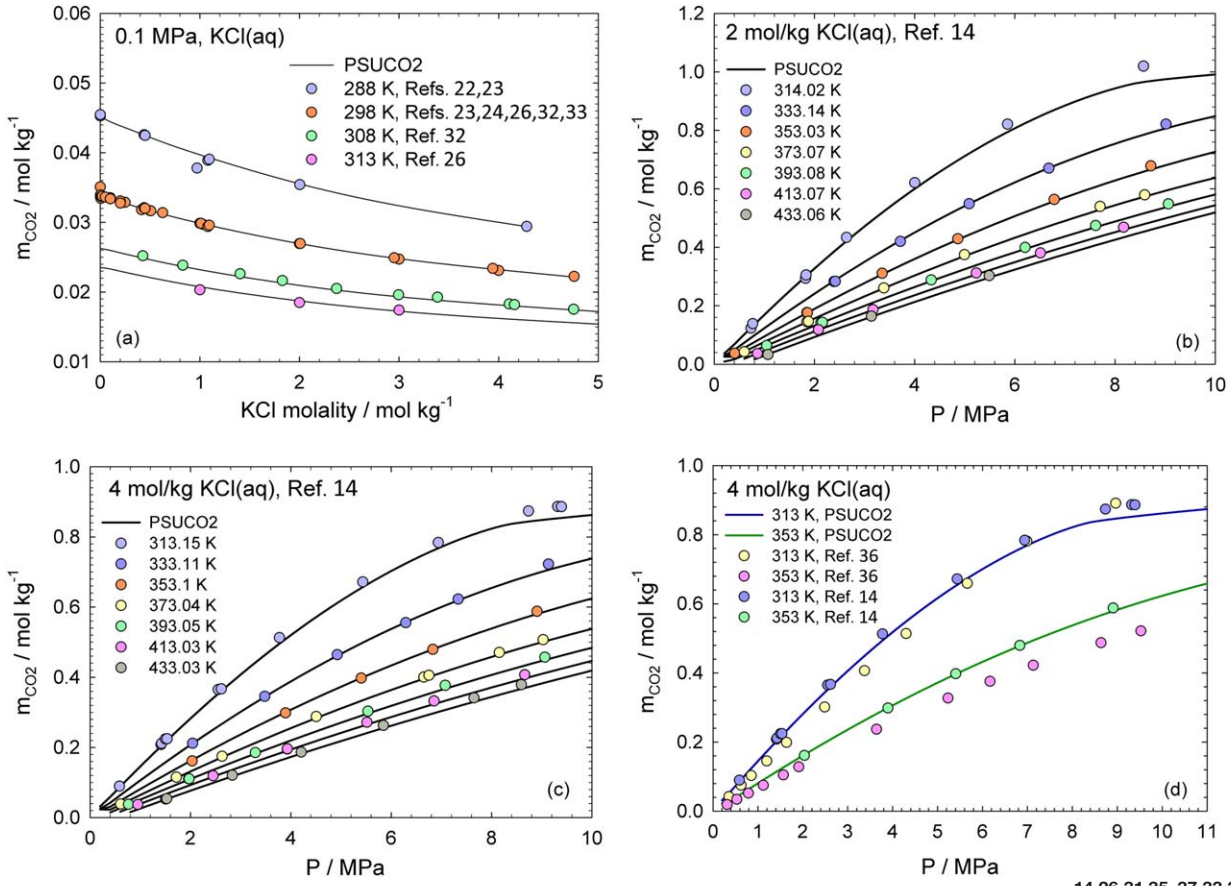

Figure 8. (a–d). Comparison of the model calculations against the experimental CO_2 solubility[14,26,31,35–37,33,34] in aqueous KCl solutions.

(a) 0.1 MPa, 288–313 K, 0–4.75 mol kg^{-1} KCl; (b) 0.4–9.1 MPa, 314–433 K, and 2 mol kg^{-1} KCl; (c) 0.6–9.4 MPa, 313–433 K, and 4 mol kg^{-1} KCl; (d) Comparison of the experimental CO_2 solubility between Pérez-Salado Kamps[14] and Kiepe et al.[34] at the same *P-T-x* conditions, the modeling results are in excellent agreement with the experimental results reported by Pérez-Salado Kamps.[14][Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

calculated CO_2 solubilities in aqueous NaCl and KCl solutions, as well as in aqueous $CaCl_2$ and $MgCl_2$ solutions, are identical from these models. OLI Studio 9.0.6 performs very well in calculating CO_2 solubility in the aqueous KCl, $CaCl_2$, and $MgCl_2$ solutions when compared with our experimental results, but OLI calculated results for the CO_2-Na_2SO_4-H_2O system also deviate from the experimental CO_2 solubility measured in this study (Figure 4b).

The calculated CO_2 solubility from the PSUCO2 model shows a remarkable agreement when compared with the previously published experimental data in various CO_2-salt-H_2O system (Figures 5–8). However, at same *P-T-x* conditions, a large discrepancy of experimental results for the CO_2-KCl-H_2O system between Pérez-Salado Kamps et al.[14] and Kiepe et al.[34] was observed, and the calculated results from the PSUCO2 model support the experimental CO_2 solubility reported by Pérez-Salado Kamps et al. (Figure 8d).[14]

The H_2O solubility in the CO_2-rich phase can also be calculated by the proposed PSUCO2 model. Reliable experimental data are desirable to evaluate the model performance at elevated temperatures and pressures. At high temperatures and pressures, the experimental H_2O solubility in the CO_2-rich phase reported by Takenouchi and Kennedy[46] and Tödheide and Franck[47] are significantly different. Later on, to resolve this discrepancy, Mather and Franck[48] used the so-called "synthetic" experimental method to study the phase equilibria of the CO_2-H_2O system. Initially, known amounts of CO_2 and H_2O 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 stated their measured the dew points (at 498.15–546.15 K and 1100–2640 bar) of H_2O in the CO_2-rich phase support the experimental results of Tödheide and Franck.[47] In Figure 9a, the calculated H_2O solubility in the CO_2-rich phase among the different models (PSUCO2, OLI, and SP2010) were compared with the experimental data[46,47,49,50] at 298 and 423 K and up to 50 MPa. At 298 K, the differences among the three models are rather small (Figure 9a). All three models are capable of predicting the phase change (Figure 9a, enlarged view) from gaseous to liquid CO_2-rich phase[15] at 298 K as compared with the experimental data.[49,50] At 423 K, the PSUCO2 and SP2010 models agree well with the experimental data,[47] but the calculated results from OLI gradually deviate from the results of the other models (PSUCO2 and SP2010) in predicting H_2O solubility in the CO_2-rich phase at 423 K when pressure increases from 15 to 50MPa (Figure 9a).

For a CO_2-salt-H_2O system, the PSUCO2 model calculated results (as shown in Figure 9b) demonstrate that the different salt species in the aqueous phase will influence the H_2O solubility in the CO_2-rich phase. Based on comparison between Figures 9b and 9c, a larger activity of H_2O yields a greater solubility of H_2O in the CO_2-rich phase among

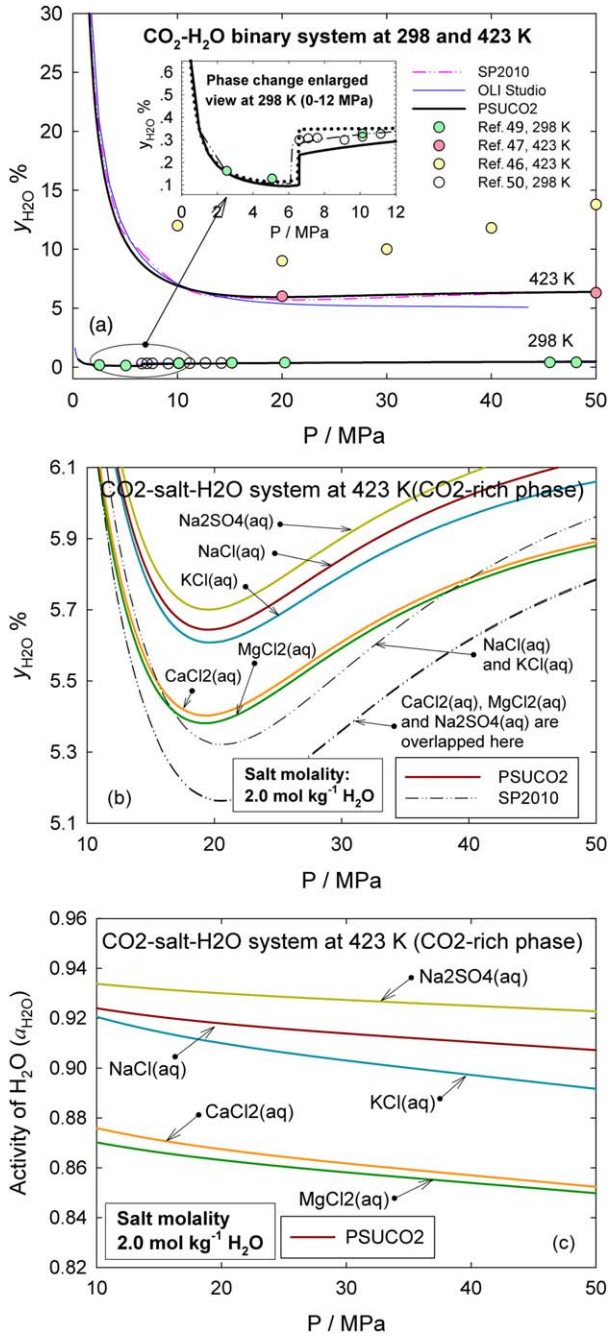

Figure 9. (a–c). Comparison of the model calculated H_2O solubility in the CO_2-rich phase for different CO_2-salt-H_2O systems.

(a) Comparison calculated H_2O solubility in the CO_2-rich phase for the binary CO_2-H_2O system by different models (SP2010, OLI, and PSUCO2); (b) Model calculated H_2O solubility in the CO_2-rich phase at 423 K in the CO_2-salt-H_2O systems. Given the same salt molality (e.g., 2 mol kg^{-1}), the differences of H_2O solubility in various single-salt aqueous solutions are quite large, whereas the SP2010 model reflects a relatively smaller variation of H_2O contents in the CO_2-rich phase caused by different salt species in the aqueous phase than does PSUCO2; (c) the PSUCO2 model calculated activity of H_2O in the aqueous phase for different CO_2-salt-H_2O systems at 423 K. Calculations made by OLI Studio 9.0.6 in Fig. 9a are under following conditions: (1) enable the second liquid phase, (2) use MSE model, (3) stream inflows contains 55.5082 mol water and 5 mol CO_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

different CO_2-salt-H_2O systems. However, for the same salt species the increase of the H_2O activity does not guarantee increased H_2O solubility in the CO_2-rich phase.

As described above, the Pitzer model is used to calculate the activity of dissolved CO_2 (a_{CO_2}) and the activity of H_2O (a_{H_2O}) in a CO_2-salt-H_2O system. Once a_{CO_2} and a_{H_2O} in mixed electrolyte solutions are evaluated, the CO_2 solubility in mixed-salt aqueous solutions may be calculated within the same thermodynamic framework. However, while the Pitzer model provides the thermodynamic framework to calculate the activity coefficient of CO_2 (neutral species) in mixed electrolyte solutions, a detailed discussion of Pitzer equations agrees that when a salt mixture presents in the aqueous phase, the number of required parameters increases significantly in Pitzer equations.[51] These parameters must be determined by thermodynamic experimental data for multicomponent systems. However, for CO_2-mixed-salt-H_2O system, there is a lack of experimental data of CO_2 solubility in mixed-salt aqueous solutions (e.g., NaCl + $CaCl_2$, NaCl + $MgCl_2$, NaCl + KCl, $CaCl_2$ + $MgCl_2$, $CaCl_2$ + Na_2SO_4, etc.), therefore, the approach using the Pitzer model to predict CO_2 solubility in mixed-salt aqueous solution at elevated temperatures and pressures is still not available for us.

However, based on the calculated CO_2 solubility in aqueous single-salt solutions, the CO_2 solubility in aqueous mixed-salt solution can be evaluated by the additivity rule of Setchenow coefficients for each single-salt species. The salting-out effect of single-salt species on dissolved CO_2 can be represented the Setschenow coefficient (K_s^i), which is calculated by the classical Setschenow equation as below[52]

$$K_s^i = \frac{1}{C_s^i} \log \frac{C_{CO_2}^o}{C_{CO_2}^i} \tag{13}$$

where C_s^i is the molarity of the ith salt species in a single-salt electrolyte solution, mol L^{-1}; $C_{CO_2}^o$ is the CO_2 molarity in pure water, mol L^{-1}; and $C_{CO_2}^i$ is the CO_2 molarity in the single-salt aqueous solution with ith salt species. The proposed PSUCO2 model is capable of calculating Setschenow coefficients (K_s^{NaCl}, $K_s^{MgCl_2}$, $K_s^{CaCl_2}$, $K_s^{Na_2SO_4}$, and K_s^{KCl}) for corresponding single-salt aqueous solutions. The Setschenow coefficient of a mixed-salt solution (K_s^{Mix}) can be evaluated using the additivity rule of Setschenow coefficients in each involved single-salt solution. The detailed method to calculate K_s^{Mix} based on the obtained K_s^{NaCl}, $K_s^{MgCl_2}$, $K_s^{CaCl_2}$, $K_s^{Na_2SO_4}$, and K_s^{KCl} can be found in Zhao et al.[53]

Conclusions

A new set of CO_2 solubility data in aqueous $CaCl_2$, $MgCl_2$, Na_2SO_4, and KCl solutions were measured at temperatures from 323 to 423 K, the ionic strengths from 0 to 6 mol kg^{-1} and a pressure of 15 MPa. The comparisons of experimental results based on the same concentration scale (ionic strength or salt percent by weight) showed that (1) the solubility of CO_2 in aqueous solutions in the presence of different salt species are quite different; (2) the solubility of CO_2 in $CaCl_2$(aq) and $MgCl_2$(aq) solutions are close to each other; and (3) given the same type of electrolyte (with the same anion), a cation with greater charge density in the aqueous phase has more significant salting-out effect on dissolved CO_2 than that with smaller charge density.

The previously developed CO_2 solubility model for the CO_2-NaCl-H_2O system was extended to the systems of CO_2-$CaCl_2$-H_2O, CO_2-Na_2SO_4-H_2O, CO_2-$MgCl_2$-H_2O, and CO_2-

KCl-H_2O by fitting a new set of Pitzer model parameters for each system. Pitzer model provides highly-accurate correlation results of CO_2 solubility in single-salt aqueous solutions, however, the use of Pitzer model for mixed-salt aqueous system at elevated temperatures and pressures is not recommended due to too many model parameters need to be evaluated.

Comparisons against literature data reveal a clear improvement of the proposed PSUCO2 model among the published models in predicting CO_2 solubility in aqueous single-salt solutions at temperatures from 288 to 433 K and pressures up to 71 MPa. The applicable *P-T-x* range of the proposed PSUCO2 model is 288–523 K, 0.1–150 MPa, and salt concentration up to saturation conditions.

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Notations

Uppercase

AAD % = average absolute deviation
A^{ϕ} = Debye–Hückel slope for osmotic coefficient
$B_{CO_2\text{-salt}}$ = combined Pitzer interaction parameter for the CO_2-salt-H_2O system
$C_{CO_2\text{-}CO_2\text{-salt}}$ = combined Pitzer triple interaction parameter for the CO_2-salt-H_2O system
$C_{ca}C^{\phi}_{ca}$ = Pitzer's model parameters
I = molality scale ionic strength, mol $kg^{-1}(H_2O)$
N_p = Total number of measured point
P = pressure, MPa
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_i = parameters for calculating combined Pitzer interaction parameters
b = constant in Pitzer's activity model, b=1.2 $kg^{1/2}$ $mol^{-1/2}$
k^{o}_{H,CO_2} = Henry's constant, bar mol^{-1} kg
m_a, m_c = molality of dissolved anion and cation ions in the aqueous phase, mol kg^{-1}
m_{CO_2} = molality of CO_2 in the aqueous phase, mol kg^{-1}
$m^{o}_{CO_2}$ = molality of CO_2 in the pure water, mol kg^{-1}
$m^{calc}_{CO_2,i}$ = calculated molality of CO_2 by CO_2 solubility models, mol kg^{-1}
$m^{exp}_{CO_2,i}$ = experimental CO_2 solubility taken from literature, mol kg^{-1}
m_{salt} = molality of salt species in aqueous solution
q_i = parameters for calculating Pitzer ion-ion binary interaction parameters for the binary salt-H_2O systems
$\overline{v}_{co_2}$ = an empirical determined parameter in the proposed CO_2 solubility model, cm^3 mol^{-1}
$\overline{v}_w$ = partial molar volume of water, cm^3 mol^{-1}
x_{CO_2}, y_{CO_2} = mole fraction of CO_2 and H_2O in the aqueous phase

Greek

α_1 = a constant for Pitzer's model, α_1=2.0 $kg^{0.5}$ $mol^{-0.5}$
$\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$ = Pitzer ion-ion binary interaction parameters for Salt-H_2O systems
γ_{CO_2} = activity coefficient of dissolved CO_2 in the aqueous salt solutions
$\gamma^{o}_{CO_2}$ = activity coefficient of dissolved CO_2 in the pure water
λ_{nc}, λ_{na} = Pitzer interaction parameters between neutral species and ions
λ_{nn}, μ_{nnn} = Pitzer interaction parameters for neutral species
$\mu^{(g)}_{CO_2}$, $\mu^{(aq)}_{CO_2}$ = chemical potential of CO_2 in both the CO_2-rich phase and the aqueous phase for a binary CO_2-H_2O system
$\mu^{(g)}_{CO_2}$, $\mu^{(aq)}_{CO_2}$ = chemical potential of CO_2 in both the CO_2-rich phase and the aqueous phase for a ternary CO_2-salt-H_2O system
v^+, v^- = stoichiometric number of cations and anions of a dissolved salt
ξ_{nca}, μ_{nna}, μ_{nnc} = Pitzer triple interaction parameters between neutral species and ions
ϕ = osmotic coefficient
φ_{CO_2}, φ_{H_2O} = fugacity coefficient of CO_2 and H_2O, computed by the modified RK EoS
φ^{s}_{w} = fugacity coefficient of pure H_2O, computed by IAPWS-95 EoS

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Appendix : Additional Model Equations

The Pitzer equations for the activity coefficient of dissolved CO_2 and the osmotic coefficient of water are shown below as Eqs. A1 and A2, respectively[54]

$$\ln\gamma_{CO_2} = 2m_{CO_2}\lambda_{nn} + 3m_{CO_2}^2\mu_{nnn} + 2\lambda_{nc}m_c + 2\lambda_{na}m_a + m_a m_c \xi_{nca} + 6m_{CO_2}m_c\mu_{nnc} + 6m_{CO_2}m_a\mu_{nna} \tag{A1}$$

$$\begin{aligned}\phi - 1 = {} & \frac{2}{m_a + m_c + m_{CO_2}} \\ & \{-A^\phi \frac{I^{1.5}}{I + bI^{0.5}} + m_a m_c[\beta_{ca}^{(0)} + \beta_{ca}^{(1)}\exp(-\alpha_1 I^{0.5}) \\ & + (m_a|z_a| + m_c|z_c|)C_{ca}] \\ & + \frac{1}{2}m_{CO_2}^2\lambda_{nn} + m_{CO_2}^3\mu_{nnn} + m_{CO_2}m_c\lambda_{nc} + 3m_{CO_2}^2 m_c\mu_{nnc} \\ & + m_{CO_2}m_a\lambda_{na} + 3m_{CO_2}^2 m_a\mu_{nna} + m_{CO_2}m_a m_c\xi_{nca}\}\end{aligned} \tag{A2}$$

In these equations, m_{CO_2} is the molality of CO_2; m_a and m_c are, respectively, the molality of anions and cations in the aqueous phase. In Eq. 2, $C_{ca} = 0.5C_{ca}^{\phi}/|z_c z_a|^{0.5}$, A^ϕ is the Debye–Hückel slope for the osmotic coefficient, and $b = 1.2$ kg$^{1/2}$ mol$^{-1/2}$, $\alpha_1 = 2.0$ kg$^{1/2}$ mol$^{-1/2}$. I is the ionic strength based on the molal concentration scale. The empirical equations for calculating the Pitzer binary ion-ion interaction parameters ($\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, and C_{ca}) were taken from literature and summarized in the Appendix. The Pitzer pure CO_2 interaction parameters (λ_{nn} and μ_{nnn}) in the temperature range 273.15–573.15 K can be found in Zhao et al.[10]

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