An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar

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Abstract

A thermodynamic model for the solubility of carbon dioxide (CO_2) in pure water and in aqueous NaCl solutions for temperatures from 273 to 533 K, for pressures from 0 to 2000 bar, and for ionic strength from 0 to 4.3 m is presented. The model is based on a specific particle interaction theory for the liquid phase and a highly accurate equation of state for the vapor phase. With this specific interaction approach, this model is able to predict CO_2 solubility in other systems, such as CO_2–H_2O–$CaCl_2$ and CO_2–seawater, without fitting experimental data from these systems. Comparison of the model predictions with experimental data indicates that the model is within or close to experimental uncertainty, which is about 7% in CO_2 solubility.
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Keywords: CO_2 solubility; CO_2 thermodynamics; Specific interaction modeling; Aqueous CO_2 solution; Solubility model; Equation of state

1. Introduction

The extensive study of fluid inclusions from hydrothermal, sedimentary metamorphic and igneous rocks has shown that H_2O, CO_2 and NaCl are the most common species in geological fluids (Fyfe et al., 1978; Roedder, 1984). Accurate prediction of CO_2 solubility over a wide range of temperature, pressure and ionic strength ($T-P-m$) is important to the analysis of fluid inclusion data (Roedder, 1984; Duan et al., 1992a; Dubessy et al., 2001), to the studies of the carbonate precipitation and to the tracing of the global carbon cycle (Butcher et al., 1992; Millero, 1995; Riley and Skirrow, 1975). It is also essential for designing certain separation equipment in the chemical or oil-related industries (Li and Ngheim, 1986; Rumpf et al., 1994). Because of its importance, there have been many experimental studies on the solubility of CO_2 in pure water and in aqueous NaCl solutions. There has also been extensive theoretical effort on modeling the CO_2 solubility in aqueous solutions. Although several models on CO_2 solubility have been

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published, few can predict CO_2 solubility in wide T–P–m range with accuracy close to experiment. For many temperature–pressure–composition conditions, CO_2 solubilities are still unknown.

Based on the EOS of Peng–Robinson, Henry's law and the scaled-particle theory, Li and Ngheim (1986) presented a model (L–N model) to predict phase equilibrium of oil, gas and water/brine mixtures. This model is also intended to calculate the solubility of CO_2 in pure water up to 473 K and in NaCl solutions with NaCl up to 4 m. However, it is in general not accurate to predict the solubility of CO_2 in aqueous NaCl solutions. Harvey and Prausnitz (1989) developed an EOS (H–P model) to predict CO_2 solubility in pure water and in aqueous NaCl solutions at elevated pressures. However, it overestimates CO_2 solubility by more than 10–20% in NaCl solutions. Zuo and Guo (1991) extended the Patel–Teja EOS to phase equilibrium calculations for electrolyte solutions (Z–G model). The Z–G model is no more accurate than the H–P model for CO_2 solubility. For example, it underestimates CO_2 solubility by more than 12% in 20 wt.% NaCl solutions at high pressures (>1000 bar) and overestimated CO_2 solubility by

more than 10% in 6 wt.% NaCl solution at moderate pressures. Some of the comparisons of these models will be shown in Section 4.

In this article, we present a model covering a large T–P–m range in the CO_2–H_2O–NaCl system and in other aqueous systems using an approach proposed by Duan et al. (1992a). In this approach, the chemical potential of CO_2 in the vapor phase is calculated using the equation of state (Duan et al., 1992b), and the chemical potential of CO_2 in the liquid phase is described by the specific interaction model of Pitzer (1973). This will be discussed in the next section. To disentangle the controversy over the experimental measurements, the available data are reviewed in Section 3. We found that most of the major data sets are consistent. The parameters are evaluated from as many experimental data as possible. The resulted model is compared with experimental data in Section 4. Comparison with experimental data indicates that the resulting model can predict CO_2 solubility in pure water from 273 to 533 K and from 0 to 2000 bar, and in aqueous NaCl solutions up to high temperature, pressure and ionic strength (273–533 K, 0–2000 bar, 0–4 m) with accuracy close to

Table 1
Measurements of CO_2 solubility

Authors	Solution	T (K)	P (bar)	N[a]
Wiebe and Gaddy (1939)	Water	323–373	25–710	29
Wiebe and Gaddy (1940)	Water	285–313	25–510	42
Morrison and Billett (1952)	Water	286–348	1.02–1.40	19
Malinin (1959)	Water	473–603	98–490	79
Todheide and Franck (1963)	Water	323–623	200–3500	109
Takenouchi and Kennedy (1964)	Water	383–623	100–1500	116
Zawisza and Malesinska (1981)	Water	323–473	1–54	33
Müller et al. (1988)	Water	373–473	3–80	49
King et al. (1992)	Water	288–298	60–250	37
Markham and Kobe (1941)	0–4 m NaCl	273–313	1.02–1.09	18
Harned and Davis (1943)	0–3 m NaCl	273–323	1.02–1.14	66
Ellis and Golding (1963)	0–2 m NaCl	445–610	25–200	54
Takenouchi and Kennedy (1965)	0–4.28 m NaCl	423–723	100–1400	123
Malinin and Savelyeva (1972)	0–4.5 m NaCl	298–348	47.92	16
Malinin and Kurorskaya (1975)	0–6 m NaCl	298–423	47.92	16
Gehrig (1980)	1–4.3 m NaCl	408–800	30–2800	29
Drummond (1981)	0–6.5 m NaCl	290–673	35–400	509
Nighswander et al. (1989)	0–0.17 m NaCl	353–473	20–100	67
Rumpf et al. (1994)	4–6 m NaCl	313–433	1–100	63
Prutton and Savage (1945)	0–3.9 m $CaCl_2$	348–394	10–700	142

[a] Number of measurements.

experiments (<7% in CO_2 solubility). More importantly, this model can be accurately extrapolated to other aqueous electrolyte solution systems such as aqueous $CaCl_2$, $MgCl_2$ and $(NH_4)_2SO_4$ solutions and seawater without using experimental data from those systems.

2. Phenomenological description of gas solubility as a function of composition, pressure and temperature

CO_2 solubility in aqueous solutions is determined from the balance between its chemical potential in the liquid phase $\mu_{CO_2}^l$ and that in the gas phase, $\mu_{CO_2}^v$. The potential can be written in terms of fugacity in the vapor phase and activity in the liquid phase as

$$\begin{aligned}\mu_{CO_2}^v(T,P,y) &= \mu_{CO_2}^{v(0)}(T) + RT\ln f_{CO_2}(T,P,y)\\ &= \mu_{CO_2}^{v(0)}(T) + RT\ln y_{CO_2}P\\ &\quad + RT\ln\varphi_{CO_2}(T,P,y)\end{aligned} \quad (1)$$

$$\begin{aligned}\mu_{CO_2}^l(T,P,m) &= \mu_{CO_2}^{l(0)}(T,P) + RT\ln a_{CO_2}(T,P,m)\\ &= \mu_{CO_2}^{l(0)}(T,P) + RT\ln m_{CO_2}\\ &\quad + RT\ln\gamma_{CO_2}(T,P,m)\end{aligned} \quad (2)$$

At equilibrium, $\mu_{CO_2}^l = \mu_{CO_2}^v$, and we obtain,

$$\begin{aligned}\ln\frac{y_{CO_2}P}{m_{CO_2}} &= \frac{\mu_{CO_2}^{l(0)}(T,P) - \mu_{CO_2}^{v(0)}(T)}{RT} - \ln\varphi_{CO_2}(T,P,y)\\ &\quad + \ln\gamma_{CO_2}(T,P,m)\end{aligned} \quad (3)$$

The standard chemical potential of CO_2 in liquid phase, $\mu_{CO_2}^{l(0)}$, is the chemical potential in hypothetically ideal solution of unit molality (Denbigh, 1971). The vapor phase standard chemical potential, $\mu_{CO_2}^{v(0)}$, is the hypothetically ideal gas chemical potential when the pressure is equal to 1 bar. In the parameter-

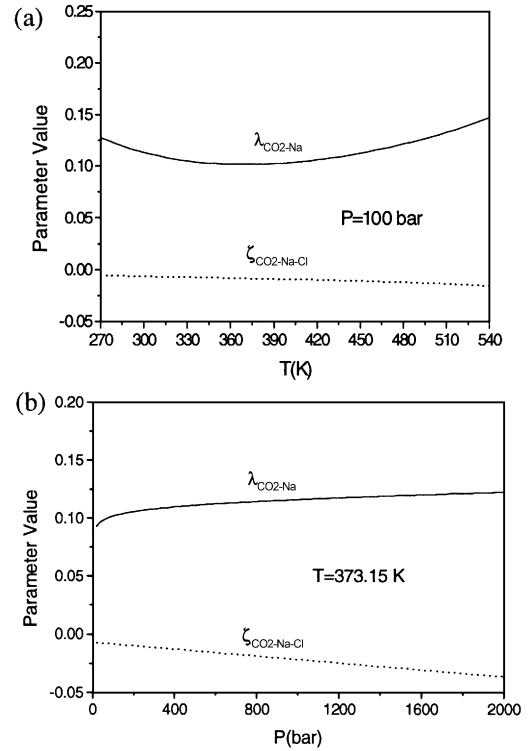Fig. 1. The values of λ_{CO_2-Na} and $\zeta_{CO_2-Na-Cl}$ as functions of (a) temperature and (b) pressure.

ization, $\mu_{CO_2}^{v(0)}$, as a reference number, can be set to any number because only the difference between $\mu_{CO_2}^{l(0)}$ and $\mu_{CO_2}^{v(0)}$ is important. Here we set it to zero for convenience. According to the equation of state of Duan et al. (1992b), the fugacity coefficient of CO_2 in the vapor phase of CO_2-H_2O mixtures differs very little from that in pure CO_2 for temperatures between 273 and 533 K. Therefore, $\ln\varphi_{CO_2}$ can be calculated from the EOS for pure CO_2 (Duan et al., 1992b) (see Appendix A). Since there are no vapor composition measurements for the $CO_2-H_2O-NaCl$ system in the temperature range of this study, we have to assume that water vapor pressure of the mixtures is the same as pure water saturation pressure. Consequently, y_{CO_2} can be approximately calculated from

$$y_{CO_2} = (P - P_{H_2O})/P \quad (4)$$

Table 2
Interaction parameters

T–P coefficient	$\mu_{CO_2}^{l(0)}/RT$	λ_{CO_2-Na}	$\xi_{CO_2-Na-Cl}$
c_1	28.9447706	− 0.411370585	3.36389723e − 4
c_2	− 0.0354581768	6.07632013e − 4	− 1.98298980e − 5
c_3	− 4770.67077	97.5347708	
c_4	1.02782768e − 5		
c_5	33.8126098		
c_6	9.04037140e − 3		
c_7	− 1.14934031e − 3		
c_8	− 0.307405726	− 0.0237622469	2.12220830e − 3
c_9	− 0.0907301486	0.0170656236	− 5.24873303e − 3
c_{10}	9.32713393e − 4		
c_{11}		1.41335834e − 5	

where P_{H_2O} is the pure water pressure, which can be taken from the steam tables (Haar et al., 1984) or can be calculated from an empirical equation (see Appendix B). The above assumption may lead to errors (up to 5%) for $\mu_i^{l(0)}/RT$ and $\ln\gamma_{CO_2}^l$. However, these errors cancel approximately in our parameterization and the effect on the calculation of CO_2 solubility is negligible. A virial expansion

Table 3
Calculated CO_2 solubility (mol/kg water) in water

P (bar)	T (K)									
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	533.15
1	0.0693	0.0286	0.0137	0.0036						
5	0.3368	0.1442	0.0803	0.0511	0.0298	0.0023				
10	0.6463	0.2809	0.1602	0.1086	0.0781	0.0480				
50		1.0811	0.6695	0.4952	0.4157	0.3767	0.3476	0.2997	0.1887	0.0392
100		1.3611	1.0275	0.8219	0.7314	0.7054	0.7131	0.7259	0.7025	0.6267
200		1.4889	1.2344	1.1308	1.1100	1.1569	1.2634	1.4171	1.5898	1.6846
300		1.5989	1.3495	1.2802	1.3184	1.4427	1.6521	1.9506	2.3334	2.6190
400		1.7005	1.4478	1.3954	1.4700	1.6535	1.9527	2.3871	2.9802	3.4700
500		1.7965	1.5368	1.4954	1.5972	1.8287	2.2059	2.7664	3.5666	4.2695
600		1.8883	1.6194	1.5857	1.7102	1.9833	2.4310	3.1102	4.1152	5.0387
700		1.9767	1.6970	1.6689	1.8131	2.1238	2.6370	3.4301	4.6390	5.7905
800		2.0622	1.7703	1.7464	1.9082	2.2535	2.8288	3.7323	5.1452	6.5318
900		2.1450	1.8399	1.8189	1.9966	2.3744	3.0089	4.0203	5.6376	7.2658
1000		2.2254	1.9062	1.8870	2.0792	2.4876	3.1790	4.2960	6.1183	7.9933
1100		2.3034	1.9692	1.9510	2.1566	2.5939	3.3401	4.5607	6.5877	8.7138
1200		2.3792	2.0292	2.0112	2.2290	2.6937	3.4927	4.8147	7.0458	9.4256
1300		2.4527	2.0864	2.0678	2.2968	2.7874	3.6372	5.0585	7.4922	10.127
1400		2.5240	2.1407	2.1210	2.3601	2.8752	3.7739	5.2919	7.9260	10.814
1500		2.5933	2.1924	2.1707	2.4192	2.9575	3.9030	5.5150	8.3460	11.485
1600		2.6605	2.2413	2.2172	2.4740	3.0341	4.0245	5.7276	8.7513	12.136
1700		2.7251	2.2875	2.2605	2.5248	3.1053	4.1385	5.9294	9.1403	12.764
1800		2.7882	2.3312	2.3007	2.5717	3.1712	4.2450	6.1202	9.5123	13.366
1900		2.8486	2.3725	2.3379	2.6146	3.2319	4.3440	6.2997	9.8655	13.938
2000		2.9071	2.4110	2.3719	2.6538	3.2875	4.4353	6.4677	10.199	14.478

of excess Gibbs energy (Pitzer, 1973) is used to obtain $\ln\gamma_{CO_2}$,

$$\ln\gamma_{CO_2} = \sum_c 2\lambda_{CO_2-c}m_c + \sum_a 2\lambda_{CO_2-a}m_a$$
$$+ \sum_c\sum_a \zeta_{CO_2-a-c}m_cm_a, \quad (5)$$

where λ and ζ are second-order and third-order interaction parameters, respectively, c and a mean cations and anions, respectively. Substituting Eq. (5) in Eq. (3), we have

$$\ln\frac{y_{CO_2}P}{m_{CO_2}} = \frac{\mu_{CO_2}^{l(0)}}{RT} - \ln\varphi_{CO_2} + \sum_c 2\lambda_{CO_2-c}m_c$$
$$+ \sum_a 2\lambda_{CO_2-a}m_a + \sum_c\sum_a \zeta_{CO_2-c-a}m_cm_a$$
$$(6)$$

In the above equation, λ's, ζ's and the dimensionless standard chemical potential, $\mu_{CO_2}^{l(0)}/RT$ are dependent

upon temperature and total pressure. Following Pitzer et al. (1984), we select the following equation for the parameters,

$$Par(T,P) = c_1 + c_2T + c_3/T + c_4T^2$$
$$+ c_5/(630 - T) + c_6P + c_7P\ln T$$
$$+ c_8P/T + c_9P/(630 - T)$$
$$+ c_{10}P^2/(630 - T)^2 + c_{11}T\ln P \quad (7)$$

Eqs. (6) and (7) form the basis of our parameterization for the model.

3. Review of solubility data of CO_2

CO_2 solubility in pure water and in aqueous NaCl solutions has been measured for a wide range of temperatures, pressures and ionic strength (Table 1).

Table 4
Calculated CO_2 solubility (mol/kg water) in 1 m aqueous NaCl solutions

P (bar)	T (K)									
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15
1	0.0557	0.0238	0.0116	0.0031						
5	0.2675	0.1185	0.0674	0.0433	0.0253	0.0020				
10	0.5109	0.2294	0.1335	0.0914	0.0660	0.0404				
50		0.8729	0.5502	0.4103	0.3447	0.3106	0.2837	0.2399	0.1467	
100		1.0958	0.8405	0.6767	0.6015	0.5759	0.5751	0.5755	0.5434	0.4236
200		1.1990	1.0072	0.9259	0.9052	0.9337	1.0035	1.1016	1.2018	1.2475
300		1.2910	1.1012	1.0456	1.0696	1.1551	1.2973	1.4926	1.7260	1.9493
400		1.3781	1.8127	1.1383	1.1881	1.3150	1.5180	1.8009	2.1607	2.5646
500		1.4620	1.2577	1.2191	1.2869	1.4458	1.6993	2.0593	2.5369	3.1192
600		1.5438	1.3282	1.2925	1.3742	1.5595	1.8565	2.2859	2.8734	3.6300
700		1.6239	1.3952	1.3604	1.4535	1.6616	1.9973	2.4900	3.1810	4.1072
800		1.7026	1.4594	1.4240	1.5264	1.7546	2.1254	2.6769	3.4659	4.5562
900		1.7801	1.5210	1.4839	1.5941	1.8402	2.2431	2.8494	3.7314	4.9796
1000		1.8565	1.5803	1.5403	1.6570	1.9193	2.3518	3.0094	3.9797	5.3785
1100		1.9318	1.6375	1.5937	1.7157	1.9925	2.4524	3.1580	4.2117	5.7527
1200		2.0061	1.6926	1.6442	1.7705	2.0603	2.5455	3.2959	4.4281	6.1016
1300		2.0795	1.7458	1.6919	1.8215	2.1231	2.6314	3.4236	4.6292	6.4241
1400		2.1517	1.7970	1.7370	1.8690	2.1810	2.7106	3.5415	4.8149	6.7192
1500		2.2231	1.8464	1.7794	1.9131	2.2343	2.7832	3.6496	4.9853	6.9855
1600		2.2935	1.8938	1.8194	1.9538	2.2830	2.8494	3.7482	5.1402	7.2222
1700		2.3624	1.9393	1.8568	1.9913	2.3273	2.9094	3.8375	5.2796	7.4281
1800		2.4308	1.9829	1.8919	2.0256	2.3674	2.9634	3.9174	5.4034	7.6028
1900		2.4976	2.0249	1.9247	2.0569	2.4035	3.0113	3.9882	5.5115	7.7453
2000		2.5635	2.0648	1.9549	2.0852	2.4354	3.0532	4.0498	5.6038	7.8558

The most extensive studies of CO_2 solubility in water are those of Wiebe and Gaddy (1939, 1940), Todheide and Franck (1963) and Takenouchi and Kennedy (1964, 1965). The data sets of Wiebe and Gaddy (1939, 1940) are the most comprehensive at the temperatures below 373 K, while the data sets of Todheide and Franck (1963) and Takenouchi and Kennedy (1964, 1965) cover the largest temperature–pressure (T–P) range (from 323 to 623 K, from 100 to 3500 bar). The data sets of Zawisza and Malesinska (1981), Müller et al. (1988) and Nighswander et al. (1989) cover the high temperature (>373 K) and low pressure (<100 bar) range, which is not covered by the data sets of Todheide and Franck (1963) and Takenouchi and Kennedy (1964, 1965). In the T–P range we are trying to model (T < 533 K, P < 2000 bar), most of CO_2 solubility data in water are consistent within errors of about 7%. A few data points of Zawisza and Malesinska (1981) and Nighswander et al. (1989) are consistent neither with their own bulk data points nor with that of Müller et al. (1988). These small number of points are discarded in the parameterization. At temperatures above 540 K, some data points of Malinin (1959) and Todheide and Franck (1963) are inconsistent with that of Takenouchi and Kennedy (1964, 1965) for pressures above 1200 bar, with a deviation more than 10%. As Carroll et al. (1991) surveyed, about 100 CO_2 solubility data sets exist for low pressures (<10 bar). Some representative data sets (Harned and Davis, 1943; Markham and Kobe, 1941; Morrison and Billett, 1952) are listed in Table 1.

The most extensive studies of CO_2 solubility in aqueous NaCl solutions are those of Takenouchi and Kennedy (1965), Gehrig (1980), Drummond (1981) and Rumpf et al. (1994). The data set of Takenouchi and Kennedy (1965) covers a large temperature–pressure–ionic strength (T–P–m) range (423–723 K, 100–1400 bar and 0–4.28 m). Gehrig (1980) extended CO_2 solubility data in 1.09 m NaCl solution

Table 5
Calculated CO_2 solubility (mol/kg water) in 2 m aqueous NaCl solutions

P (bar)	T (K)									
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15
1	0.0452	0.0200	0.0100	0.0027						
5	0.2147	0.0984	0.0572	0.0372	0.0218	0.0017				
10	0.4080	0.1895	0.1126	0.0780	0.0565	0.0346				
50		0.7135	0.4583	0.3451	0.2905	0.2608	0.2362	0.1982	0.1186	
100		0.8939	0.6978	0.5663	0.5038	0.4798	0.4743	0.4678	0.4335	0.3301
200		0.9801	0.8359	0.7729	0.7543	0.7721	0.8192	0.8834	0.9418	0.9488
300		1.0600	0.9160	0.8731	0.8898	0.9513	1.0521	1.1855	1.3343	1.4535
400		1.1377	0.9873	0.9518	0.9878	1.0803	1.2250	1.4191	1.6507	1.8781
500		1.2143	1.0542	1.0216	1.0702	1.1855	1.3655	1.6114	1.9170	2.2457
600		1.2905	1.1182	1.0859	1.1436	1.2771	1.4865	1.7771	2.1489	2.5710
700		1.3665	1.1802	1.1463	1.2108	1.3593	1.5939	1.9240	2.3554	2.8629
800		1.4425	1.2405	1.2035	1.2731	1.4343	1.6910	2.0563	2.5416	3.1266
900		1.5186	1.2994	1.2582	1.3314	1.5034	1.7797	2.1766	2.7107	3.3650
1000		1.5950	1.3571	1.3104	1.3861	1.5673	1.8610	2.2863	2.8645	3.5797
1100		1.6716	1.4136	1.3606	1.4376	1.6267	1.9356	2.3866	3.0040	3.7715
1200		1.7485	1.4690	1.4086	1.4860	1.6817	2.0042	2.4779	3.1301	3.9410
1300		1.8256	1.5234	1.4548	1.5316	1.7327	2.0670	2.5609	3.2433	4.0883
1400		1.9029	1.5766	1.4991	1.5745	1.7799	2.1244	2.6357	3.3440	4.2135
1500		1.9806	1.6289	1.5414	1.6148	1.8234	2.1765	2.7028	3.4322	4.3168
1600		2.0584	1.6800	1.5821	1.6524	1.8633	2.2236	2.7624	3.5084	4.3985
1700		2.1361	1.7301	1.6208	1.6876	1.8997	2.2657	2.8145	3.5727	4.4586
1800		2.2144	1.7790	1.6578	1.7202	1.9327	2.3030	2.8594	3.6254	4.4980
1900		2.2924	1.8270	1.6931	1.7505	1.9625	2.3355	2.8973	3.6666	4.5167
2000		2.3706	1.8735	1.7264	1.7783	1.9890	2.3634	2.9283	3.6967	4.5157

up to 2800 bar. The measurements of Drummond (1981) are the most extensive at lower pressures (<400 bar). Besides, Ellis and Golding (1963), Malinin and Savelyeva (1972) and Malinin and Kurorskaya (1975) also published some CO_2 solubility data in aqueous NaCl solutions. However, there are some disagreements among these data. A few data points of Drummond (1981) measured during the pressure increasing process are not consistent with those measured in the pressure decreasing process. The deviation between them is 8–15%. The data of Takenouchi and Kennedy (1965) at 100 bar diverge sharply from that of Drummond (1981) and Rumpf et al. (1994). We have no reliable criterion to determine which data are more accurate. So we include all these inconsistent data in the parameterization, although they only account for a small portion of the whole database. We note that experimental measurements of CO_2 solubility in NaCl solutions at high pressure (>400 bar) and low temper-

ature (<423 K) range and in the high ionic strength (>4.3 m) range are absent.

CO_2 solubility data in other salt than NaCl aqueous solutions at elevated pressures are very limited. Prutton and Savage (1945) published some experimental CO_2 solubility data in aqueous $CaCl_2$ solutions from 384 to 394 K and from 10 to 700 bar with molality up to 3.9 m.

4. Parameterization and comparison with experimental data

To calculate the CO_2 solubility as a function of temperature, pressure and salt composition, we need to determine the parameters λ's and ζ's for Na^+ and Cl^- in liquid as well as the standard chemical potential $\mu_{CO_2}^{l(0)}$ in Eq. (6). Since measurements can only be made in electronically neutral solutions, one of the parameters must be assigned arbitrarily (Harvie

Table 6
Calculated CO_2 solubility (mol/kg water) in 4 m aqueous NaCl solutions

| P (bar)	T (K)									
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15
1	0.0308	0.0147	0.0077	0.0021						
5	0.1425	0.0703	0.0428	0.0287	0.0171	0.0013				
10	0.2684	0.1339	0.0833	0.0593	0.0435	0.0266				
50		0.4945	0.3314	0.2554	0.2169	0.1942	0.1737	0.1430	0.0834	
100		0.6189	0.5028	0.4169	0.3733	0.3538	0.3449	0.3328	0.2999	0.2207
200		0.6849	0.6060	0.5705	0.5590	0.5679	0.5924	0.6234	0.6444	0.6253
300		0.7515	0.6717	0.6503	0.6636	0.7026	0.7624	0.8365	0.9104	0.9524
400		0.8200	0.7340	0.7170	0.7434	0.8034	0.8921	1.0042	1.1270	1.2281
500		0.8907	0.7955	0.7793	0.8140	0.8893	1.0011	1.1457	1.3122	1.4683
600		0.9639	0.8571	0.8395	0.8798	0.9671	1.0982	1.2709	1.4765	1.6829
700		1.0399	0.9194	0.8987	0.9428	1.0399	1.1875	1.3850	1.6258	1.8778
800		1.1189	0.9826	0.9573	1.0038	1.1091	1.2712	1.4909	1.7634	2.0561
900		1.2009	1.0468	1.0157	1.0633	1.1755	1.3504	1.5902	1.8914	2.2198
1000		1.2862	1.1121	1.0739	1.1216	1.2395	1.4254	1.6837	2.0107	2.3697
1100			1.1787	1.1321	1.1789	1.3015	1.4979	1.7719	2.1219	2.5062
1200			1.2464	1.1902	1.2352	1.3615	1.5668	1.8553	2.2254	2.6295
1300			1.3155	1.2485	1.2907	1.4197	1.6326	1.9340	2.3215	2.7394
1400			1.3858	1.3068	1.3453	1.4761	1.6956	2.0082	2.4101	2.8360
1500			1.4575	1.3651	1.3991	1.5308	1.7557	2.0777	2.4912	2.9189
1600				1.4235	1.4519	1.5837	1.8130	2.1428	2.5648	2.9884
1700				1.4817	1.5039	1.6349	1.8674	2.2033	2.6309	3.0440
1800				1.5400	1.5549	1.6843	1.9190	2.2593	2.6895	3.0862
1900				1.5983	1.6050	1.7319	1.9676	2.3107	2.7405	3.1148
2000				1.6563	1.6541	1.7777	2.0132	2.3575	2.7838	3.1302
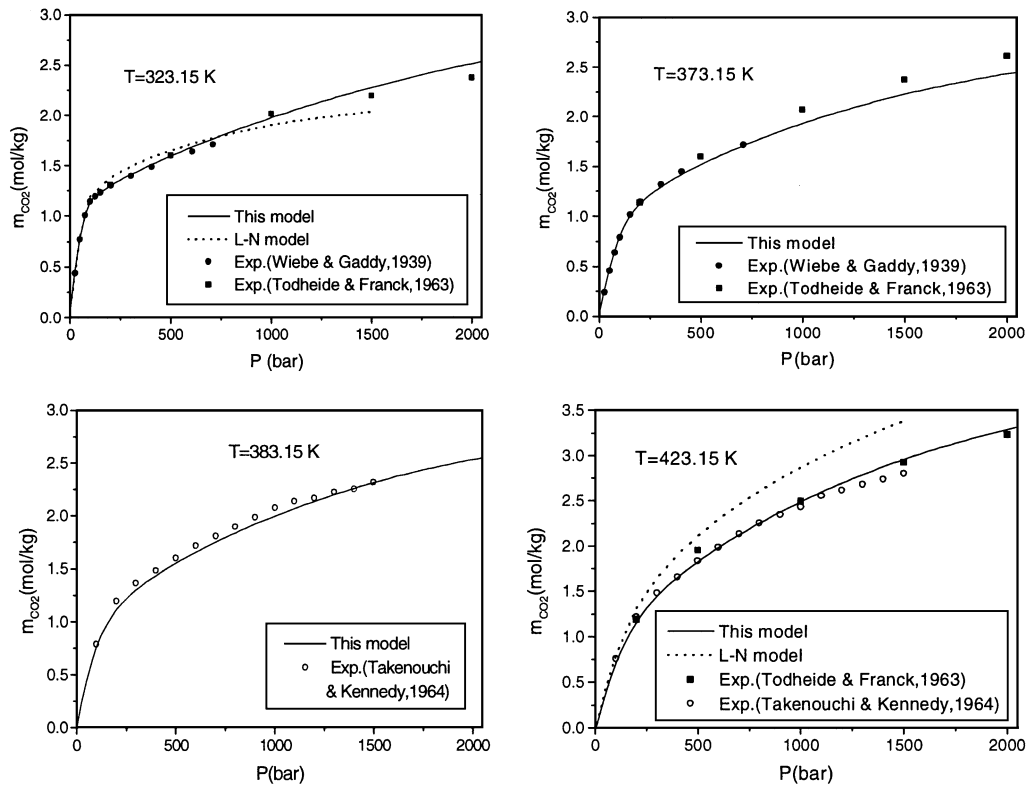
Fig. 2. CO_2 solubility in pure water (the model of this study vs. experimental data and other models).

and Weare, 1984). We set λ_{CO_2-Cl} to zero and fit the remaining parameters. $\mu_{CO_2}^{l(0)}/RT$ was first evaluated using the CO_2 solubility data in pure water with a

standard error of 4.5%. λ_{CO_2-Na} and $\zeta_{CO_2-Na-Cl}$ were then evaluated simultaneously by least square fitting of solubility data in aqueous NaCl solutions with a
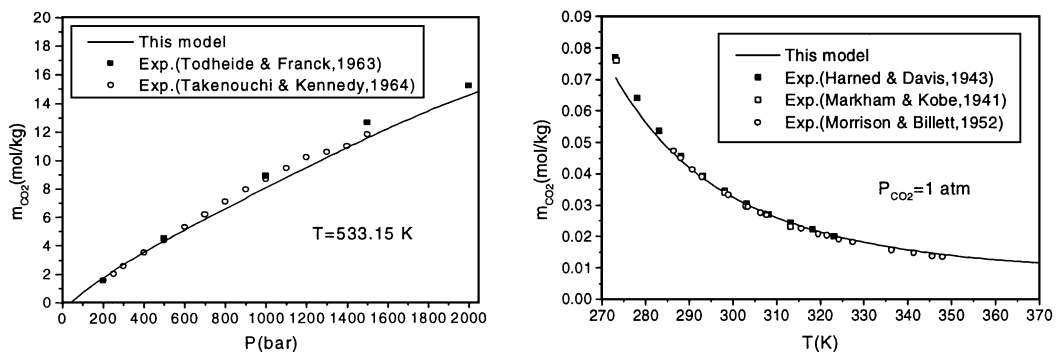

Fig. 3. CO_2 solubility in pure water (the model of this study vs. experimental data and other models).

standard error of 5.5%. The third-order interaction parameter, $\zeta_{CO_2-Na-Cl}$, is lower than the second-order interaction parameter λ_{CO_2-Na} by about one order of magnitude (Fig. 1). Since the change of CO_2 solubility with pressure at temperatures above 538 K differs sharply from that at temperatures below 538 K (Takenouchi and Kennedy, 1964; Todheide and Franck, 1963), it is beyond the capability of this model to predict such an abrupt change. The temperature- and pressure-dependent coefficients are listed in Table 2.

By substituting the parameters into Eq. (6), the CO_2 solubility in pure water and aqueous NaCl solutions (0–4.3 m, 273–533 K, 0–2000 bar) can be calculated. Solubilities in pure water and in 1, 2 and 4 m NaCl solutions calculated from this model are compiled in Tables 3–6, respectively. Figs. 2–4 show the agreement between the experimental data and our model. It can be seen from these figures that most experimental data can be represented by this model adequately, within or close to experimental uncertainty (about 7%). Figs. 2–4 also suggest that our
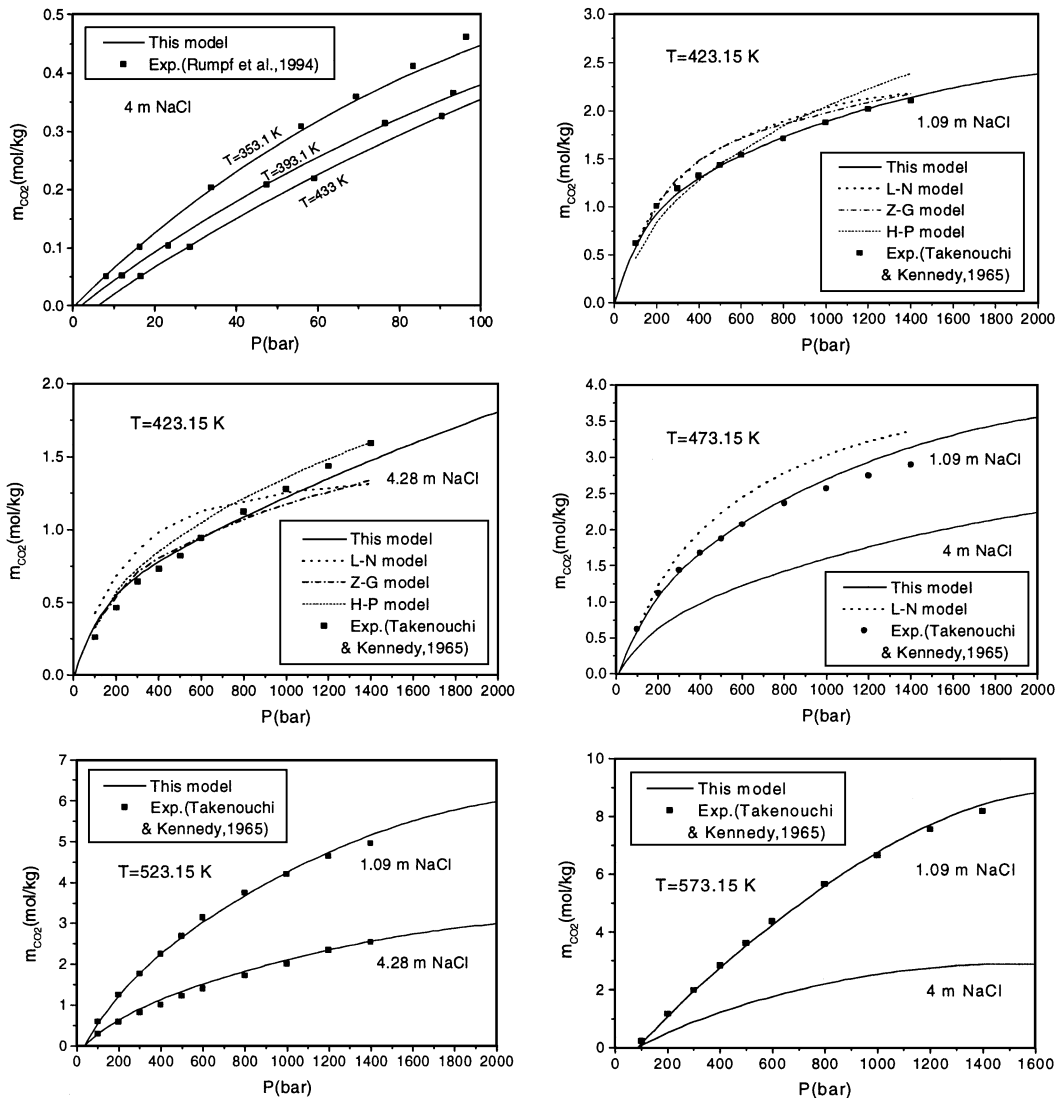
Fig. 4. CO_2 solubility in aqueous NaCl solutions (the model of this study vs. experimental data and other models).

model not only covers wider $T-P-m$ range, but also is more accurate than previous models. For example, the L–N model overestimates CO_2 solubility in pure water at 423 and 473 K with 7–25% of deviation from experimental data. Furthermore, the L–N model cannot predict CO_2 solubility in aqueous NaCl solutions with errors far greater than experiments. The deviation of it from the experimental solubility data in aqueous NaCl solution in 473 K (except the data at 100 bar) is more than 10%, well above experimental uncertainty. The H–P model overestimates CO_2 solubility in 6 wt.% NaCl solution by more than 10% when pressures are above 1000 bar, while it overestimates CO_2 solubility in 20 wt.% NaCl solution by more than 15% at moderate pressures (<600 bar). The Z–G model underestimates CO_2 solubility in 20 wt.% NaCl solution by more than 10% at high pressures (>1000 bar), while it overestimates CO_2 solubility in NaCl solution by more than 10% at moderate pressures (<500 bar).

Gehrig (1980) reported the only experimental data set with pressures above 1500 bar (up to 2800 bar). It can be seen from Table 7 that these data are accurately reproduced by our model. In the $T-P-m$ range covered by our model, the solubility of CO_2 increases with the increase of pressure and decreases with the increase of ionic strength. However, CO_2 solubility varies more dramatically with temperature. Fig. 5 shows that at low pressures (<100 bar) CO_2 solubility decreases gradually with temperature. At higher pres-
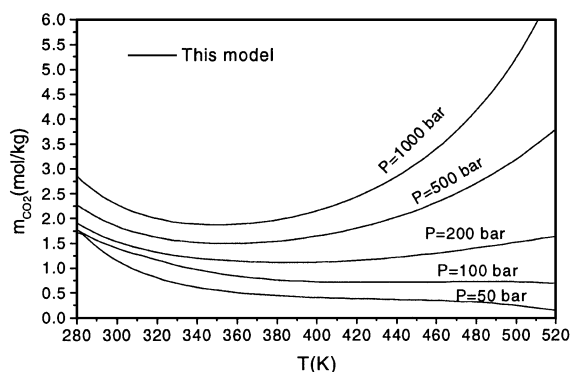

Fig. 5. The isobaric minimum solubilities of CO_2 in pure water.

sures (≥ 100 bar), CO_2 solubility decreases with temperature at first, and then it increases with temperature. The isobaric minimum solubility points vary from about 423 K at 100 bar to about 353 K at high pressures as displayed by Fig. 5.

The heat of solution of CO_2 in water can be derived from the solubility model:

$$-\frac{\Delta H^{l(0)} - \Delta H^{v(0)}}{RT^2} = \frac{\partial}{\partial T}\left(\frac{\mu^{l(0)} - \mu^{v(0)}}{RT}\right)$$
$$= c_2 - c_3/T^2 + 2c_4 T + c_5/(630-T)^2$$
$$+ c_7 P_{H_2O}/T - c_8 P_{H_2O}/T^2 + c_9 P_{H_2O}/(630-T)^2$$
$$+ 2c_{10}P_{H_2O}^2/(630-T)^3 \quad (8)$$

where $\Delta H^{l(0)} - \Delta H^{v(0)}$ is the heat of solution per mole, P_{H_2O} is the pure water pressure. Fig. 6 compares

Table 7
CO_2 solubility (mol/kg water) in aqueous NaCl solution at high pressure

T (K)	P (bar)	NaCl (m)	m_{CO_2} (a)	m_{CO_2} (b)
423.15	1458	1.09	2.3583	2.1653
413.15	1965	1.09	2.3583	2.2356
408.15	2180	1.09	2.3583	2.2304
507.15	1400	1.09	4.0906	4.3492
489.15	2015	1.09	4.0906	4.1579
483.15	2404	1.09	4.0906	4.0486
476.15	2717	1.09	4.0906	3.8015
573.15	887	1.09	6.0728	6.1371
528.15	1670	1.09	6.0728	5.9239
520.15	2307	1.09	6.0728	5.9451
520.15	2635	1.09	6.0728	5.9429

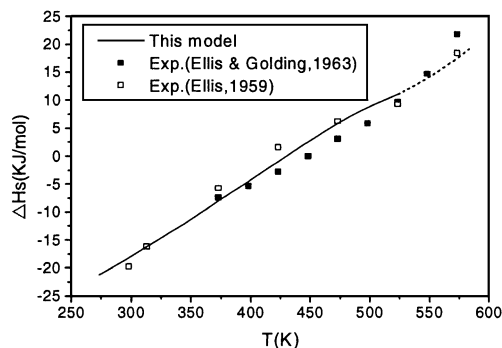(a) Data of Gehrig (1980); (b) this model.

Fig. 6. The heat of solution of CO_2 in water (the model of this study vs. experimental data).

the experimental heat of solution (Ellis, 1959; Ellis and Golding, 1963) with the results calculated from Eq. (8). It can be seen from Fig. 6 that our model can predict the heat of solution of CO_2 with remarkable accuracy. This, from another point of view, proves the reliability of the model.

5. CO_2 solubility in seawater: extrapolation of the model

The advantage of the specific interaction approach is that the model, though evaluated from binary and ternary data, can be applied to more complex systems (Weare, 1987). Natural waters often contain NaCl, KCl, $MgCl_2$, $CaCl_2$, and sulphate and carbonate salts, although NaCl is often the major component. Because of data limitations, a model directly fit to experimental measurements is possible only for CO_2–NaCl–H_2O system. In order to treat more complex systems, we included Ca^{2+}, K^+, Mg^{2+}, SO_4^{2-}, CO_3^{2-} and HCO_3^- in this model

with an approximation proposed by Duan et al. (1992a). This approach was also successfully used for the prediction of N_2 solubility (Sun et al., 2001).

As Duan et al. (1992a) proposed, the interaction parameters (λ's, ζ's) of the same charge ions have roughly the same value, and the CH_4–bivalent cation interaction parameters are about twice as large as CH_4–monovalent interaction parameters within the accuracy of experiment, which is true at different temperatures and pressures. The CH_4–anion interaction parameters are relatively small and therefore contribute little to the calculations. Hence, Duan et al. (1992a) approximated all CH_4–monovalent cation and CH_4–bivalent cation interaction parameters as λ_{CH_4-Na} and $2\lambda_{CH_4-Na}$, respectively. Here we adopt this approach to deal with the solubility of CO_2 in seawater-type brines. We approximated all CO_2–monovalent cation and CO_2–bivalent cation interaction parameters as λ_{CO_2-Na} and $2\lambda_{CO_2-Na}$, respectively. We approximate all ternary parameters as $\zeta_{CO_2-Na-Cl}$. With
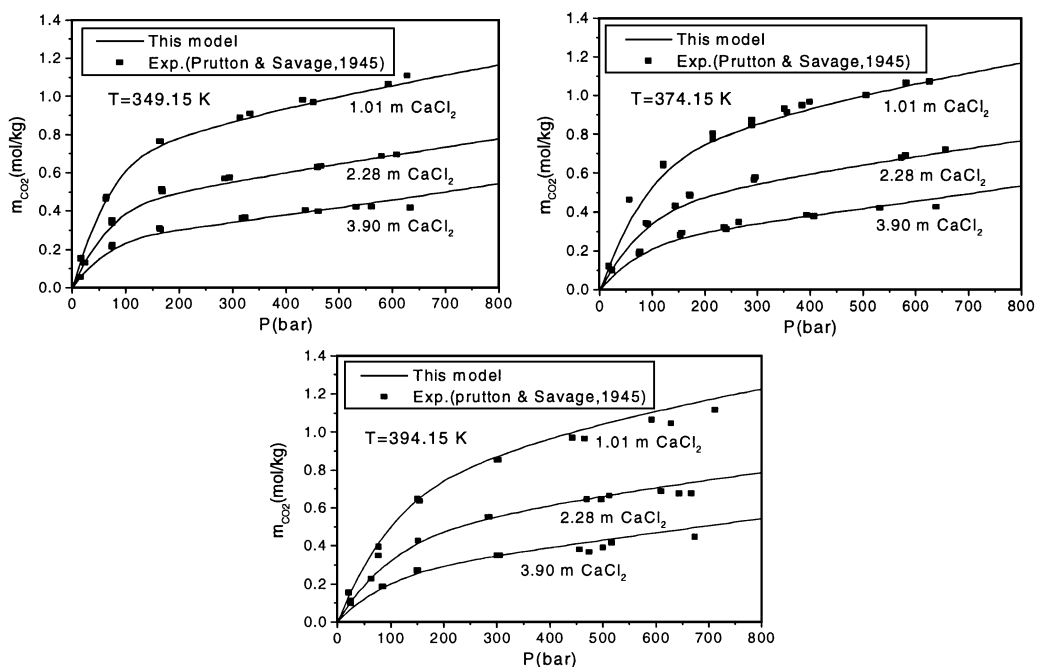

Fig. 7. The prediction of CO_2 solubility in aqueous $CaCl_2$ solutions (the model of this study vs. experimental data).
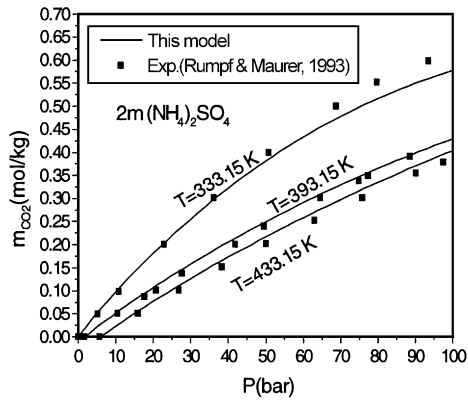
Fig. 8. The prediction of CO_2 solubility in aqueous $(NH_4)_2SO_4$ solutions (the model of this study vs. experimental data).

these approximations, the following equation is obtained.

$$
\begin{aligned}
\ln m_{CO_2} = {} & \ln y_{CO_2} \varphi_{CO_2} P - \mu_{CO_2}^{l(0)}/RT \\
& - 2\lambda_{CO_2-Na}(m_{Na} + m_K + 2m_{Ca} + 2m_{Mg}) \\
& - \zeta_{CO_2-Na-Cl} m_{Cl}(m_{Na} + m_K + m_{Mg} + m_{Ca}) \\
& + 0.07 m_{SO_4}
\end{aligned}
\tag{9}
$$

In order to test this approximation, we compared Eq. (9) with experimental data of CO_2 solubility in aqueous $CaCl_2$ solutions (Prutton and Savage, 1945), aqueous $(NH_4)_2SO_4$ solutions (Rumpf and Maurer, 1993), aqueous $MgCl_2$ solutions (Yasunishi and Yoshida, 1979) and seawater (Murray and Riley, 1971),
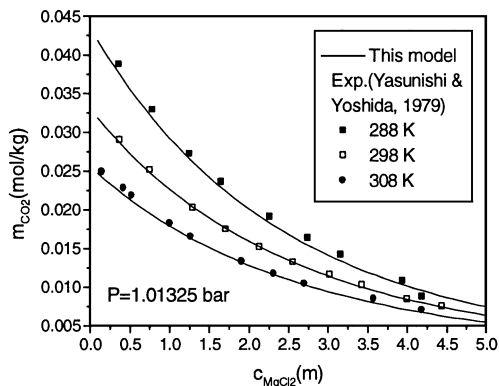

Fig. 9. The prediction of CO_2 solubility in aqueous $MgCl_2$ solutions (the model of this study vs. experimental data).
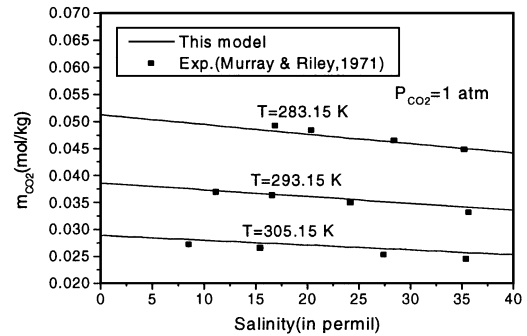

Fig. 10. The prediction of CO_2 solubility in seawater (the model of this study vs. experimental data).

respectively. Figs. 7–9 show that this approximate approach can represent CO_2 experimental solubility data in all these salt solutions with an average error of less than 5%, which is within the experimental error. Fig. 10 shows that Eq. (9) can predict CO_2 solubility in seawater with the deviation from experimental data of 3%, which is a remarkable agreement between this model and the experiment (the chemical composition of seawater is from Holland, 1978).

6. Conclusions

A CO_2 solubility model has been developed based on the equation of state of Duan et al. (1992b) and the theory of Pitzer (1973). Comparison with experimental data demonstrates that this model gives results within or close to experimental uncertainty (about 7%) in the temperature range from 273 to 533 K, for pressures from 0 to 2000 bar, and for ionic strength from 0 to 4.3 m. Following the approach adopted by Duan et al. (1992a), this model is extended to predict CO_2 solubility in more complex brines such as seawater with remarkable accuracy.

Notation

T absolute temperature in Kelvin
P total pressure; $= P_{CO_2} + P_{H_2O}$ in bar
y mole fraction of CO_2 in vapor phase
R universal gas constant; $= 0.08314467$ bar L $mol^{-1} K^{-1}$
m molality of CO_2 or salts in the liquid phase
φ fugacity coefficient

γ activity coefficient
μ chemical potential
λ_{CO_2-ion} interaction parameter
$\zeta_{CO_2-cation-anion}$ interaction parameter
Par   parameter

Subscripts
a   anion
c   cation

Superscripts
v   vapor
l   liquid
(0)   standard state
aq   aqueous solution

Acknowledgements

Appendix A. The equation of state for supercritical fluids CO_2

The equation of state for CO_2 developed by Duan et al. (1992b) has the following form:

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3}{V_r}$$
$$+ \frac{a_4 + a_5/T_r^2 + a_6/T_r^3}{V_r^2} + \frac{a_7 + a_8/T_r^2 + a_9/T_r^3}{V_r^4}$$
$$+ \frac{a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{V_r^5}$$
$$+ \frac{a_{13}}{T_r^3 V_r^2}\left(a_{14} + \frac{a_{15}}{V_r^2}\right)\exp\left(-\frac{a_{15}}{V_r^2}\right) \tag{A1}$$

where P_r, T_r and V_r are reduced pressure, reduced temperature and reduced volume, respectively. They are defined as:

$$P_r = \frac{P}{P_c} \tag{A2}$$

$$T_r = \frac{T}{T_c} \tag{A3}$$

$$V_r = \frac{V}{V_c} \tag{A4}$$

where P_c and T_c are the critical pressure and critical temperature, respectively. V_c is not the critical volume, but is defined as:

$$V_c = \frac{RT_c}{P_c} \tag{A5}$$

where R is universal gas constant, which is equal to 8.314467 Pa m^3 K^{-1} mol^{-1}. The parameters of Eq. (A1), $a_1–a_{15}$, are listed in Table A1. The mole volume V of CO_2 at a given T (K) and P is calculated as follows. First, V_r is calculated by substituting Eqs. (A2) and (A3) into Eq. (A1) for a given T (K) and P, V_r will be obtained by solving Eq. (A1). Then V is calculated from Eq. (A4). The formula to calculate fugacity coefficient of CO_2 was deduced from Eq.

Table A1
Parameters for Eq. (A1)

a_1	8.99288497e − 2
a_2	− 4.94783127e − 1
a_3	4.77922245e − 2
a_4	1.03808883e − 2
a_5	− 2.82516861e − 2
a_6	9.49887563e − 2
a_7	5.20600880e − 4
a_8	− 2.93540971e − 4
a_9	− 1.77265112e − 3
a_{10}	− 2.51101973e − 5
a_{11}	8.93353441e − 5
a_{12}	7.88998563e − 5
a_{13}	− 1.66727022e − 2
a_{14}	1.39800000e + 0
a_{15}	2.96000000e − 2

(A1) by Duan et al. (1992b), too. It has the following form:

$$\ln\varphi(T,P) = Z - 1 - \ln Z + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3}{V_r}$$
$$+ \frac{a_4 + a_5/T_r^2 + a_6/T_r^3}{2V_r^2}$$
$$+ \frac{a_7 + a_8/T_r^2 + a_9/T_r^3}{4V_r^4}$$
$$+ \frac{a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{5V_r^5} + \frac{a_{13}}{2T_r^3 a_{15}}$$
$$\times \left[a_{14} + 1 - \left(a_{14} + 1 + \frac{a_{15}}{V_r^2} \right) \right.$$
$$\left. \times \exp\left(-\frac{a_{15}}{V_r^2} \right) \right] \tag{A6}$$

Appendix B. The empirical model for pure water pressure

The empirical model to calculate pure water pressure has the following form:

$$P = (P_c T/T_c)[1 + c_1(-t)^{1.9} + c_2 t + c_3 t^2$$
$$+ c_4 t^3 + c_5 t^4] \tag{B1}$$

where T is temperature in K, $t = (T - T_c)/T_c$. T_c and P_c are the critical temperature and critical pressure of water, respectively ($T_c = 647.29$ K, $P_c = 220.85$ bar). The parameters of Eq. (B1), $c_1 - c_5$, are listed in Table B1.

Table B1
Parameters for Eq. (B1)

c_1	− 38.640844
c_2	5.8948420
c_3	59.876516
c_4	26.654627
c_5	10.637097

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