

CO₂-H₂O Mixtures in the Geological Sequestration of CO₂. II. Partitioning in Chloride Brines at 12–100°C and up to 600 bar.

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ABSTRACT

Correlations presented by Spycher et al. (2003) to compute the mutual solubilities of CO₂ and H₂O are extended to include the effect of chloride salts in the aqueous phase. This is accomplished by including, in the original formulation, activity coefficients for aqueous CO₂ derived from several literature sources, primarily for NaCl solutions. Best results are obtained when combining the solubility correlations of Spycher et al. (2003) with the activity coefficient formulation of Rumpf et al. (1994) and Duan and Sun (2003), which can be extended to chloride solutions other than NaCl. This approach allows computing mutual solubilities in a noniterative manner with an accuracy typically within experimental uncertainty for solutions up to 6 molal NaCl and 4 molal CaCl₂.

1. INTRODUCTION

In Part I of this study (Spycher et al., 2003), a noniterative approach was presented to compute the mutual solubilities of pure H₂O and CO₂ in a temperature and pressure range most relevant to the geologic sequestration of CO₂. The method was intended primarily for efficient numerical simulations of CO₂ flows. Most practical modeling applications related to CO₂ sequestration (e.g., Xu et al., 2004; Pruess et al., 2004; Garcia, 2003) deal with subsurface waters containing dissolved salts. For this reason, in Part II of this study, we extend the solubility model to include moderately saline solutions up to 6 m NaCl and 4 m CaCl₂. As before, the objective is to compute in the most efficient manner the solubility of CO₂ in the aqueous phase, as well as the H₂O solubility in the compressed-gas phase at equilibrium with the aqueous phase.

Several theoretical studies of the CO₂-H₂O-NaCl system have been published to date, following various approaches and equations of state (EOS). Two of the more comprehensive solubility models developed for this system (Bowers and Helgeson, 1983; Duan et al., 1995) lie outside the pressure-temperature-composition (P-T-X) range of interest here. These studies covered elevated pressures and temperatures mostly relevant to the study of hydrothermal systems and fluid inclusions. More recently, Duan and Sun (2003) presented a model for CO₂ solubility in NaCl and other electrolyte solutions applicable to a wide P-T-X range (0–2000 bar, 0–260°C, 0–4.3 m NaCl), overlapping low temperatures and moderate pressures applicable to the investigation of geologic CO₂ sequestration. Their model relies on an exhaustive set of experimental data from the literature and, according to the authors, reproduces published solubilities of CO₂ in NaCl and CaCl₂ solutions, as well as in seawater, with accuracies close to experimental uncertainty. One drawback of Duan and Sun's model, however, is that it relies on a fifth-order virial EOS (Duan et al., 1992) that cannot be efficiently implemented in numerical flow simulations. Also, this model was not intended to compute the H₂O solubility in the compressed CO₂ gas phase, which is one of our objectives. Nevertheless, in their study, Duan and Sun (2003) present useful Pitzer expressions (Pitzer, 1973) and parameters to compute activity coefficients for aqueous CO₂, which are needed to account for salting-out effects. When taking into account assumptions made by these authors, their activity coefficient formulation can be used with our solubility correlations (Spycher et al. 2003) to yield, in a noniterative manner, CO₂ solubilities with an accuracy comparable to their results, as discussed later.

Models presented by Li and Nghiem (1986) and Enick and Klara (1990) make use of simpler and more efficient cubic EOS. Duan et al. (2003) show that the model of Li and Nghiem (1986), based on a Peng-Robinson EOS, is not as accurate as theirs and, therefore, this model is not further evaluated here. Enick and Klara (1990) fitted a large number of solubility measurements to a Henry's-law/Peng-Robinson-EOS model, using an approach similar to that followed in Spycher et al. (2003). They then extended their solubility model to include electrolyte solutions by correlating solubilities with total dissolved solids (on a weight percent basis), using a large set of experimental and field

data. In their correlation, however, these authors did not distinguish between the various types of dissolved salts in the solutions for which CO₂ solubilities were regressed (NaCl, CaCl₂, and unspecified brines). Because their correlation for saline solutions inevitably shows significant scatter and is approximate at best, it was not considered further.

Rumpf and Maurer (1993) presented a comprehensive solubility model for CO₂ in electrolyte solutions. Their model relied on solution-chemistry correlations similar to those adopted in the present study, but used a standard virial EOS truncated after the second term to compute fugacity coefficients. Rumpf et al. (1994) fitted this model to their own measurements of CO₂ solubility from 40 to 160°C and up to ~100 bar, in 4 and 6 m NaCl solutions. These authors used Pitzer expressions similar to those adopted by Duan and Sun (2003) to compute activity coefficients. As shown later in this study, their activity coefficient formulation can be extended and combined with our solubility model (Spycher et al., 2003) to cover our entire P-T range of interest (12–100°C and up to 600 bar) with an accuracy as good as, if not better than, that of Duan and Sun's model.

Because reasonable aqueous CO₂ solubilities can be determined without considering non-ideal mixing effects in the gas phase, other studies have focused primarily on the aqueous phase without integrating an accurate solubility model for the compressed gas phase. Such studies include those of Ellis and Golding (1963), Malinin and Savelyeva (1972), Malinin and Kurovskaya (1975), Drummond (1981), and Cramer (1982), all of whom conducted their own CO₂ solubility experiments. These authors determined Henry's constants for pure H₂O and saline solutions, from which salting-out effects could be quantified, as further discussed later and in Appendix A-1. Nesbitt (1984) and Barta and Bradley (1985) developed similar models using experimental data from others, but further expanded the formulation of activity coefficients for aqueous CO₂ using Pitzer expressions.

In all studies discussed above, the solubility of CO₂ in water was expressed through some form of gas-liquid partitioning function relating either directly or indirectly to a thermodynamic equilibrium constant. If an EOS was used, this was done merely to

account for gas phase non-ideality. With this “Henry’s law” or “solution chemistry” approach, the effect of dissolved salts on CO₂ solubility is treated by using an activity (or salting-out) coefficient expressing the departure from solubility in pure water. This approach is followed here as well. In the last decade or so, however, other solubility models have been developed that make use of one single EOS (e.g., Peng-Robinson) to compute the properties of both the aqueous and compressed-gas phases at equilibrium. These models, reported primarily in the chemical engineering literature, have been applied to pure CO₂-H₂O systems (e.g., Shyu et al., 1997) and to systems including electrolyte solutions (e.g., Harvey and Prausnitz, 1989; Zuo and Guo, 1991; Soreide and Whitson, 1992; Sorensen et al., 2002; Masoudi et al., 2004). The main drawback of these models is that an iterative procedure must be used to solve the EOS twice, once for the gas-phase composition and a second time for the liquid-phase composition. Furthermore, while conceptually elegant, these models have not been shown to be superior to traditional “Henry’s law” models and produce large errors when their parameters are extrapolated beyond the range of measured solubilities, particularly in multicomponent systems (e.g., Patel et al., 2001). For these reasons, and because of their incompatibility with the more traditional correlations adopted in Spycher et al. (2003), these models were not considered further.

2. SOLUBILITY MODEL

The formulation of the basic model (Spycher et al., 2003) is extended with an activity coefficient for aqueous CO₂ and a correction to the activity of water to account for the effects of dissolved salts. The extended formulation is presented below, followed by a review of available models and/or data from which activity coefficients for aqueous CO₂ can be derived.

2.1 Extended Solubility Correlations

The reader is referred to Spycher et al. (2003) for the derivation of the basic correlations and a description of conventions and standard states. In the P–T range of interest here, dissolved salts are essentially nonvolatile and, therefore, the extended formulation hardly

changes. The water mole fraction in the CO₂-rich phase ($y_{\text{H}_2\text{O}}$) and the CO₂ mole fraction in the aqueous phase (x_{CO_2}) are respectively expressed as:

$$y_{\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}}^0 a_{\text{H}_2\text{O}}}{\Phi_{\text{H}_2\text{O}} P_{\text{tot}}} \exp\left(\frac{(P - P^0) \bar{V}_{\text{H}_2\text{O}}}{R T}\right) \quad (1)$$

and

$$x_{\text{CO}_2} = \frac{\Phi_{\text{CO}_2} (1 - y_{\text{H}_2\text{O}}) P_{\text{tot}}}{55.508 \gamma'_x K_{\text{CO}_2(\text{g})}^0} \exp\left(-\frac{(P - P^0) \bar{V}_{\text{CO}_2}}{R T}\right) \quad (2)$$

In these equations, K^0 is the thermodynamic equilibrium constant for each component at temperature T and reference pressure $P^0 = 1$ bar, for respective reactions $\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_2\text{O}_{(\text{g})}$ and $\text{CO}_{2(\text{aq})} \rightleftharpoons \text{CO}_{2(\text{g or l})}$. P is total pressure, \bar{V} is the average partial molar volume of each pure condensed phase over the pressure range $P^0 - P$, Φ is the fugacity coefficient of each component in the CO₂-rich (compressed gas) phase, and R is the gas constant. The effect of dissolved salts is expressed through $a_{\text{H}_2\text{O}}$, the activity of liquid water, and γ'_x , an activity coefficient for aqueous CO₂. For consistency with the formulation and values of K^0 developed in our initial model, γ'_x is on a mole fraction scale and is unity when no salts are present (i.e., $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$). Note that by equating the water activity to water mole fraction and setting $\gamma'_x = 1$, Equations (1) and (2) revert to the formulation for pure water presented in Spycher et al. (2003).

Parameters and equations for computing K^0 and Φ , as well as values of \bar{V} , were reported in Spycher et al. (2003) and are unchanged here. Values of $a_{\text{H}_2\text{O}}$ are approximated as discussed below, and various existing models for computing γ'_x are reviewed later in this paper.

Accurate values of water activity for solutions of various electrolytes can be obtained using the Pitzer ion interaction model (Pitzer 1973) (e.g., Rumpf and Maurer, 1993). However, in a salinity range up to ionic strength around 6 molal (below halite saturation), the model can be simplified by assuming that the water activity equals its mole fraction on the basis of a fully ionized salt. Deviations in computed $y_{\text{H}_2\text{O}}$ values resulting from

this assumption are evaluated later ($< \sim 8\%$ at ionic strength < 6 m). Note that the effect of these deviations on computed CO_2 solubilities (through Equation 2) is one to two orders of magnitude smaller, because $y_{\text{H}_2\text{O}}$ in Equation (2) typically remains quite small (a few percent or less at temperatures below 100°C and pressures above 25 bars or so).

Equations (1) and (2) are solved as previously by setting:

$$A = \frac{K_{\text{H}_2\text{O}}^0}{\Phi_{\text{H}_2\text{O}} P_{\text{tot}}} \exp\left(\frac{(P - P^0) \bar{V}_{\text{H}_2\text{O}}}{R T}\right) \quad (3)$$

$$B = \frac{\Phi_{\text{CO}_2} P_{\text{tot}}}{55.508 \gamma'_x K_{\text{CO}_2(\text{g})}^0} \exp\left(-\frac{(P - P^0) \bar{V}_{\text{CO}_2}}{R T}\right) \quad (4)$$

Taking the water mole fraction as a reasonable approximation of water activity, we rewrite Equation (1) as

$$y_{\text{H}_2\text{O}} = A (1 - x_{\text{CO}_2} - x_{\text{salt}}) \quad (5)$$

and the mutual solubilities are then computed as:

$$y_{\text{H}_2\text{O}} = \frac{(1 - B - x_{\text{salt}})}{(1/A - B)} \quad (6)$$

$$x_{\text{CO}_2} = B (1 - y_{\text{H}_2\text{O}}) \quad (7)$$

In Equations (5) and (6), x_{salt} is the mole fraction of the dissolved salt on a fully ionized basis and including dissolved CO_2 . It is defined as:

$$x_{\text{salt}} = \frac{\nu m_{\text{salt}}}{55.508 + \nu m_{\text{salt}} + m_{\text{CO}_2(\text{aq})}} \quad (8)$$

where m stands for molality and ν is the stoichiometric number of ions contained in the dissolved salt (i.e., 2 for NaCl, 3 for CaCl₂, etc.). Accordingly, the CO₂ molality is expressed from the mole fraction as

$$m_{\text{CO}_2} = \frac{x_{\text{CO}_2}(\nu m_{\text{salt}} + 55.508)}{(1 - x_{\text{CO}_2})} \quad (9)$$

or also as

$$m_{\text{CO}_2} = \frac{x_{\text{CO}_2} 55.508}{x_{\text{H}_2\text{O}}} \quad (10)$$

It is more practical to use the salt molality instead of mole fraction as an input parameter because it is independent from the CO₂ solubility. For this reason, after some manipulations, Equation (6) is redefined as:

$$y_{\text{H}_2\text{O}} = \frac{(1 - B) 55.508}{(1/A - B)(\nu m_{\text{salt}} + 55.508) + \nu m_{\text{salt}} B} \quad (11)$$

By computing fugacity coefficients as presented in Spycher et al. (2003), Equations (7) and (11) can be solved without iteration to provide the mutual solubilities of CO₂ and H₂O-salt solutions.

2.2 Activity Coefficients for Aqueous CO₂

Studies by Duan and Sun (2003), Rumpf et al. (1994), He and Morse (1993), Barta and Bradley (1985), Nesbitt (1984), Cramer (1982), and Drummond (1981) present data and/or equations from which activity coefficients can be derived for aqueous CO₂ in NaCl and other electrolyte solutions. Activity coefficient values from these studies, however, are not all directly comparable and yield a significant scatter (Figure 1), for various reasons discussed below and in Appendix A.1. Note that all these studies show a temperature dependence of salting-out effects, but only that of Duan and Sun (2003) also include a pressure dependence to reasonably reproduce experimental solubilities.

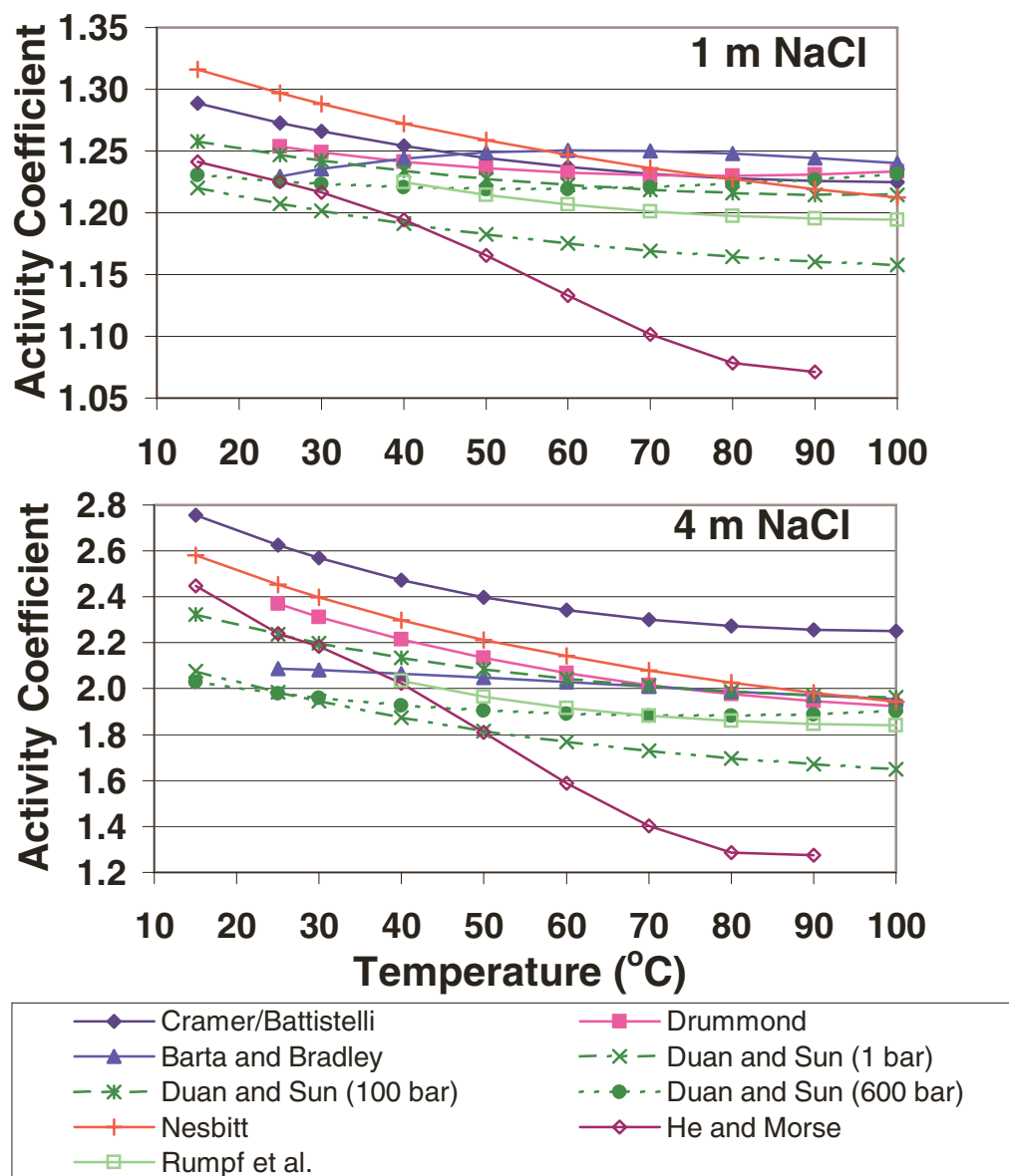


Figure 1. Activity coefficients for aqueous CO_2 from various sources (see text and Appendix A.2). Data from Cramer (1982) (and regressed by Battistelli, 1997) and Nesbitt (1984) are on a mole fraction scale; other data are on a molality scale. As discussed in the text, data from these sources are not directly comparable, yielding significant scatter.

He and Morse (1993) determined activity coefficients of aqueous CO_2 at 1.032 bar (1 atm) from 0 to 90°C for solutions of various compositions (0.1–3 m HCl, 0.5–6 m NaCl, 0.1–5 m KCl, 0.1–5 m CaCl_2 , 0.1–5 m MgCl_2 , 0.01–3 m Na_2SO_4 , 0.01–0.9 m K_2SO_4 and

0.1–4 m MgSO₄). These authors computed activity coefficients on a molal scale from measurements of Henry's law ratios (Equation A-1). They used Henry's constants (k_H) for saline solutions determined from their own experimental data, but a Henry's constant at infinite dilution (k_H^0) determined by others (Plummer and Busenberg, 1982). Their activity coefficients deviate significantly from other values shown in Figure 1, possibly because of inconsistencies between their measurements and adopted k_H^0 value. These authors fitted their activity coefficients to a Pitzer formulation with temperature-dependent ion-interaction parameters. Their regression with temperature appears to have been conducted on the same number of data points as fit parameters, which could explain the somewhat wavy behavior displayed in Figure 1. For these reasons, their activity coefficient formulation was not considered further.

Barta and Bradley (1985) regressed the experimental data of Ellis and Golding (1963) and Drummond (1981) for solutions up to 6.5 m NaCl, covering a P-T range around 20–400°C and 1–400 bar, using a Pitzer ion-interaction model. These authors fitted these data to expressions yielding Henry's constants, as a function of temperature. Activity coefficients on a molality scale (γ'_m), with the convention that $\gamma'_m \rightarrow 1$ as $m_{\text{salt}} \rightarrow 0$, were derived from their Henry's law formulation (using Equation A-1). The values obtained in this way are within the range of other data (Figure 1) but display a convex instead of concave trend with temperature. These authors were not able to regress simultaneously data for pure water and for NaCl solutions, and possibly overfitted their results. Therefore, their model was not considered either.

In the remaining cited studies, CO₂ solubilities in pure water and in saline solutions were simultaneously considered, presenting an advantage by reducing the risk of inconsistencies when evaluating salting-out effects. Duan and Sun (2003) simultaneously fitted a Pitzer ion-interaction model and a thermodynamic equilibrium formulation to a large number of solubility data for pure water and electrolyte solutions, as a function of both pressure and temperature. The experimental data regressed by Duan and Sun (2003) cover a wide P-T-X range spanning 0–260°C, 0–2000 bar, 0–6.5 m NaCl and 0–3.9 m CaCl₂. Their activity coefficient formulation is given in Appendix A.2. This model,

however, does not yield γ'_x values that can be used directly in Equation (2). This is because these authors assumed ideal mixing and did not take into account salt effects when expressing the partial pressure of H₂O in the gas phase (however, these effects were indirectly absorbed in their model by other fit parameters expressing chemical potential). Therefore, in their regression, the CO₂ partial pressure remains the same over pure and saline water, such that the pressure terms in Henry's ratios in Equation A-1 cancel out. As such, their activity coefficient formulation yields the quantity $\gamma^* = m_o/m$, where m_o is the CO₂ molality in pure water and m the molality in saline water (at the same given P and T). Their activity coefficient formulation can be implemented with our solubility model by first applying our correlations for pure water (setting $x_{\text{salt}} = 0$ and $\gamma'_x = 1$) to determine m_o , then computing the CO₂ solubility in saline solutions as $m = m_o/\gamma'$. The composition of the gas phase is then determined directly from Equation (5) after converting the salt and aqueous CO₂ molalities to mole fractions (Equations 8 and 10).

Rumpf et al. (1994) fitted the correlations of Rumpf and Maurer (1993) to their CO₂ solubility measurements in the range 40–160°C and 5 – 96 bar, at 4 and 6 m NaCl. In doing so, these authors determined Pitzer ion-interaction parameters for activity coefficient expressions similar to those implemented by Duan and Sun (2003) (Appendix A.2). In their limited P-T range, Rumpf et al. (1994) neglected the effect of pressure on these parameters and included a temperature dependence only on the binary interaction parameter. In their analysis, Rumpf et al. (1994) used a Henry's constant for pure solutions previously fitted to published data using the same model (Rumpf and Maurer, 1993), thus providing consistency. Their expression yields activity coefficients on a molality scale (γ'_m) with the convention that $\gamma'_m \rightarrow 1$ as $m_{\text{salt}} \rightarrow 0$ (Appendix A.2). For use with Equations (2) and (4), these coefficients were converted to a mole fraction scale with the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$, as shown in Appendix A.2.

Battistelli et al. (1997) regressed, as a function of temperature, salting-out coefficients determined by Cramer (1982) for NaCl solutions from 0 to 300°C. Cramer (1982) used his own experimental data up to 240°C, 62 bar, and 1.95 m NaCl, as well as data from others up to ~330°C and ~200 bar at similar NaCl concentrations. The regression

equation from Battistelli et al. (1997) is given in Appendix A.2 and can be used to compute activity coefficients through Equation A-2. Cramer's salting-out coefficients were derived on the basis of Henry's constants (Equation A-1) expressed in terms of mole fraction (and later correlated to a Setchenow equation expressed in terms of molality). Therefore, the Cramer/Battistelli model provides activity coefficients on a mole fraction scale (γ'_x), with the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$, which can be entered directly into Equations (2) and (4) without further correction. Note that Cramer (1982) did not see a need to take pressure into account in his fit of salting-out coefficients.

Using primarily his own experimental data, Drummond (1981) provided a useful regression of Henry's constants as a function of both temperature and salt molality for solutions up to around 6.5 m NaCl and a P-T range covering approximately 20–400°C and 1–400 bar. He expressed Henry's law in terms of molality, and obtained a reasonable fit of Henry's constants without introducing a pressure dependency. Activity coefficients on a molal scale (γ'_m) can be derived from his data, with the convention that $\gamma'_m \rightarrow 1$ as $m_{\text{salt}} \rightarrow 0$ (Appendix A.2). Conversion to a mole fraction scale with the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$ (Appendix A.2) yields activity coefficients within about 5% of the values given by the Cramer/Battistelli regression.

Nesbitt (1984) derived a simple relation to compute activity coefficients on a mole fraction scale (γ_x) with the convention that $\gamma_x \rightarrow 1$ as $x_{\text{H}_2\text{O}} \rightarrow 1$ (Appendix A.2). He fitted his formulation to existing experimental data covering a P-T-X range 0–500°C, 1–1500 bar, and 0–6 m NaCl. For use with Equation (4), his model must be corrected for the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$ (Appendix A.2).

Note that the activity coefficient formulation of Nesbitt (1984), as well as the molality- to mole fraction-scale conversion required with activity coefficients derived from Drummond (1981) and Rumpf et al. (1994), introduce a dependency of the activity coefficient on CO₂ solubility. This requires further manipulation of Equations (7) and (11) to solve these equations directly, because B in Equation 11 is no longer independent of x_{CO_2} . A more practical alternative, adopted here, is to simply iterate between

Equations (7) and (11). Because the coupling between B and x_{CO_2} is weak, values of γ'_x always converge within 3–4 iterations without any provisions to speed convergence.

3. RESULTS

CO₂ solubilities calculated using Equations (3) to (11), in combination with the various activity coefficient formulations discussed earlier and in Appendix A.2, were compared to both experimental and computed data reported in the literature (Table 1). Results of these comparisons are discussed below.

Most experimental data on CO₂ solubility in aqueous electrolyte solutions have been summarized in Scharlin (1996). Very few experimental data have been published on CO₂ solubility in saline solutions at low temperatures and high pressures. Prutton and Savage (1945) reported solubility for CaCl₂ solutions near 76 and 101°C up to pressures of ~650 bar. For NaCl solutions, usable data at temperatures below 100°C are limited to pressures up to ~100 bar. These data include CO₂ solubilities measured by Rumpf et al. (1994), Nighswander et al. (1989), Drummond (1981), Malinin and Kurovskaya (1975), and Malinin and Savelyeva (1972).

Because of the lack of experimental solubility data at low temperatures and high pressures, we first compare our results to the computed CO₂ solubilities tabulated by Duan and Sun (2003) at 30, 60, and 90°C and 1–600 bar for solutions up to 4 m NaCl (Figure 2). Duan and Sun (2003) fitted their solubility model to all the experimental data mentioned above, and to data from other sources covering a much wider P-T range than considered here. According to these authors, their model reproduces experimental data close to or within experimental uncertainty (estimated by the authors at around 7%).

Combining the activity coefficient formulation of Duan and Sun (2003) (Appendix A.2) and the solubility correlations presented earlier, the CO₂ solubilities reported by Duan and Sun (2003) (i.e., computed using their full model) are reproduced with a root-mean-square error (RMSE) around 2% at all salt molalities (Table 1 and Figure 2). This deviation expresses differences between the pure-water solubilities computed by each

Table 1. Deviations, as root mean square error (RMSE), between predicted CO₂ solubilities (Equations 3–11) and available experimental and computed data below ~100°C for NaCl and CaCl₂ solutions, using various activity coefficient formulations from the literature, as discussed in the text and in Appendix A.2.

Solubility Data Source	P-T-X range covered below ~ 100°C				Model deviations for various activity coefficient formulations				
	T (°C)	P (bar)	Aqueous Solution	Nb. Points	Duan and Sun	Rumpf et al.	Cramer/Battistelli	Drummond	Nesbitt
Computed Data					RMSE (%)	RMSE (%)	RMSE (%)	RMSE (%)	RMSE (%)
Duan and Sun (2003)	30-90	1-600	pure water	30	1.6	1.6	1.6	1.6	1.6
	30-90	1-600	1 m NaCl	30	1.6	2.9	3.0	3.2	3.7
	30-90	1-600	2 m NaCl	30	1.6	4.2	4.1	4.6	6.0
	30-90	1-600	4 m NaCl	30	1.7	6.7	8.2	9.4	10.0
Experimental Data									
Drummond (1981)	31-100	39-58	pure water	11	7.8	7.8	7.8	7.8	7.8
	27-100	42-65	1 m NaCl	14	7.3	7.8	8.8	6.2	8.8
	28-100	42-68	2 m NaCl	15	3.6	2.2	2.2	4.3	2.3
	22-100	40-67	3 m NaCl	17	3.1	3.2	2.3	2.4	6.1
	20-100	35-59	4 m NaCl	17	7.9	4.1	10	11	2.1
	24-100	35-54	6 m NaCl	16	5.6	9.2	13	11	15
Malinin and Savelyeva (1972)	25-100	~48	pure water	5	4.3	4.3	4.3	4.3	4.3
Malinin and Kurovskaya (1975)	25-100	~48	0.4-1.1 m NaCl	6	4.9	4.7	4.5	5.8	4.7
	25-100	~48	1.8-2.2 m NaCl	5	4.5	4.2	4.5	4.7	5.4
	25-100	~48	2.6-3.2 m NaCl	5	4.7	4.0	4.8	6.1	5.7
	25-100	~48	4-5.9 m NaCl	7	5.5	4.8	11	9.3	11
Rumpf et al. (1994)	50	11-58	pure water	7	0.96	0.96	0.96	0.96	0.96
	40-80	5-96	4 m NaCl	22	4.1	2.2	5.3	6.3	5.5
	40-80	6-92	6 m NaCl	16	6.2	2.1	18	16	6.0
Nighswander et al. (1989)	80-81	23-102	pure water	8	3.7	3.7	3.7	3.7	3.7
	80-81	40-99	0.18 m NaCl	8	3.4	3.4	3.5	3.3	3.5
Pruett and Savage (1945)	101	58-623	pure water	14	5.0	5.0	5.0	5.0	5.0
	76-101	16-628	~1 m CaCl ₂	28	6.0	5.7	20	17	16
	76-101	22-657	~2.3 m CaCl ₂	25	5.5	4.3	40	26	39
	76-101	15-638	~4 m CaCl ₂	20	6.8	8.7	61	41	77
Malinin and Savelyeva (1972)	25-100	~48	pure water	5	4.3	4.3	4.3	4.3	4.3
Malinin and Kurovskaya (1975)	20-100	~48	0.2-1.3 m CaCl ₂	10	4.3	3.7	19	16	13
	20-100	~48	1.9-2.4 m CaCl ₂	5	3.6	3.3	40	32	31
	20-100	~48	3-3.4 m CaCl ₂	2	7.1	9.5	58	48	51
	20-100	~48	3.9-6.0 mCaCl ₂	3	6.5	6.1	72	49	95

model. The other activity coefficient formulations (Appendix A.2) produce somewhat larger deviations but still reasonably good results, with an RMSE increasing from ~3% at 1 m NaCl up to ~10% at 4m NaCl (Table 1). Note that Duan and Sun (2003) limit their model application to 4 m NaCl, although these authors seem to have fitted solubilities at concentrations up to 6 m NaCl.

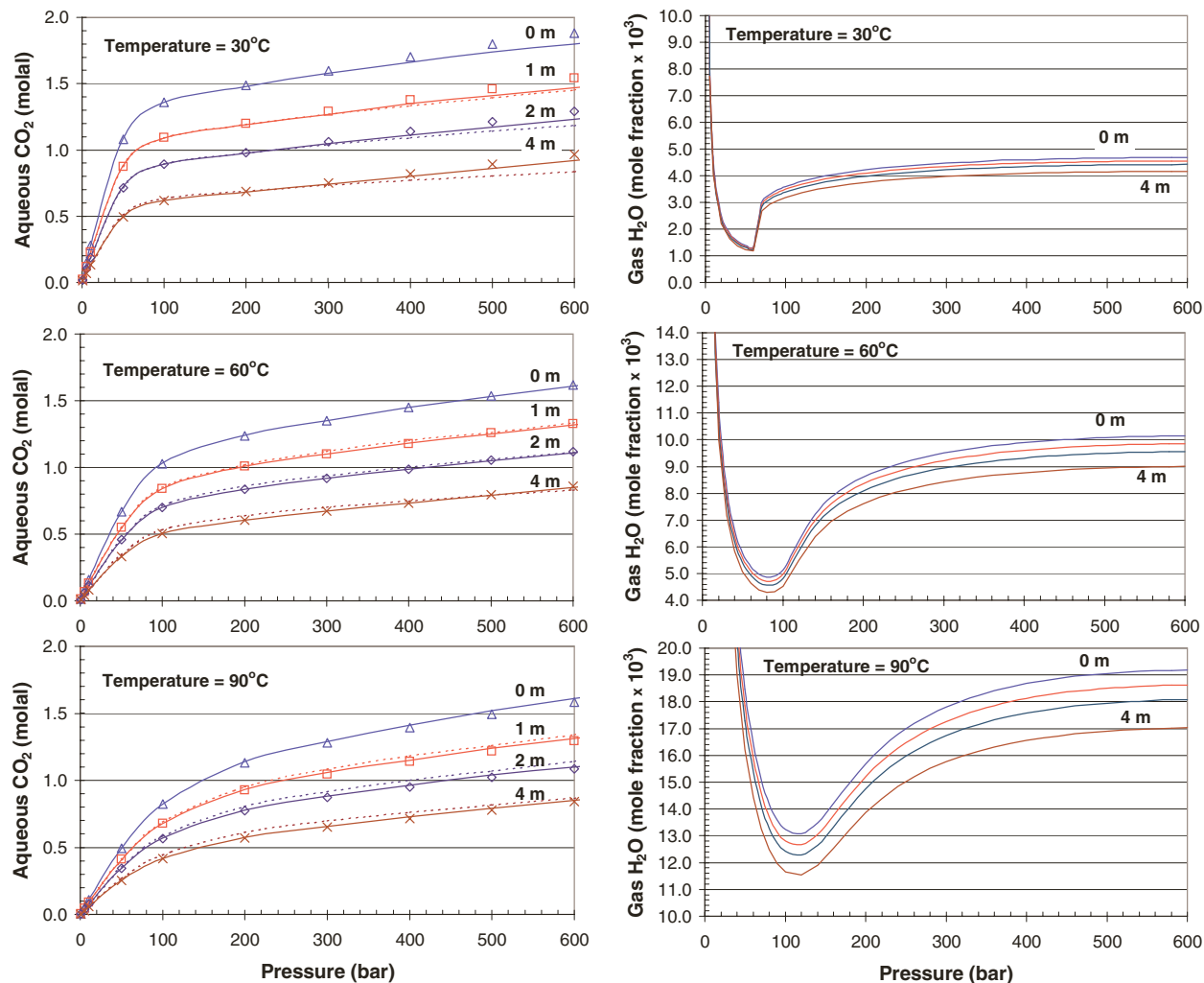


Figure 2. Predicted mutual solubilities of CO₂ and H₂O (Equations 3-11) using the activity coefficient formulations of Duan and Sun (2003) (solid lines) and Rumpf et al. (1984) (dashed lines) (see text and Appendix A.2). CO₂ solubilities computed by Duan and Sun (2003) using their full solubility model are also shown for comparison (symbols).

No experimental or computed data were available for comparing water concentrations in the compressed gas phase ($y_{\text{H}_2\text{O}}$) for saline CO₂-H₂O solutions (Figure 2). As discussed earlier, the accuracy of $y_{\text{H}_2\text{O}}$ directly relates (through Equation 1) to the accuracy of the liquid water activity, which is approximated in our model by the liquid water mole fraction (on the basis of a fully ionized salt). The deviation between water mole fraction and activity was evaluated using osmotic coefficient values reported by Pitzer et al.

(1984) for sodium chloride solutions and by Ananthaswamy and Atkinson (1985), Phutela and Pitzer (1983), and Holmes et al. (1994) for calcium chloride solutions. In our P–T range of interest, assuming that $a_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}}$ leads to computed $y_{\text{H}_2\text{O}}$ values deviating positively from “true” values by about 1, 3, 5, and 8% for solutions 3, 4, 5, and 6 m NaCl, and about 0.4, 5, 15, and 30% for solutions 1, 2, 3, and 4 m CaCl_2 (ionic strength 3, 6, 9, and 12), respectively. For these ranges in composition, differences between activity and mole fraction due solely to temperature and pressure remain below ~1% for NaCl solutions and below ~10% for CaCl_2 solutions (the temperature effect being largely dominant). These approximate deviations in $y_{\text{H}_2\text{O}}$ do not include the average fit error around 5% (Spycher et al., 2003) determined from experimental data for the pure CO_2 - H_2O system.

Results of our solubility model combined with the various activity coefficient formulations (Appendix A.2) were also compared directly to experimental solubilities (Table 1 and Figures 3–4). For pure water, our correlations reproduce the experimental CO_2 solubilities of Drummond (1981) within about 8%, and other solubility data listed in Table 1 within less than 5%, even though none of these data was included in the original regression (Spycher et al., 2003). For NaCl solutions, the various activity coefficient formulations reproduce experimental data with RMSE values generally less than 10%. The activity coefficient formulations from Duan and Sun (2003) and Rumpf et al. (1994) provide the best results. The latter reproduces best the solubilities measured by Rumpf et al. (1994) at 6 m NaCl, which is to be expected, because their activity coefficient formulation was fitted to these data.

The various activity coefficient formulations were also tested against data for CaCl_2 solutions. Duan and Sun (2003) extended their formulation to deal with salts other than NaCl by assuming that interaction parameters for ions with the same charge have roughly the same values. The same method was used, here, to extend the formulation of Rumpf et al. (1994) to CaCl_2 solutions (Appendix A.2). The activity coefficient formulation from Drummond (1981) and Cramer (1982) were extended to CaCl_2 solutions by using ionic strength in place of salt molality. The formulation of Nesbitt (1984) was extended

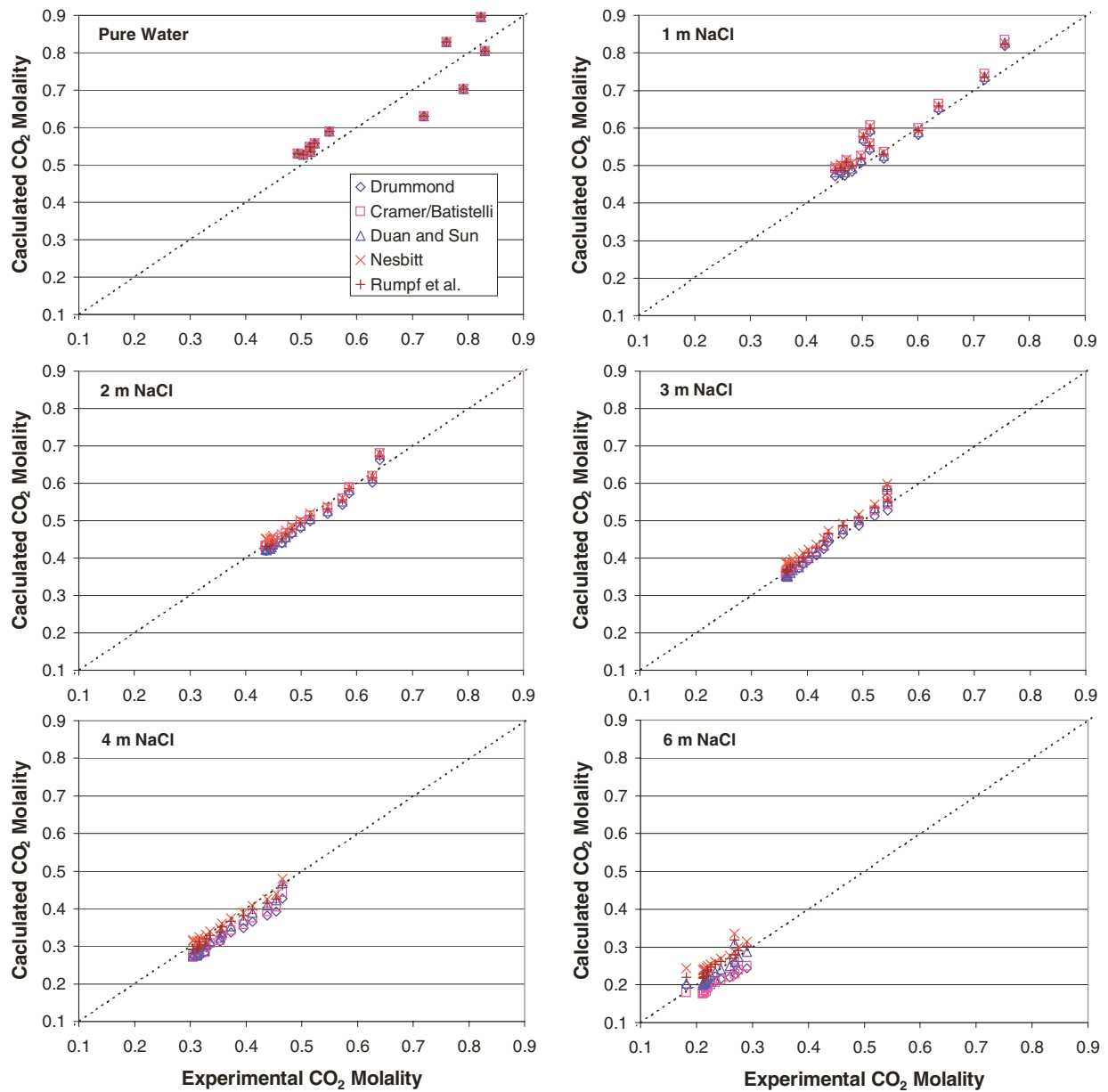


Figure 3. Predicted (Equations 3-11) versus measured (Drummond, 1981) CO₂ solubilities in NaCl solutions, using various activity coefficient formulations (symbols) as discussed in the text and Appendix A.2. The P-T range of the experimental data is approximately 20–100°C and 35–68 bar (see Table 1).

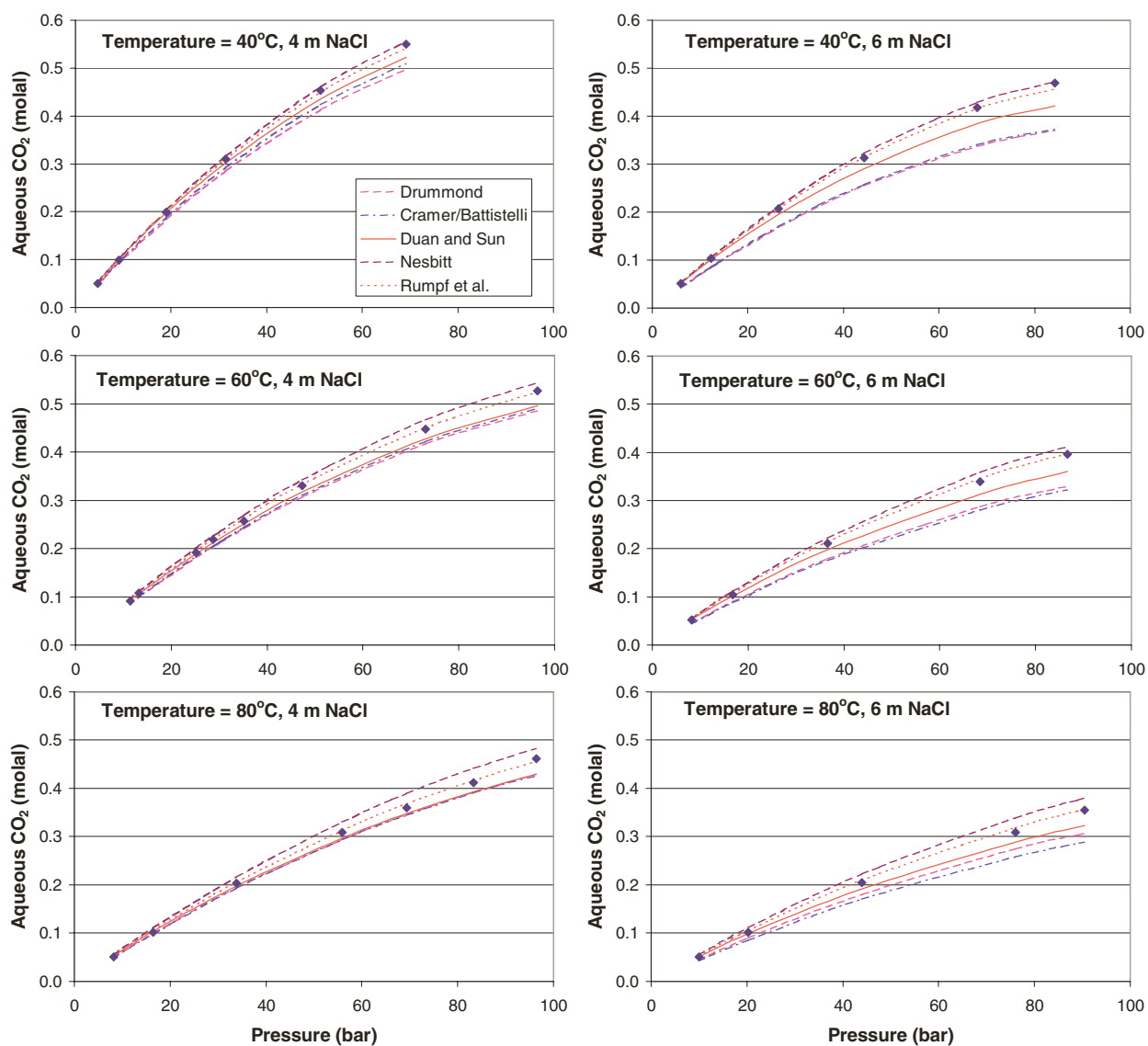


Figure 4. Predicted (Equations 3-11) (lines) and measured (Rumpf et al., 1994) (symbols) CO₂ solubilities in NaCl solutions, using various activity coefficient formulations as discussed in the text and Appendix A.2.

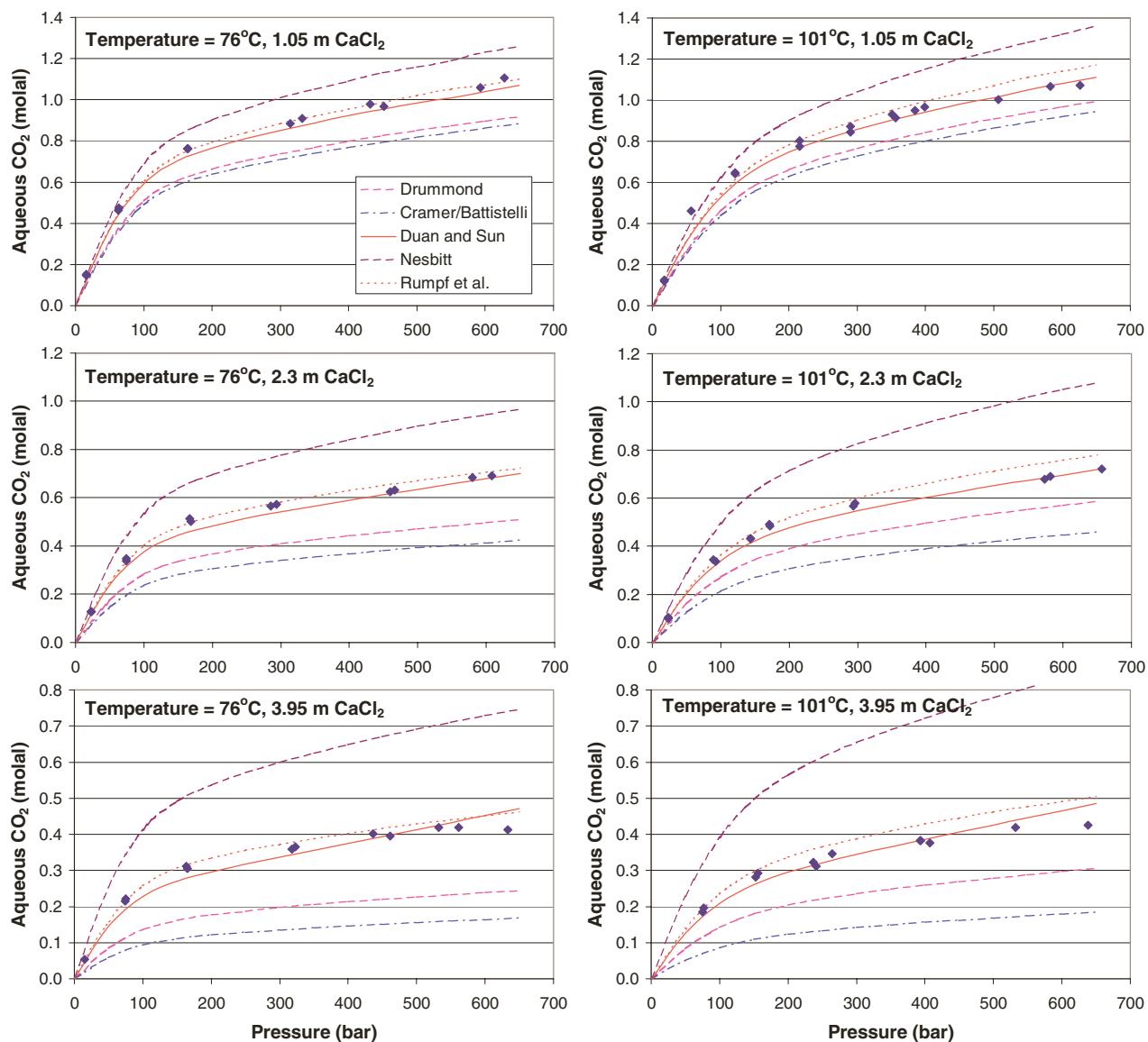


Figure 5. Predicted (Equations 3-11) (lines) and measured (Prutton and Savage, 1945) (symbols) CO₂ solubilities in CaCl₂ solutions, using various activity coefficient formulations as discussed in the text and Appendix A.2.

using CaCl_2 mole fractions (on a fully ionized basis) in place of NaCl mole fractions. As expected, the activity coefficient expression of Duan and Sun (2003) and Rumpf et al. (1994) are clearly superior in reproducing solubilities in CaCl_2 solutions, showing similar RMSE values within a 3–10% range for solutions up to 6 m CaCl_2 , compared to deviations up to 95% with the other formulations (Table 1). Note that even though the computed CO_2 solubility is reasonably accurate up to 6 m CaCl_2 , large errors in computed $y_{\text{H}_2\text{O}}$ values ($>30\%$) are expected to occur at concentrations > 4 m CaCl_2 because $a_{\text{H}_2\text{O}}$ is approximated by $x_{\text{H}_2\text{O}}$ in Equation 1.

4. DISCUSSION AND CONCLUSIONS

For NaCl solutions up to 2 molal, all activity coefficient formulations provide reasonable CO_2 aqueous solubilities within $\sim 10\%$ of the experimental and computed reference data shown in Table 1. At molalities up to 6 m NaCl and 4 m CaCl_2 , the activity coefficient expressions of Duan and Sun (2003) and Rumpf et al. (1994) provide more accurate results, reflecting the superiority of the Pitzer formulation over simpler models. Overall, the activity coefficient formulation of Rumpf et al. (1994) yields slightly smaller RMSE values relative to experimental data, most visibly (and expectedly) so when comparing results against the solubility measurements made by these authors at 6 m NaCl (Figure 4). However, in the absence of more experimental data at these salinities and at high pressures, it is difficult to assess which of these two formulations is more accurate. Note that the formulation of Rumpf et al. (1994) yields good results within a P-T range significantly larger than the range covered by these authors when regressing their data (pressures limited to ~ 100 bar and no temperatures below 40°C). Also, their formulation (which is only a function of temperature) yields an accuracy similar to that of Duan and Sun's formulation (which is pressure and temperature dependent), indicating that within the pressure range considered here (up to ~ 600 bars) a pressure correction to activity coefficients is not necessary.

Using the activity coefficient formulation of Duan and Sun (2003) allows computing the mutual solubilities of CO_2 and H_2O in a noniterative manner. As discussed earlier, the formulation of Rumpf et al. (1994) is most easily implemented using a few iterations

because of the (weak) dependence of activity coefficients on the CO₂ solubility (introduced by the conversion from a molality to a mole fraction scale). This is not seen as a disadvantage, however, because the type of iterative procedure and equations involved would not significantly decrease performance when implemented into large numerical simulations. In any case, using either approach, the EOS required to calculate mutual solubilities is solved noniteratively (Spycher et al., 2003).

By combining either of these two activity coefficient formulations (Appendix A.2) with our solubility correlations, mutual CO₂-H₂O solubilities in the range 12–100°C, 1–600 bar, and 0–6 m NaCl (or 4 m CaCl₂) can be computed in a direct manner, yielding CO₂ solubilities with an accuracy (typically < 7%) within the spread of experimental data. It must be recalled, however, that CO₂ aqueous solubilities computed above ~100 bar at temperatures below ~100°C may have a large uncertainty, because they rely on very few experimental data points. As more experimental data become available in this P-T range, a refit of ion-interaction parameters, as done previously by Duan and Sun (2003) and Rumpf et al. (1994), but using our solubility correlations, may increase the model confidence and accuracy for applications to geologic CO₂ sequestration.

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Appendix A

Activity Coefficient Formulations for Aqueous CO₂

A.1 General Considerations

The usual approach to determining activity coefficients of dissolved gases in water is to make use of the relationship

$$\ln(\gamma) = \ln(k_H / k_H^0) \quad (\text{A-1})$$

where k_H and k_H^0 is the ratio of gas fugacity (f) to aqueous molality (m) or mole fraction (x) (Henry's constant) in saline and pure water, respectively (i.e., $k_H = f/m$ or $k_H = f/x$, as discussed below).

When using Equation A-1, the definition and concentration units used for expressing k_H and k_H^0 are crucial in the definition of γ . Fundamentally, k_H^0 should be a true equilibrium constant extrapolated to conditions of infinite dilution (at ~ 1 bar, or water saturation pressure above 100°C), in which case Equation (A-1) yields a “true” activity coefficient, depending not only on salt concentration but also on the concentration of the dissolved gas (i.e., the convention that $\gamma \rightarrow 1$ as x_{CO_2} or $m_{\text{CO}_2} \rightarrow 0$). Practically, however, k_H^0 is often taken as the ratio of the gas fugacity to the gas solubility in pure water but not extrapolated to infinite dilution. In this case, the activity coefficients obtained with Equation (A-1) are unity in pure water (i.e., $\gamma' \rightarrow 1$ as x_{salt} or $m_{\text{salt}} \rightarrow 0$), and can be related to the salting-out coefficient, k_s , through the Sechenow equation

$$\ln(\gamma') = k_s m_{\text{salt}} \quad (\text{A-2})$$

Note that the salt molality (m_{salt}) in Equation A-2 is commonly replaced by ionic strength for salts other than 1:1 electrolytes.

The difference between γ and γ' can be evaluated using expressions presented by Diamond and Akinfiev (2003) to compute the activity coefficient of CO_2 in pure water. In our P-T range of interest, the difference is always less than 7%. Note that this difference is absorbed into the values of $K_{\text{CO}_2}^0$ in Equations 2 and 4, because these values were fitted to experimental data assuming unit activity coefficient in the absence of

dissolved salts (Spycher et al., 2003). Therefore, for consistency, values of activity coefficients (γ'_x) introduced into Equations 2 and 4 should be corrected for the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$, even though the correction is not very large.

At elevated salt concentrations, a more important difference in activity coefficient values obtained with Equation A-1 results from the concentration units in the expression of Henry's law. If Henry's constants are defined in terms of mole fractions (e.g., Cramer, 1982), then the activity coefficients are on a mole fraction scale (γ_x), even though they might be related to a salting-out coefficient (through Equation A.2) using molality (as was done by Cramer, 1982). If Henry's constants are defined in terms of molality (e.g., Drummond 1981), then the activity coefficients derived through Equation A-2 are on a molality scale (γ_m). The relationship between both types of coefficients can be derived from fundamental thermodynamic relations (e.g., Denbigh, 1983, p. 278) and is given by

$$\gamma_m = \gamma_x / \left(1 + \frac{\sum m_i}{55.508} \right) = \gamma_x x_{\text{H}_2\text{O}} \quad (\text{A-3})$$

where the summation of molalities m_i is across all dissolved species in solution. As mentioned previously, values of activity coefficients (γ'_x) in Equations (2) and (4) should always be on a mole fraction scale, for consistency with the derivation of these equations (Spycher et al., 2003).

Smaller differences in activity coefficient values derived through Equation A-1 may also arise if experimental k_{H}° values are not extrapolated to water saturation pressures (or ~ 1 bar at $T < 100^{\circ}\text{C}$). Other small differences may also result from the method used to calculate the gas fugacity necessary to determine k_{H} and k_{H}° . If partial pressure (P_i) is used instead of fugacity ($f_i = \phi_i P_i = \phi_i y_i P_{\text{total}}$), errors in γ values calculated through Equation A-1 will be primarily caused by the difference between the CO_2 gas mole fraction (y_i) over pure and saline water (the difference between fugacity coefficient values (ϕ_{CO_2}) over pure and saline water is negligible in our P-T range of interest).

A.2. Activity Coefficient Expressions from the Literature

Duan and Sun (2003)

The activity coefficient formulation presented by Duan and Sun (2003) is a Pitzer formulation fitted to experimental solubility data. It takes the following form:

$$\begin{aligned} \ln(\gamma^*) = & 2\lambda(m_{\text{Na}} + m_{\text{K}} + 2m_{\text{Ca}} + 2m_{\text{Mg}}) \\ & + \xi m_{\text{Cl}} (m_{\text{Na}} + m_{\text{K}} + m_{\text{Ca}} + m_{\text{Mg}}) - 0.07 m_{\text{SO4}} \end{aligned} \quad (\text{A-4})$$

with

$$\begin{aligned} \lambda = & -0.411370585 + 6.07632013 \times 10^{-4} T + 97.5347708 / T - 0.0237622469 P / T \\ & + 0.0170656236 P / (630 - T) + 1.41335834 \times 10^{-5} T \ln(P) \\ \xi = & 3.36389723 \times 10^{-4} - 1.98298980 \times 10^{-5} T + 2.12220830 \times 10^{-3} P / T \\ & - 5.24873303 \times 10^{-3} P / (630 - T) \end{aligned}$$

where T is temperature in degrees Kelvin (ranging from 273 to 533 K), P is pressure in bar (ranging from 0 to 2000 bar), m are molalities (for ionic strength ranging from 0 to 4.3 m, but up to ~6 m NaCl and 4 m CaCl₂ in our P-T range of interest). The activity coefficient calculated in this way is not a “true” activity coefficient and is related to the CO₂ solubility by the following relationship (see main text):

$$\gamma^* = m_{\text{CO2}}^0 / m_{\text{CO2}} \quad (\text{A-5})$$

where m_{CO2}^0 is the aqueous CO₂ molality in pure water at P and T and m_{CO2} is the aqueous CO₂ molality in a saline solution with a composition defined by m_{Na} , m_{K} , m_{Ca} , m_{Mg} , m_{Cl} and m_{SO4} at the same P and T .

Rumpf et al. (1994)

This model makes use of a Pitzer formulation similar to that adopted by Duan and Sun (2003). Their model yields activity coefficients on the molality scale, with the convention that $\gamma'_m \rightarrow 1$ as $m_{\text{salt}} \rightarrow 0$. Rumpf et al. (1994) use solubility correlations (Rumpf and Maurer, 1993) without simplifications, and their activity coefficients are

appropriate for use in Equations (2) and (4) after conversion to a mole fraction scale, as shown below. The activity coefficients are given by

$$\ln(\gamma'_m) = 2 m_{\text{salt}} B^{(0)} + 3 m_{\text{salt}}^2 \Gamma \quad (\text{A-6})$$

with

$$B^{(0)} = 0.254 - 76.82/T - 10656/T^2 + 6312 \times 10^3/T^3$$

$$\Gamma = -0.0028$$

where T is temperature in degrees Kelvin (ranging from 313 to 433 K) and m_{salt} is NaCl molality (up to 6 molal). For extension to other chloride solutions, we extend their model using the same simplifications as proposed by Duan et al. (1992) (and applied by Duan et al. 2003), based on the assumption that interaction parameters for ions with the same charge have roughly the same values. Doing so yields

$$\ln(\gamma'_m) = 2 B^{(0)} (m_{\text{Na}} + m_{\text{K}} + 2m_{\text{Ca}} + 2m_{\text{Mg}}) + 3 \Gamma m_{\text{Cl}} (m_{\text{Na}} + m_{\text{K}} + m_{\text{Ca}} + m_{\text{Mg}}) \quad (\text{A-7})$$

where m stands for the molality of each individual ion in solution. For compatibility with Equations (2) and (4), the activity coefficients are converted (Equation A-3) to a mole fraction scale and convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$ using the following relationship:

$$\gamma'_x = \gamma'_m \left(1 + \frac{m_{\text{CO2(aq)}} + \sum m_{i \neq \text{CO2(aq)}}}{55.508} \right) \bigg/ \left(1 + \frac{m_{\text{CO2(aq)}}}{55.508} \right) \quad (\text{A-8})$$

Cramer (1982)/Battistelli et al. (1997)

This model is derived from salting-out coefficients (k_s) reported by Cramer (1982), for NaCl solutions, and regressed as a function of temperature by Battistelli et al. (1997).

The model takes the form:

$$\log_{10}(\gamma'_x) = k_s m_{\text{salt}} \quad (\text{A-9})$$

with

$$k_s = 1.19784 \times 10^{-1} - 7.17823 \times 10^{-4} T + 4.93854 \times 10^{-6} T^2 - 1.03826 \times 10^{-8} T^3 \\ + 1.08233 \times 10^{-11} T^4$$

where T is temperature in degrees centigrade (ranging 0 – 350°C) and m_{salt} is NaCl molality (ranging 0–1.95 m). As discussed earlier, values of γ'_x in this particular case are on a mole fraction scale, with the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$, and can be used directly in Equations (2) and (4) without further correction.

Drummond (1981)

Drummond (1981) reported regression equations to compute Henry's law constants as a function of temperature and NaCl molality. From his Henry's law expressions and Equation A-1, the following activity coefficient formulation can be derived:

$$\ln(\gamma'_m) = (-1.0312 + 1.2806 \times 10^{-3} T + 255.9 / T) m_s \\ - (0.4445 - 1.606 \times 10^{-3} T) m_s / (m_s + 1) \quad (\text{A-10})$$

where T is temperature in degrees Kelvin (for ~20 – 400°C) and m_s is NaCl molality (for 0–6.5 m). The activity coefficient values given by this equation are on a molality scale with the convention that $\gamma'_m \rightarrow 1$ as $m_s \rightarrow 0$. Identical expressions have been derived by others for implementation into geochemical modeling codes (e.g., Wolery 1986). For compatibility with Equations (2) and (4), these activity coefficients are converted to a mole fraction scale, with the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$, using Equation A-8.

Nesbitt (1984)

Nesbitt (1984) developed a simple formulation applicable to NaCl solutions, yielding true activity coefficients on a mole fraction scale as follows:

$$\ln(\gamma_x) = A (x_{\text{H}_2\text{O}}^2 - 1) \quad (\text{A-12})$$

with (after corrections of typographical errors on the original paper)

$$A = - \exp (1.281 \times 10^{-5} \times T^2 - 9.606 \times 10^{-3} T + 9.445) / (1.98717 T)$$

where T is temperature in degrees Kelvin (ranging from 273 to 440 K; the author provides other coefficients for higher temperatures) and $x_{\text{H}_2\text{O}}$ is the water mole fraction (on the basis of a fully ionized salt, up to 6 m NaCl). Conversion for compatibility with Equations (2) and (4) with the convention that $\gamma'_x \rightarrow 1$ as $x_{\text{salt}} \rightarrow 0$ is carried out by expressing the water mole fraction in Equation (A-12) in terms of the mole fractions of other components (i.e., $x_{\text{H}_2\text{O}} = 1 - x_{\text{salt}} - x_{\text{CO}_2}$), then subtracting from Equation (A-12) the result of that equation for $x_{\text{salt}} = 0$. These manipulations yield the following revised expression:

$$\ln(\gamma'_x) = A (-2x_{\text{NaCl}} + 2x_{\text{NaCl}}x_{\text{CO}_2(\text{aq})} + x_{\text{NaCl}}^2) \quad (\text{A-13})$$

where A remains the same function of temperature as shown above.