PARAMETER ESTIMATION IN COMPLEX ALGEBRAIC MODELS: SOLUBILITY OF CO_2 IN BRINE

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A new form to calculate the activity coefficient of CO_2 in aqueous solutions of chloride salts is presented. The model is coupled with an external solubility model to verify its performance against experimental data in temperature range of 50ºC-120ºC and pressures up to 200 bar, showing the model gives more accurate results than some well-known solubility models. Moreover, it presents a procedure to estimate parameters in complex algebraic models via MATLAB®, testing seven built-in optimization algorithms and mapping both individual and joint confidence interval.

Keywords: parameter estimation, carbon dioxide, activity, solubility, brine

Introduction

Models for the activity coefficient of CO_2 (γ_{CO_2}) in brine is a topic of interest when phase equilibria is involved, e.g. in carbon sequestration, CO_2-induced metal corrosion, enhanced oil recovery (EOR) and other petroleum or environmental applications [1]. Many thermophysical fluid properties depend on the content of CO_2 in water or brine, as it determines the pH the chemistry of the resulting solution. For example, the dissolution rate of carbonate minerals are highly dependent on the pH of the carbonated brine in EOR. The presence of salts from seawater or from the dissolution of the formation rock reduce the molality of CO_2 in equilibrium condition mainly due to a change in γ_{CO_2}, so it should be modeled to predict fluid chemistry correctly [1,9].

Any model should deliver the best representation of the real-world phenomena. In this sense, parameter estimation is an optimization problem and must be described statistically in terms of confidence intervals subjected a level of confidence. These calculations were performed using MATLAB® [4] and the adjusted model was compared with other well-known models in the literature to verify its potential uses.

Method

A CO_2-brine solubility model was used to test an external model that computes the activity coefficient of CO_2 (γ_{CO_2}) [9]. This work slightly changed the formulation of this solubility model so it is applicable even when the salts are present simultaneously, providing information both on the molality of CO_2 (m_{CO_2}) in the brine and the composition of the CO_2-rich phase at equilibrium condition.

Duan and Sun (2003) [1] developed the most accurate activity model to be integrated into the solubility model, but it does not provide a true activity coefficient [9], as it just relates m_{CO_2} in pure water and brine at the same system conditions. Thus, this model cannot be used in chemical equilibrium (i.e. speciation calculations). Rumpf et al. (1994) [7] developed the second most accurate model but only for specific chloride salts so it is not easily extendable. This work attempts to create a model that could be used for chloride salts in general and provides a true activity coefficient.

Activity models like electrolyte-NRTL or Pitzer represent a wider variety of ions but their implementation is difficult, as the model requires too many input parameters.

This work developed a simpler solution to capture the behavior of γ_{CO_2} by extending the formulation of Drummond (1981) [2] to aqueous solutions of chloride salts in general. The original formulation was developed only for aqueous solutions of NaCl., The modified γ_{CO_2} in a molality scale is given in eq. (1) and can be used for speciation calculations up to pH = 6 with fairly good agreement with Pitzer models.

$$ln(\gamma_{CO_2,m}) = \left(-1.0312 + 1.2806 \times 10^{-3}T + \frac{255.9}{T}\right) m_{NaCl,eq} - (0.4445 - 1.606 \times 10^{-3}T)\left(\frac{m_{NaCl,eq}}{m_{NaCl,eq} + 1}\right) \tag{1}$$

The value of $\gamma_{CO_2,m}$ must be converted to the molar fraction scale to be incorporated into the solubility model. This conversion is performed by eq. (2), making the procedure iterative but it converges in few iterations [9].

$$\gamma_{CO_2,m} = \frac{\gamma_{CO_2,x}}{\left(1 + \frac{\sum m_i}{55.508}\right)}\left(1 + \frac{m_{CO_2}}{55.508}\right) \tag{2}$$

This new modification relies on parameters that express the molality of salts in terms of NaCl equivalents instead of using the ionic strength as in Spycher et al. (2005), which yielded poor results. In the modification of this work, the molality of each ion (m_i) is calculated assuming complete dissociation of each molal of salt (m_k) in water, according to eq. (3), which uses the stoichiometric coefficients ($\nu_{i,k}$) given in Table 1.

$$m_i = \sum \nu_{i,k} m_k \tag{3}$$

Table 1 Stoichiometric coefficients for each chloride salt.

k / i	NaCl	$CaCl_2$	$MgCl_2$
Na^+	1	0	0
Cl^-	1	2	2
Ca^{2+}	0	1	0
Mg^{2+}	0	0	1

The effect of each ion is considered by eq. (4) according to a parameter h_i that weights the molality of the ion in the solution.

$$m_{NaCl,equivalent} = \frac{1}{2}\left(\sum_{i=1}^{N} m_i h_i\right) \tag{4}$$

The initial hypothesis for the alterations in Drummond (1981) was that the charge and the amount of the ions have similar impact in γ_{CO_2}. In addition, it assumes that γ_{CO_2} obeys the same dependence on temperature for other salts as NaCl does. This was changed the form of eq. (4) to account for effects such as ionic radius and other properties difficult to include into the model. As such, the ion charge just serves as initial guess for the optimization algorithm to find the value of h_i.

The parameters were adjusted using seven different MATLAB® commands to compare their convergence speed and ascertain the final value. The algorithm that was most successful for minimizing the Least Sum of Squared Errors (LSE) was the hybrid Particle Swarm Optimization (PSO) and interior point, but it is also the most time consuming (~10 s), as it took >17500 objective function evaluations. On the other hand, the SIMPLEX of the MATLAB® command *fminsearch* was the fastest (<< 1s).

All algorithms used in this work are included in MATLAB® Global Optimization Toolbox™ or Optimization Toolbox™. Moreover, a stochastic algorithm (PSO) was used to ensure a global minimum. The non-default settings of each algorithm were FuctionTolerance, which was set to 10^{-8} and StepTolerance, set to 10^{-10}. The deterministic algorithms were one applied more time at these settings after it converged to assure the best results. The initial guess for all deterministic algorithms was 2 for each parameter. In addition, the PSO used a particle swarm size of 500 in the search region of [0.1 3] and does not need an initial guess. The objective function is shown in eq. (5).

$$f_{obj} = \sum_{i=1}^{n_{meas}} \left(m_{CO_2,meas} - m_{CO_2,,model}\right)^2 \tag{5}$$

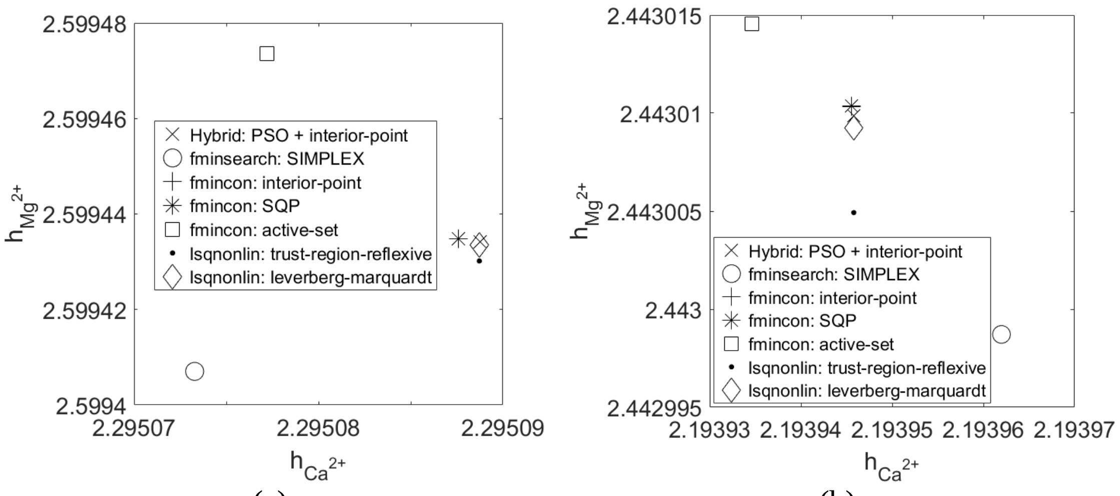
Results and discussion

The model was trained with 99 data points taken from [3,10] and validated against 84 data points taken from [6,11]. These authors performed experiments to determine the content of CO_2 in solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$. The results are summarized in Table 2. Later, the validation data was combined with the training dataset to reduce the confidence interval (CI) for the parameters, as shown in Figure 1.

Table 2 General information and results for each parameter estimation procedure

Dataset used for training	First adjustment	Second adjustment
Liu et al. (2011) [3]	✓	✓
Tong et al. (2013) [10]	✓	✓
Prutton and Savage (1945) [6]		✓
Zhao et al. (2015) [11]		✓
LSE for the best fit (PSO+ interior point)	1.208	1.681
Number of measurements (n_{meas})	99	183
Number of parameters (n_{par})	2	
$h_{Ca^{2+}}$ with significance level $\alpha = 5\%$	2.2951±0.4414	2.1939±0.1940
$h_{Mg^{2+}}$ with significance level $\alpha = 5\%$	2.5994±0.5646	2.4430±0.3563

The quality of Modified Drummond (2018) is shown in Figure 2 also comparing the results with the literature [1,7,9]. As can be seen, the new model outperformed the others in mild temperatures and low pressures (< 200 bar), even when preserving the original structure of Drummond (1981). In addition, Table 3 shows validation for h_{MgCl_2}.



(a) (b)

Figure 1 Results for (a) first adjustment and (b) second adjustment.

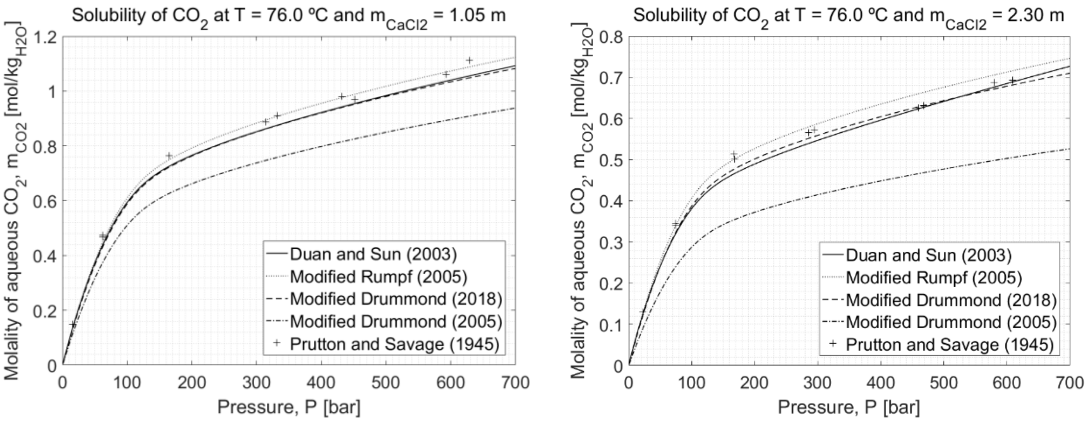


Figure 2 Validation of the modified Drummond (2018) for the first adjustment – $CaCl_2$.

Table 3 Validation of the modified Drummond (2018) at P = 150 bar – $MgCl_2$

T [K]	m_{MgCl_2} [mol/kgH$_2$O]	m_{CO_2} [mol/kgH$_2$O]			Error M1 (%)	Error M2 (%)
		Measured	Model from 1st adjustment	Model from 2nd adjustment		
323	0.333	1.071	1.041	1.047	2.8	2.2
323	0.667	0.961	0.896	0.906	6.7	5.7
323	1.000	0.834	0.777	0.789	6.8	5.4
323	1.333	0.743	0.676	0.689	9.0	7.2
323	1.667	0.671	0.589	0.603	12.3	10.1
323	2.000	0.609	0.513	0.528	15.7	13.3
373	0.333	0.875	0.846	0.850	3.3	2.8
373	0.667	0.767	0.743	0.749	3.2	2.3
373	1.000	0.664	0.591	0.669	10.9	-0.7
373	1.333	0.594	0.531	0.600	10.7	-1.1
373	1.667	0.533	0.531	0.540	0.5	-1.4
373	2.000	0.483	0.477	0.487	1.3	-0.9

The model tends to underestimate the value for the experimental molality of CO_2, which is demonstrated in Figure 3. This is a consequence from preserving the parameters originally estimated by Drummond (1981) and setting $h_{Na^+} = h_{Cl^-} = 1$.

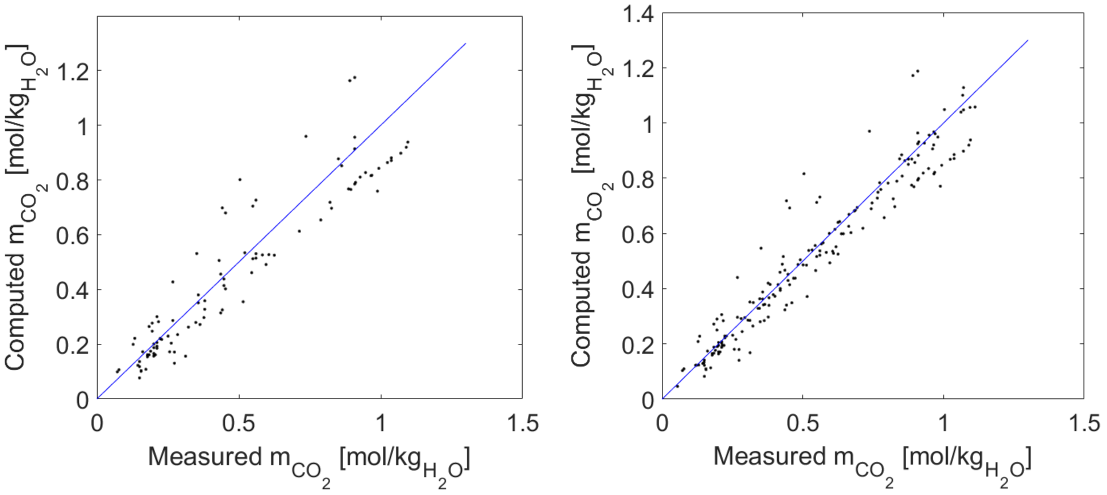


Figure 3 Comparison between model and experimental results for (a) first adjustment and (b) second adjustment. The algorithm used was PSO + interior point.

The covariance matrix was obtained using the approximation given in eq. (6), where the Hessian matrix is computed using a central differencing scheme of second order (CDS-2). The objective function must be redefined from eq. (5) to eq. (7) to use this equation, where the Mean Sum of Squared Errors (MSE) is computed from eq. (8). In this setting, the MSE value serves as an estimation of the variance of the experimental points. In addition, the least sum of squared errors (LSE) is computed from eq. (9). This approximation has the major advantage that the size of the Hessian matrix does not depend on the number of points, so it can be faster to compute for large datasets [8].

$$C \cong 2H_a^{-1} \tag{6}$$

$$f_{obj,aux} = \sum_{i=1}^{n_{meas}} \frac{\left(m_{CO_2,meas} - m_{CO_2,,model}\right)^2}{MSE} \tag{7}$$

$$MSE = \frac{LSE}{n_{meas} - n_{par}} \tag{8}$$

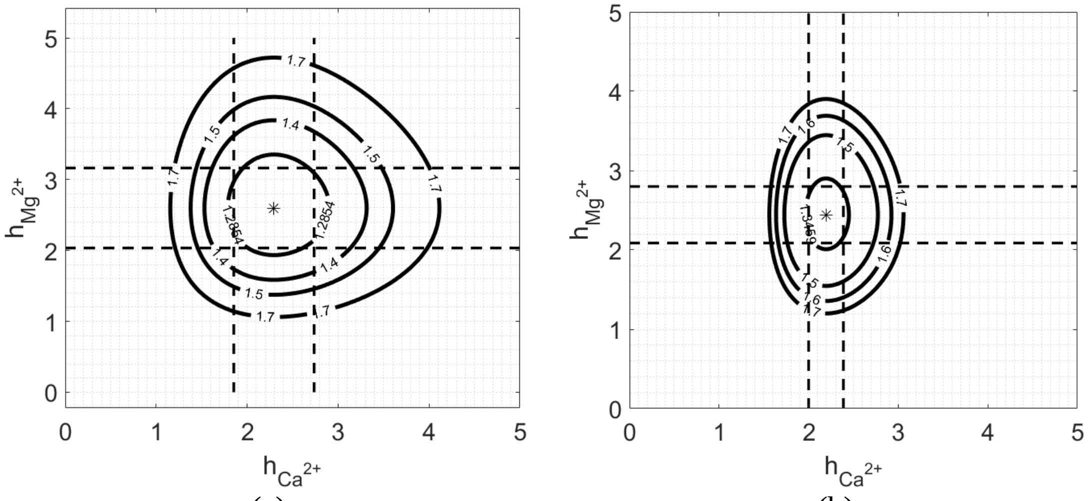
$$LSE = \min\left(f_{obj}(h_i)\right) = \min(SSE) \tag{9}$$

The individual confidence interval (CI) for each parameter is obtained using eq. (10) using the Student t-distribution, retrieved from the MATLAB® command *tinv*.

$$h_i \pm t_{\left(1-\frac{\alpha}{2},n_{meas}-n_{par}\right)}\sqrt{C_{jj}} \tag{10}$$

The joint confidence region is determined by the area that satisfies eq. (11), where F_{value} is retrieved from the F distribution by the MATLAB® command *finv*. The resulting region is presented in Figure 4, where the boundary is 1.2854 and 1.3459 for the first and second adjustment, respectively.

$$SSE \leq LSE\left(1+\frac{n_{par}}{n_{meas}-n_{par}}F_{value_{\left(1-\alpha,n_{par},n_{meas}-n_{par}\right)}}\right) \tag{11}$$



(a) (b)

Figure 4 Joint confidence region for the (a) first adjustment and (b) second adjustment.

The solubility model

Spycher et al. (2005) [9] developed a solubility model of CO_2 in a synthetic brine made of chloride salts and tested their model in single-salt solutions of NaCl or $CaCl_2$.

In short, the hypotheses of the model are: (1) the modified Redlich-Kwong EoS represents the vapor phase well, (2) ions and salts are non-volatile, (3) the H_2O content in the vapor phase is negligible, (4) classical mixing rules capture the correct mixture behavior, (5) the activity of water is close to unity and (6) all inorganic carbon is CO_2.

Classical mixing rules for the intermolecular attraction parameter $a_{RK,mix}$ and the volume parameter $b_{RK,mix}$ yield a_{RK,CO_2} and b_{RK,CO_2}. The parameters from the modified Redlich-Kwong equation of state (EoS) take the form of eq. (12) to (15) [9].

$$a_{RK,CO_2} = 7.54 \times 10^7 - 4.13 \times 10^4 T \text{ valid for } 283\ K < T < 380\ K \tag{12}$$

$$a_{RK,H_2O-CO_2} = 7.89 \times 10^7 \text{ bar } cm^6\ K^{0.5} mol^{-2} \tag{13}$$

$$b_{RK,CO_2} = 27.80\ cm^3/mol \tag{14}$$

$$b_{RK,H_2O} = 18.18\ cm^3/mol \tag{15}$$

The solution of the modified Redlich-Kwong EoS determines the molar volume of the H_2O-rich phase and the CO_2-rich phase. The root corresponding to the stable phase should be selected [9] and inserted in eq. (16) to compute the fugacity coefficient of CO_2 and H_2O (ϕ_i), where λ denotes all chemical species other than i that are present in the vapor phase. Although there are numerical procedures to solve cubic EoS, the analytical approach is computationally faster and much simpler [5]. Despite well documented, the analytical solution is often overlooked, but is recommended in this case.

$$
\begin{aligned}
\ln(\phi_i) = ln\left(\frac{V_{mix}}{V_{mix} - b_{RK,mix}}\right) + \left(\frac{b_{RK,i}}{V_{mix} - b_{RK,mix}}\right) \\
- \left(\frac{2\sum_{i=1}^{NC} y_i a_{RK,\lambda-i}}{RT^{1.5} b_{RK,mix}}\right) ln\left(\frac{V_{mix} + b_{RK,mix}}{V_{mix}}\right) \\
+ \left(\frac{a_{RK,mix} b_{RK,i}}{RT^{1.5} b_{RK,mix}^2}\right)\left[ln\left(\frac{V_{mix} + b_{RK,mix}}{V_{mix}}\right)\right. \\
\left. - \left(\frac{b_{RK,mix}}{V_{mix} + b_{RK,mix}}\right)\right] - ln\left(\frac{P_{eq} V_{mix}}{RT}\right)
\end{aligned}
\tag{16}
$$

Values of Henry's law constants for CO2 in water $K_{H_2O,T,P}$ and $K_{CO_2,T,P}$ vary according to a function of temperature (expressed in °C), as in eq. (17) to (19) [9].

$$
\begin{gathered}
log\left(K_{H_2O,T,P_{ref}}\right) = -2.209 + 0.03097\,T - 0.0001098\,T^2 + 2.048 \times 10^{-7}\,T^3 \\
\text{valid for } 10\,°C < T < \ 110\,°C
\end{gathered}
\tag{17}
$$

$$
\begin{gathered}
log\left(K_{CO_{2(g)},T,P_{ref}}\right) = \ 1.189 + 0.001304\,T + 5.446 \times 10^{-5}\,T^2 \\
\text{valid for } 12\,°C < T < \ 110\,°C
\end{gathered}
\tag{18}
$$

$$
\begin{gathered}
log\left(K_{CO_{2(l)},T,P_{ref}}\right) = 1.169 + 0.01368\,T - 5.380 \times \ 10^{-5}\,T^2 \\
\text{valid for } 12\,°C < T < \ 31\,°C
\end{gathered}
\tag{19}
$$

The selection of the value of $K_{CO_2,T,P_{ref}}$ follows eq. (20) and (21).

$$\text{If } T < 31°\text{C } and\ V_{mix} < 94 \text{ cm}^3 \rightarrow K_{H_2O,T,P_{ref}} = K_{CO_{2(l)},T,P_{ref}} \tag{20}$$

$$Otherwise\ K_{H_2O,T,P_{ref}} = K_{CO_{2(g)},T,P_{ref}} \tag{21}$$

The properties of the system were lumped and arranged in the form of A and B as in equations (22) and (23).The averaged partial molar volumes over the range of the model, i.e.the P-T grid of 1-601 bar and 280-380 K, are given in eq. (24) and (25).

$$A = \frac{K_{H_2O,T,P_{ref}}}{\phi_{H_2O} P_{eq}} exp\left(\frac{\left(P_{eq} - P_{ref}\right)\bar{V}_{H_2O}}{RT}\right) \tag{22}$$

$$B = \frac{\phi_{CO_2} P_{eq}}{55.508\gamma_{x,CO_2} K_{CO_2,T,P_{ref}}} exp\left(-\frac{\left(P_{eq} - P_{ref}\right)\bar{V}_{CO_2}}{RT}\right) \tag{23}$$

$$\bar{V}_{H_2O} = 18.1\ cm^3/mol \tag{24}$$

$$\bar{V}_{CO_2} = 32.6\ cm^3/mol \tag{25}$$

Finally, the system is solved using eq. (26) and (27), while eq. (28) converts the molar fraction of CO2 in the H2O-rich phase (x_{CO_2}) to molality of CO2 (m_{CO_2}).

$$y_{H_2O} = \frac{(1 - B)55.508}{[(1/A) - B]\left(\sum \nu_{tot,k} m_k + 55.508\right) + \left(\sum \nu_{tot,k} m_k\right)B} \tag{26}$$

$$x_{CO_2} = B\left(1 - y_{H_2O}\right) \tag{27}$$

$$m_{CO_2} = \frac{x_{CO_2}.\left(\sum \nu_{tot,k} m_k + 55.508\right)}{\left(1 - x_{CO_2}\right)} \tag{28}$$

Conclusion

A CO_2 activity model was developed for brines of chloride salts and tested for $CaCl_2$ and $MgCl_2$. All algorithms are in agreement for both the adjustments. Comparison with experimental results show the relative deviation is about 9% for validation data. Also, a cation with greater charge density seems to imply in a stronger salting-out effect.

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