Lawrence Berkeley National Laboratory
LBL Publications

Title

A Thermodynamic Model For Mutual Solubility Of Water And CO2 In Brines

Permalink

https://escholarship.org/uc/item/2fv6k5rp

Authors

Spycher, Nicolas
Pruess, Karsten
Moridis, George

Publication Date

2004-06-25

A THERMODYNAMIC MODEL FOR MUTUAL SOLUBILITY OF WATER AND CO$_2$ IN BRINES

Nicolas Spycher[*], Karsten Pruess, George Moridis

Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720

Abstract

Modeling of CO$_2$ disposal into saline formations requires accurate formulation for the PVT properties and mutual solubility of CO$_2$ and water as a function of temperature, pressure and salinity. We have previously developed a numerically efficient thermodynamic model for phase partitioning in the CO$_2$-H$_2$O system without salinity. Our formulation included provisions to deal with the non-ideality of CO$_2$ at near-critical conditions and was shown to provide an excellent match to experimental data in the range 12–100°C and up to 600 bar. The present paper reports some results obtained by extending this formulation to account for dissolved salts in the aqueous phase. Our main focus is on the partitioning of CO$_2$ and H$_2$O components between the different fluid phases.

Introduction

Evaluating the feasibility of CO$_2$ geologic sequestration requires intensive numerical simulations of multiphase fluid flow. These simulations require the calculation of pressure-temperature-composition (P-T-X) data for mixtures of CO$_2$ and H$_2$O under moderate pressures and temperatures. A non-iterative approach was developed previously [1] to compute the mutual solubility of pure H$_2$O and CO$_2$ in a temperature and pressure range most relevant to the geologic sequestration of CO$_2$. The method was intended primarily for efficient fluid-flow simulations. For application to real systems, we extended this solubility model to include moderately saline solutions up to ionic strengths of about 6 molal. This was accomplished by including, into the original formulation, activity coefficients for aqueous CO$_2$ derived from several literature sources, primarily for NaCl solutions [2]. Here, we report preliminary results obtained by combining our solubility model [1] with the activity coefficient formulation developed by [3] to compute, in a non-iterative manner, the solubility of CO$_2$ in NaCl and CaCl$_2$ solutions, as well as the H$_2$O solubility in the compressed-gas phase at equilibrium with these solutions.

Solubility Model

The basic solubility model for the pure components is presented in detail in [1]. This model was developed based on equating chemical potentials in the gas and aqueous phases, and using a modified Redlich-Kwong (RK) equation of state to calculate fugacity coefficients of CO$_2$ and H$_2$O in the compressed gas phase. The mixing rules implemented in this model have a standard form but assume infinite H$_2$O dilution in the CO$_2$-rich phase, allowing the use of a non-iterative algorithm for computing mutual solubilities at given pressures and temperatures. The model was fitted to a large number of published experimental data on the mutual solubility of CO$_2$ and H$_2$O (403 data points) to yield RK interaction parameters and equilibrium solubility constants for liquid and gaseous CO$_2$.

The basic solubility model was extended using activity coefficient expressions for aqueous CO$_2$ [3]. These authors presented a model to compute the solubility of CO$_2$ in electrolyte solutions covering a wide P-T range (0–2000 bar and 0–260°C). Their solubility model, however, relies on a complex virial EOS that needs to be solved iteratively and, therefore, is inefficient for implementation into numerical flow simulations. However, the activity coefficient expressions and parameters reported by these authors [3] can be combined with our solubility model [1] as follows. Because of various assumptions made by [3], the activity coefficients from their model are not "true" activity coefficients (in a thermodynamic sense) but yield the quantity $\gamma^* = m_o/m$, where m_o is the CO$_2$ molality in pure water and m the molality in saline water (at the same given P and T). We can thus use our non-iterative model to compute m_o (using Equations 13 and 14 from [1]), then compute the CO$_2$ solubility in saline solutions as:

$$m = m_o/\gamma^* \qquad (1)$$

---

[*]Corresponding author: Tel. (510) 495-2388, Fax. (510) 486-6115, E-mail: nspycher@lbl.gov

Knowing the CO_2 solubility, the mole fraction of H_2O in the gas phase (y_{H_2O}) is then computed as:

$$y_{H2O} = A\,(1 - x_{CO2} - x_{salt})\qquad\qquad(2)$$

where x_{CO2} and x_{salt} are the mole fractions of aqueous CO_2 and dissolved salt, respectively, on the basis of a fully ionized salt, and A is a parameter defined by Equation (11) in [1]. More details on this approach are being reported in [2].

Results

Our extended model yields CO_2 solubilities in NaCl and $CaCl_2$ solutions with an accuracy comparable to that reported by [3] but without recourse to an iterative procedure. CO_2 solubilities computed using our extended model at 30, 60, and 90°C and 0–4 m NaCl differ from those computed by [3] by a root-mean-square error (RMSE) < 2% (Figure 1). Comparisons with experimental data for NaCl and $CaCl_2$ solutions (Figure 2) yield an RMSE < 7%. It should be noted that the activity coefficient model [3] relies on a fit of a large number of experimental data for both NaCl and $CaCl_2$ solutions covering a wide P-T range, but lacking points for NaCl solutions at temperatures < ~100°C and pressures > ~100 bar. Therefore, for NaCl solutions, the model cannot be tested against experimental data at pressures > ~100 bar. However, results for $CaCl_2$ solutions to pressures > 600 bar are quite good (Figure 2b).

Conclusion

Many CO_2-H_2O solubility models have been published in the literature. However, these models either do not cover our entire P-T range of interest, or involve complex correlations requiring an iterative solution. The non-iterative procedure developed in [1], and extended here for saline solutions, reproduces experimental solubilities with sufficient accuracy for the study of geologic CO_2 disposal and enough simplicity to avoid degrading the performance of numerical fluid-flow simulations.

Acknowledgments

References

1. Spycher, N., Pruess, K., Ennis-King, J. 2003. CO_2-H_2O mixtures in the geological sequestration of CO_2. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar. *Geochimica Cosmochimica Acta* 67, 3015-3031
2. Spycher, N., and Pruess, K. 2004. (In Preparation).
3. Duan, Z., Sun, R., 2003. An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 257 to 533 K and from 0 to 2000 bar. *Chemical Geology* 193, 257–271
4. Rumpf, B., Nicolaisen, H., Ocal, C., Maurer, G., 1994. Solubility of carbon dioxide in aqueous solutions of sodium chloride: experimental results and correlation. *J. Solution Chem.* 23, 431–448
5. Prutton, C.F., and Savage, R.L., 1945. The solubility of carbon dioxide in calcium chloride-water solutions at 75, 100, 120°C and high pressures. *J. Am. Chem. Soc.* 67, 1550–1554
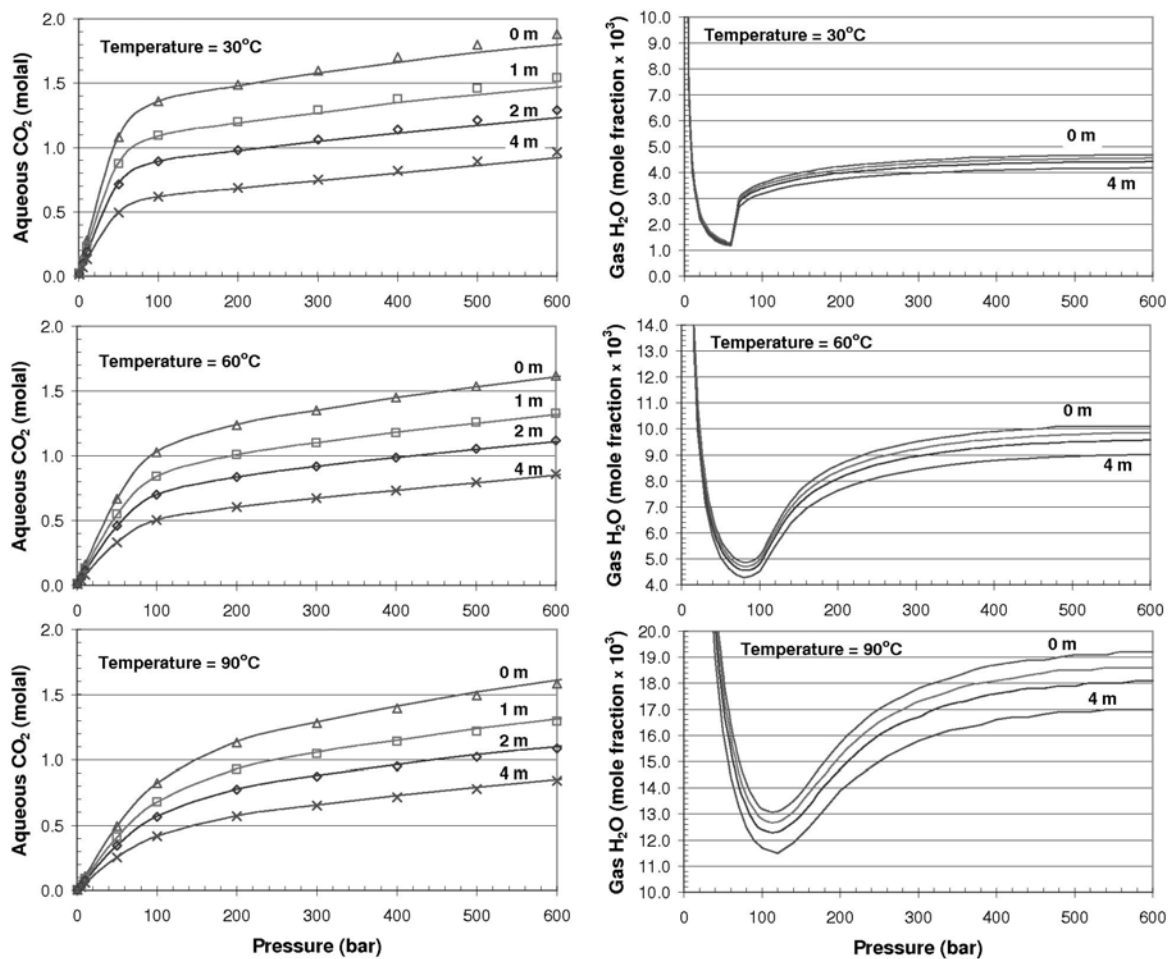
Figure 1. Predicted mutual solubilities of CO_2 and H_2O (solid lines) and CO_2 solubilities computed by [3] at 1, 2, 3, and 4 m NaCl (symbols), as a function of pressure and temperature.
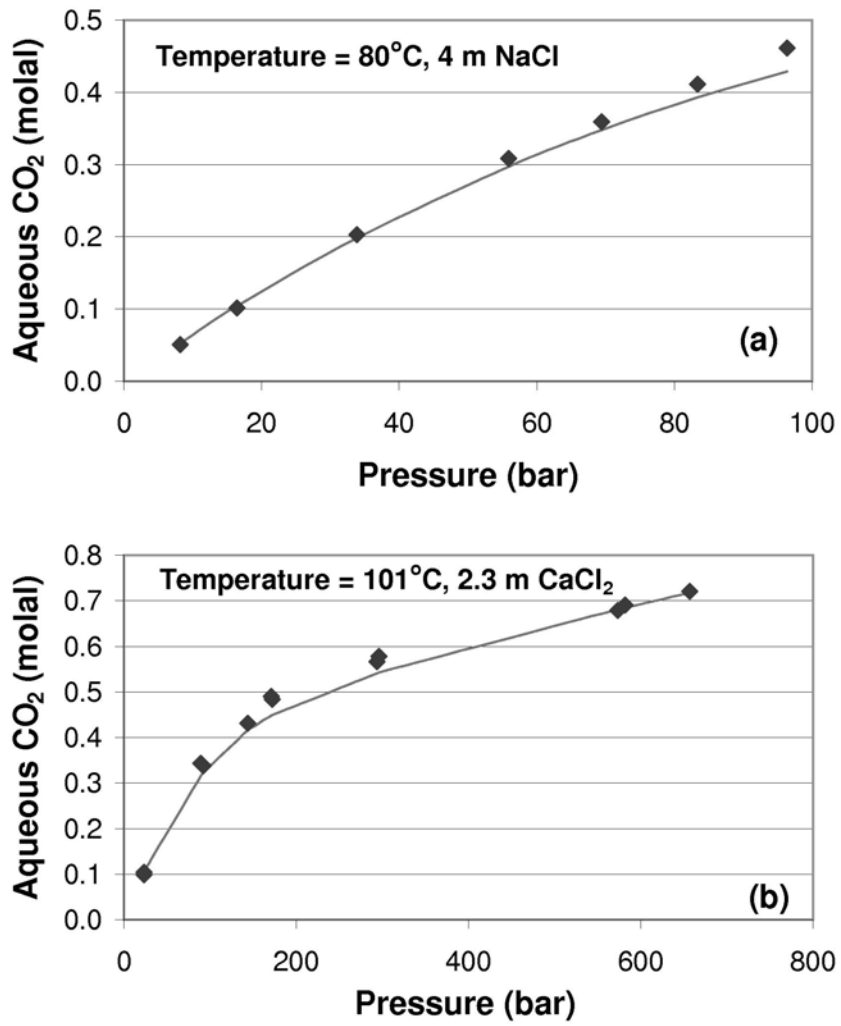
Figure 2. Predicted solubility of CO_2 (solid lines) and experimental data (symbols) as a function of pressure reported at: a) 80°C and 4 m NaCl [4] and b) 101°C and 2.3 m $CaCl_2$ [5].