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A THERMODYNAMIC MODEL FOR MUTUAL SOLUBILITY OF WATER AND CO₂ IN BRINES

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Abstract

Modeling of CO₂ disposal into saline formations requires accurate formulation for the PVT properties and mutual solubility of CO₂ and water as a function of temperature, pressure and salinity. We have previously developed a numerically efficient thermodynamic model for phase partitioning in the CO₂-H₂O system without salinity. Our formulation included provisions to deal with the non-ideality of CO₂ 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 CO₂ and H₂O components between the different fluid phases.

Introduction

Evaluating the feasibility of CO₂ 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 CO₂ and H₂O under moderate pressures and temperatures. A non-iterative approach was developed previously [1] to compute the mutual solubility 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 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 CO₂ 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 CO₂ in NaCl and CaCl₂ solutions, as well as the H₂O 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 CO₂ and H₂O in the compressed gas phase. The mixing rules implemented in this model have a standard form but assume infinite H₂O dilution in the CO₂-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 CO₂ and H₂O (403 data points) to yield RK interaction parameters and equilibrium solubility constants for liquid and gaseous CO₂.

The basic solubility model was extended using activity coefficient expressions for aqueous CO₂ [3]. These authors presented a model to compute the solubility of CO₂ 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 CO₂ 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 CO₂ solubility in saline solutions as:

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

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Knowing the CO₂ solubility, the mole fraction of H₂O in the gas phase ($y_{\text{H}_2\text{O}}$) is then computed as:

$$y_{\text{H}_2\text{O}} = A (1 - x_{\text{CO}_2} - x_{\text{salt}}) \quad (2)$$

where x_{CO_2} and x_{salt} are the mole fractions of aqueous CO₂ 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 CO₂ solubilities in NaCl and CaCl₂ solutions with an accuracy comparable to that reported by [3] but without recourse to an iterative procedure. CO₂ 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 CaCl₂ 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 CaCl₂ 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 CaCl₂ solutions to pressures > 600 bar are quite good (Figure 2b).

Conclusion

Many CO₂-H₂O 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 CO₂ disposal and enough simplicity to avoid degrading the performance of numerical fluid-flow simulations.

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Figure 1. Predicted mutual solubilities of CO₂ and H₂O (solid lines) and CO₂ 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 CO₂ (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 CaCl₂ [5].