

# **Review of the Thermodynamic Properties and their Prediction Using an Equation of State for the System CO<sub>2</sub>/H<sub>2</sub>O/Electrolyte Mixtures**

By

Ioannis N. Tsimpanogiannis, Rajesh Pawar, James W. Carey, and Peter C. Lichtner  
Hydrology, Geochemistry and Geology Group, EES-6,  
Los Alamos National Laboratory, Los Alamos, NM 87545

## **ABSTRACT**

The feasibility of carbon dioxide (CO<sub>2</sub>) sequestration by methods such as oceanic disposal, injection into oil reservoirs/saline aquifers, chemical capture, etc., depends, in part, on knowledge of the chemical interactions between CO<sub>2</sub>-rich and H<sub>2</sub>O-rich phases. In this paper we provide an overview of the literature on the experimental and modeling studies performed on the highly non-ideal CO<sub>2</sub>/H<sub>2</sub>O/electrolytes mixture. The goal of this study is to evaluate the accuracy of some of the equations of state (EoS) reported in the literature. The importance of EoS-based formulations stems from the fact that they provide us with the ability to predict the amount of CO<sub>2</sub> dissolved in the water-rich phase (which affects the sequestration capacity), and the amount of H<sub>2</sub>O dissolved in the CO<sub>2</sub>-rich phase. The thermodynamic properties considered in this work include densities, the solubility of CO<sub>2</sub> in the water-rich phase, and the solubility of H<sub>2</sub>O in the CO<sub>2</sub>-rich phase. Experimental data over a wide range of pressure (1-1500 bar) and temperature (273-400 K) are included in the study. This range covers most of the possible thermodynamic conditions that may be encountered during geologic or oceanic sequestration of CO<sub>2</sub>. We compare the accuracy of predictions for a number of the existing thermodynamic models with experimental data and examine their behavior outside the parameter range for which they were developed.

## 1. INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) has been identified as a major contributor to the global warming problem. Current estimates of CO<sub>2</sub> in the atmosphere show average levels of 370 ppm, compared to 270 ppm in the pre-industrial revolution era (Barker et al 2003). Due to the seriousness of the problem and the magnitude of the possible effects on the future climate (and thus on everyday human life), a number of studies have been undertaken to investigate possible solutions including the removing and/or disposal of the produced CO<sub>2</sub> [for an extensive list of paper see for example the special issues of *Energy Conversion Management*: vol. 38 (supplement), 1997; vol. 37 (6-8), 1996; vol. 36 (6-9), 1995; vol. 34 (9-11), 1993; vol. 33 (5-8), 1992. Also the special issue of *Waste Management*: vol. 17 (5-6), 1997].

Injection into ocean waters at various depths is one of the proposed methods for CO<sub>2</sub> disposal (see Figure 1). Depending on the injection depth, the density of CO<sub>2</sub> can be lower (CO<sub>2</sub> bubbles will move upwards due to buoyancy forces, as they dissolve), or higher (CO<sub>2</sub> will sink at the ocean-floor forming a pool) than seawater. In the second case, a multitude of interesting phenomena can take place involving chemical reactions (hydrate formation) and phase displacement in the oceanic sediments (CO<sub>2</sub> displacing formation water).

A different method of disposal is injection of supercritical CO<sub>2</sub> into oil reservoirs or saline aquifers (see Figure 1), referred to as geologic sequestration. The oil reservoir can be either depleted (in this case we are interested only in the CO<sub>2</sub> disposal process), or it can be still producing oil (in this case we are interested in enhanced oil recovery in addition to CO<sub>2</sub> sequestration). For both geologic and oceanic sequestration a range of pressures and temperatures are encountered, as well as an aqueous electrolytes phase. Therefore it is necessary to have knowledge of accurate values of thermodynamic and transport properties for the highly non-ideal system CO<sub>2</sub>/H<sub>2</sub>O/electrolytes (NaCl, MgCl<sub>2</sub>, MgSO<sub>4</sub>, CaCl<sub>2</sub>, KCl, etc.) in order to study the feasibility of CO<sub>2</sub> sequestration.

Traditionally during process design, two approaches are followed to obtain values of thermodynamic properties: experimental and predictive. While the experimental approach can yield more accurate values, it is associated with higher costs as well. Some experiments may involve costly and hard to maintain equipment, time-consuming procedures, and extreme physical conditions where the components may not be stable and as a result decompose. On the other hand, the aforementioned problems can be dealt with when using the predictive approach (with variable degrees of accuracy). In the predictive approach a model is built based on theory and using some degree of empirical observations as well, in order provide sufficient accuracy. If the model has a greater theoretical foundation compared to empiricism, then the model is expected to perform better when extrapolating to values outside the range of experimental confirmation. The ultimate test, however, is to validate the model against experimental data.

Equations of State (EoS) have contributed significantly in enhancing our ability to predict various thermodynamic properties. Their number has increased significantly (especially during recent years with the increase of computational power), since van der Waals proposed his well-celebrated EoS. A detailed review of EoS is beyond the scope of this work. However, recent reviews of EoS can be found in Valderama (2003) and Wei and Sadus (2000). Among the most popular EoS, are the cubic EoS (termed cubic because they can be cast in the form of a 3<sup>rd</sup> degree polynomial in the volume or compressibility factor) due to their simplicity and accuracy (an analytical solution can be found for 3<sup>rd</sup> degree polynomials).

It is the purpose of this work to examine a number of cubic and non-cubic equations of state for their performance to predict fluid properties for the highly non-ideal system CO<sub>2</sub>/H<sub>2</sub>O/electrolytes, including the mole fraction of dissolved CO<sub>2</sub> in the water-rich phase, the mole fraction of H<sub>2</sub>O dissolved in the carbon dioxide-rich phase, and phases densities. The remainder of the paper is organized as follows: first the approach taken in this work is described, followed by a presentation of a comparison of the different EoS considered.

## 2. APPROACH

Consider injection of CO<sub>2</sub> into a system of H<sub>2</sub>O/electrolytes. For the problem of interest we will assume that pressure,  $P$ , and temperature,  $T$ , are fixed by the surrounding environment (hydrostatic pressure, geothermal gradient). To calculate the amount of dissolved CO<sub>2</sub> in the H<sub>2</sub>O-rich phase and the amount of H<sub>2</sub>O dissolved in the CO<sub>2</sub>-rich phase a standard flash calculation (Prausnitz et al. 1999) is performed. Figure 2 depicts the  $P$ - $x$  diagram of isotherms showing the composition of gas and liquid phases in the pure CO<sub>2</sub>/H<sub>2</sub>O system with experimental data from Takenouchi and Kennedy (1964). After examining the literature it turns out that inconsistencies between the various experimental datasets exist, an important issue that needs additional work to resolve the discrepancies. A more detailed discussion about this issue is presented in Spycher et al., (2003), and Duan and Sun, (2003). Note that the red boxes in Figure 2 indicate the range of conditions of interest for this work. Roughly, the main regions of interest are pressures below 1500 bars and temperatures below 400 °C.

A number of cubic and non-cubic equations of state are examined which fall into three different groups. In the first group the researchers follow the approach of modifying the energy parameter,  $a$ , of the attractive term of the EoS. Equations that belong to this group are the Soave (Soave, 1972) modification of the Redlich-Kwong (SRK) EoS, the Peng-Robinson EoS (1979), and the Coquelet et al., (2003) modifications of PR EoS. Stryjek and Vera (1986a, b) modified the Peng-Robinson EoS by adding a component specific parameter in order to improve vapor pressure and density predictions. In order to improve further density predictions Magoulas and Tassios (1992) proposed the volume-translated modifications of PR and van der Waals EoS.

In the second group the PR EoS is used as the basic model and it is coupled with different types of binary interaction coefficients  $k_{ij}$ . Daridon et al., (1993) used a function of  $k_{ij}$  that depends on temperature and composition, while Jarne et al., (2004) used a function of  $k_{ij}$  that depends only on temperature.

In the third group a number of variations of the non-cubic equations of state developed by Duan and coworkers are examined. Duan et al., (1992) proposed a modification to the Lee-Kesler EoS, that can be component specific, thus increasing accuracy, which resulted in a non-cubic EoS. Nieva and Barragan (2003) developed a computer code using the aforementioned model applicable for temperatures above 50 °C. Duan and Sun (2003) proposed a model to incorporate the effect of electrolytes in the range 1bar-1500bar. We also examine the case of using the Duan et al., (1992) model for pure components and calculating the amount of dissolved CO<sub>2</sub> in water using Henry's law (coefficients obtained from Klauda and Sandler, 2000, or Prini et al., 2003).

## 3. RESULTS AND DISCUSSION

In Table 1 we have collected the results for all the different models examined. We report average, maximum and minimum values for the mole fraction deviations of dissolved CO<sub>2</sub> in the

water-rich phase,  $|\Delta x_{CO_2}|$  (%), and H<sub>2</sub>O dissolved in the carbon dioxide-rich phase,  $|\Delta x_{H_2O}|$  (%), for the pure CO<sub>2</sub>/ H<sub>2</sub>O system. The comparisons are between predicted values and experimental data using the database compiled by Spycher et al., (2003). The database contains 281 experimental points from 285K-383K and 1bar-770bar. At the bottom of Figure 3 the mathematical definition of the various deviations is indicated. In Figure 3 the aforementioned deviations are shown as a function of pressure (including all temperatures for which data is available) for the three models with better overall performance than the others. Note that the deviations increase at high pressures for the cubic EoS, as expected, while the Duan and coworkers non-cubic EoS performs well at high pressures but is less satisfactory at lower pressures (approximately less than 10 bars). This result is explainable if we consider the range of data used for the development of the above models. Here, it is worth mentioning that EoS like SRK, PR, t-PR perform relatively well, even though they do not apply to polar or associating (water) fluids.

While for the pure CO<sub>2</sub>/ H<sub>2</sub>O system a vast number of models exist, in the presence of electrolytes the choices are very limited. In this work we report results only for the model proposed by Duan and Sun (2003). The results for the experimental data of Nighswander et al., (1989) are shown in Figure 4 for two isotherms (40 °C and 80 °C) and three different values of NaCl molality. Again, higher deviation is observed for lower pressures.

#### 4. CONCLUSIONS

In this work a number of cubic and non-cubic equations of state were examined for their ability to predict fluid properties, including the mole fraction of dissolved CO<sub>2</sub> in the water-rich phase, the mole fraction of H<sub>2</sub>O dissolved in the carbon dioxide-rich phase, and phase densities for the highly non-ideal system water/carbon dioxide/electrolytes. The following conclusions were reached in this study:

1. Inconsistencies between the various experimental datasets in the literature have been identified, which is an important issue that needs resolution.
2. In general, when increasing the number of parameters used in an EoS, more accurate results are obtained. EoS with component specific parameters tend to perform better (e.g. compare between PR-SV and SRK EoS).
3. The smaller errors in the predictions of  $x_{CO_2}$  compared with  $y_{H_2O}$ , is due to smaller values of  $y_{H_2O}$ .
4. The Duan and Sun (2004) non-cubic EoS provided the most accurate predictions when applied to pressures higher than 10 bar. For lower pressure values, higher deviations were observed and is not that obvious which other EoS performs better.
5. Systematic differences in the observed and calculated values show that improvements in the accuracy of the predictions are required (see for example Figure 4).
6. Additional investigation needs to be undertaken, including but not limited to the effect of interaction parameters  $k_{ij}$  on the considered EoS, examining more refined EoS and/or considering more sophisticated mixing rules (e.g. EoS/G<sup>E</sup> models).
7. Additional experimental work is needed with emphasis on the carbon dioxide-rich phase.

## ACKNOWLEDGEMENTS

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## NOMENCLATURE

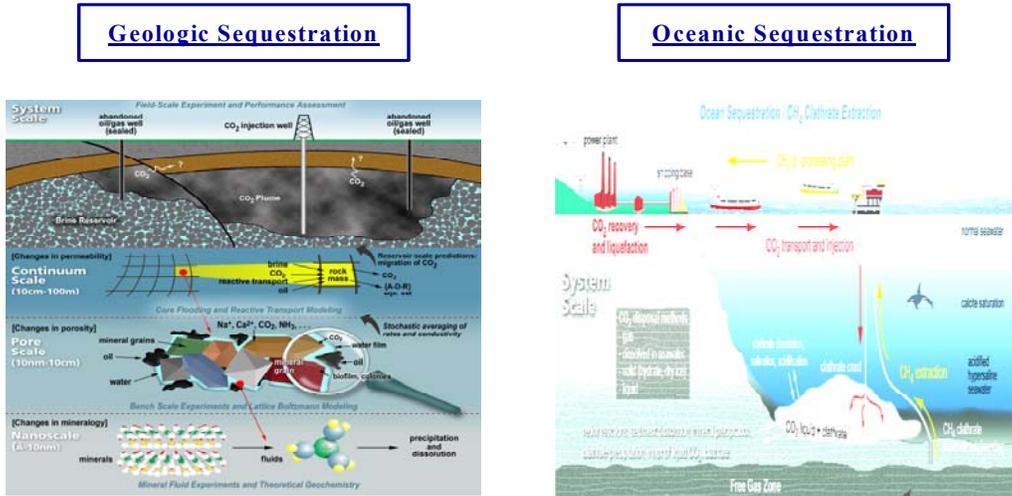
EoS	Equation of State
SRK	Soave-Redlich-Kwong
PR	Peng-Robinson
PR-SV	PR-Stryjek-Vera
t-PR	volume translated PR
t-vdW	volume translated van der Waals
Duan	EoS by Duan et al., 1992
H1	Henry's coefficients from Klauda and Sandler, 2000
H2	Henry's coefficients from Prini et al., 2003

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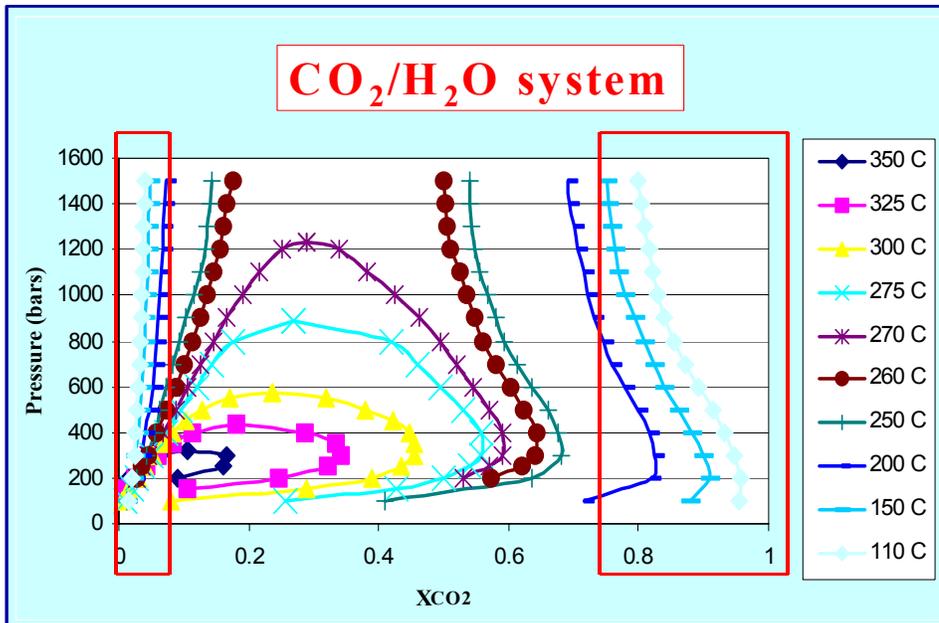
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**Figure 1:** Schematic representation of geologic and oceanic sequestration of carbon dioxide.

## Carbon Dioxide Sequestration Schemes



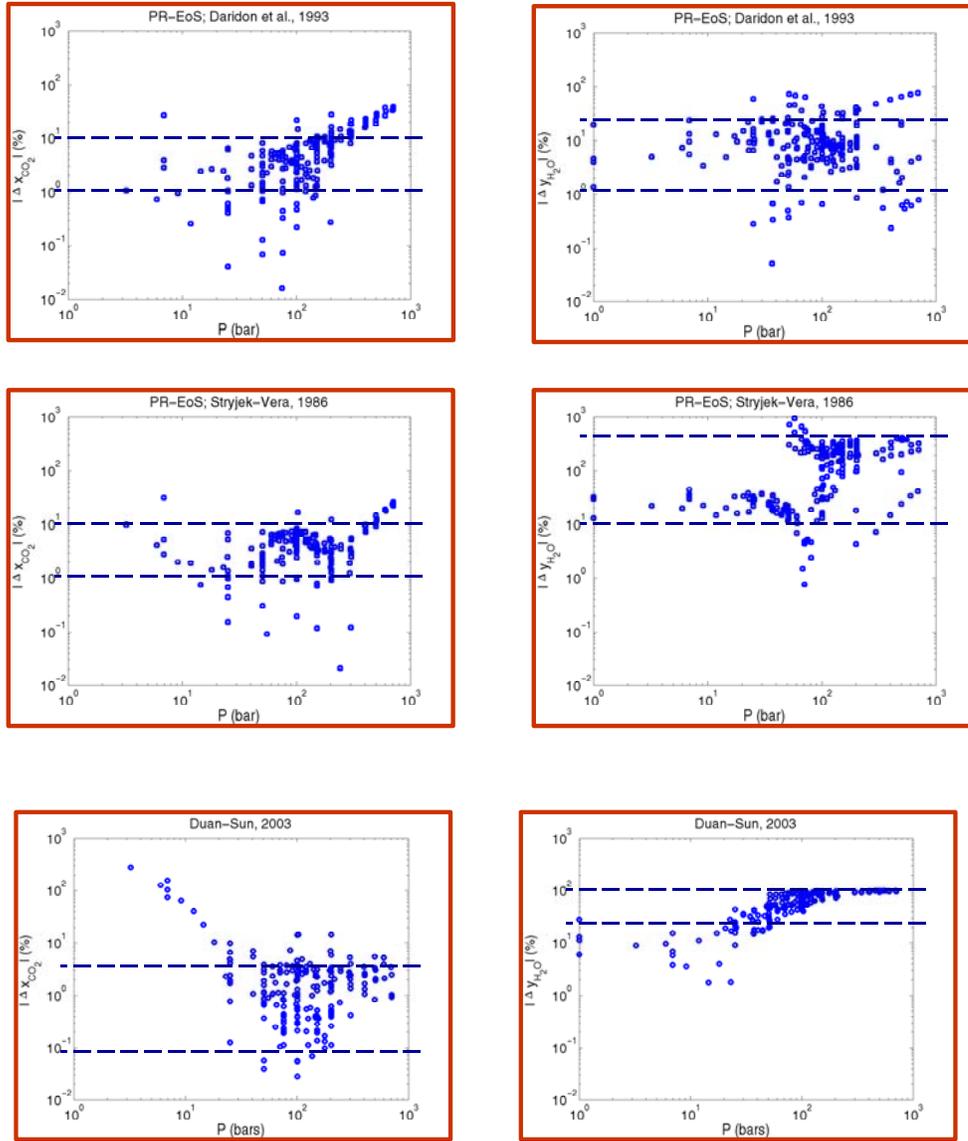
**Figure 2:** P-x diagram of isotherms showing the composition of gas and liquid phases in the pure CO<sub>2</sub>/H<sub>2</sub>O system (experimental data from Takenouchi and Kennedy, 1964). Red squares denote the range of interest.



**Table 1:** Results for comprehensive comparison of various EoS models. Deviations between predicted values and experimental data using the database of Spycher et al., (2003).

Used Model	$\Delta x_{CO_2}$   (%)			$\Delta y_{H_2O}$   (%)		
	aver	max	min	aver	max	min
SRK (1972)	11.54	58.83	0.083	108.3	403.5	0.352
PR-Original (1979)	6.56	35.21	0.022	132.1	504.8	0.259
PR-SV (1986a)	5.17	31.09	0.020	151.2	1318.0	0.751
PR-SV2 (1986b)	5.16	31.08	0.023	151.3	1319.0	0.807
t-PR (1992)	6.60	35.34	0.039	122.9	472.5	0.249
t-vdW (1992)	22.43	127.9	0.002	109.5	404.6	0.775
PR-(Daridon et al., 1993)	7.43	38.72	0.007	12.98	76.37	0.052
PR-(Jarne et al., 2004)	8.29	40.58	0.065	512.6	1457.4	6.354
PR-(Coquelet et al., 2004) $k_{ij}=0.0$	6.37	36.54	0.017	155.9	590.2	0.207
PR-(Coquelet et al., 2004) $k_{ij}=0.1$	7.02	39.43	0.035	52.55	206.4	0.8416
PR-(Coquelet et al., 2004) $k_{ij}=0.2$	7.36	40.72	0.030	11.01	77.04	0.004
Duan-NB Data with $T > 50$ °C	41.40	1024.0	0.648	190.0	4141.0	1.865
Duan-H1	14.72	441.3	0.040	na	na	na
Duan-H2	14.86	438.2	0.108	na	na	na
Duan-Sun (2003) All Data	6.33	277.0	0.028	63.52	98.41	1.768
Duan-Sun (2003) Data with $P > 10$ bar	2.39	40.21	0.028	66.43	98.41	1.768

**Figure 3:** Performance of various EoS models. Mole fraction deviations of dissolved CO<sub>2</sub> in the water-rich phase, and H<sub>2</sub>O dissolved in the carbon dioxide-rich phase as a function of pressure for the pure CO<sub>2</sub>/ H<sub>2</sub>O system. Comparison between predicted values and experimental data using the database of Spycher et al., (2003).



$$|\Delta x_{CO_2}|(\%) = \left( \frac{100}{N} \right) \sum_{i=1}^N \left| \frac{x_{CO_2}^{exp} - x_{CO_2}^{calc}}{x_{CO_2}^{exp}} \right|_i$$

$$|\Delta y_{H_2O}|(\%) = \left( \frac{100}{N} \right) \sum_{i=1}^N \left| \frac{y_{H_2O}^{exp} - y_{H_2O}^{calc}}{y_{H_2O}^{exp}} \right|_i$$

$N$ : number of experimental data  
*exp*: experimental values  
*calc*: calculated values

**Figure 4:** Comparison between predicted values and experimental data for the system CO<sub>2</sub>/H<sub>2</sub>O/NaCl using the Duan and Sun (2003) non-cubic EoS model (experimental data from Kiepe et al., 2003).

