

## A FULLY NON-ITERATIVE TECHNIQUE FOR PHASE EQUILIBRIUM AND DENSITY CALCULATIONS OF CO<sub>2</sub>+BRINE SYSTEM AND AN EQUATION OF STATE FOR CO<sub>2</sub>

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### **ABSTRACT**

Any mutual solubility or phase equilibrium calculations require iterations in order to attain desired convergence in fugacity measurements from which equilibrium compositions are obtained. In this monograph a fully non-iterative technique is approached for calculating phase equilibrium compositions of CO<sub>2</sub> in brine water and that of H<sub>2</sub>O in CO<sub>2</sub> rich phase. As an essential part of this computations process, an empirical volume explicit Equation of State (EoS) for CO<sub>2</sub> with having only 8 parameters is presented. The volumetric data and calculated results of phase compositions using this EoS are compared with the literature values. They exhibit good agreement with less than 2% deviation. A modified scheme of CO<sub>2</sub>+brine density calculation is also shown. More so, the manner in which this EoS can improve computational efficiency following the non-iterative technique with respect to other EoS's used in petroleum reservoir simulation is illustrated. This shows that the proposed technique can be even more than 1000 times faster than conventional phase equilibrium computations after integrating with numerical simulation of CO<sub>2</sub> flows in reservoir.

### **INTRODUCTION**

It is very well known that CO<sub>2</sub> is the major contributor to the global warming problem. Recent surveys of CO<sub>2</sub> in the atmosphere show average levels of 377 ppm, compared to 280 ppm in the pre-industrial revolution era (late 18<sup>th</sup> century) (Houghton, 2005). The burning of fossil fuels and other anthropogenic activities drive a dramatic increase in the concentration of atmospheric CO<sub>2</sub>. Capturing CO<sub>2</sub> from major sources (like power industries) and its storage in deep geologic formations has been considered as a means to lessen global warming (Ormerod, 1994). Injection into saline aquifers, abandoned oil and gas reservoirs, and

unmineable coal seams are among possible ways for this purpose. Injection into deep saline aquifers provides the highest storage capacity (Piri et al., 2005). This type of aquifers can provide storage capacity of up to 11<sup>13</sup> tons of CO<sub>2</sub> which is enough to store several hundred years of CO<sub>2</sub> emissions (Ormerod, 1994; Orr, 2004; Piri et al., 2005). CO<sub>2</sub> will dissolve over time in the interstitial solution of the aquifer and in some formations it would slowly react with minerals to carbonates, which would lock up the CO<sub>2</sub> permanently. Suitable aquifers would have also a cap rock of low permeability to minimize CO<sub>2</sub> leakage (Portier and Rochelle, 2005).

Predicting the sequestration potential and long term behavior of man-made geologic reservoirs requires computations of pressure, temperature and composition properties of CO<sub>2</sub>+Brine mixtures at depths where temperature is not that high (<100 °C), however, pressure may reach several hundred bar. Thermodynamically, in this range, CO<sub>2</sub>-rich gas or liquid phase and H<sub>2</sub>O-rich liquid phase typically exists. The amount of H<sub>2</sub>O in the CO<sub>2</sub>-rich phase is quite small; it can fairly be approximated as pure CO<sub>2</sub>. On the other hand, H<sub>2</sub>O in the CO<sub>2</sub> rich phase displays very non-ideal mixing behavior (King et al., 1992; Spycher and Reed, 1988; Spycher et al., 2003).

The objective of this study is to develop a fully non-iterative algorithm for phase equilibrium calculations of CO<sub>2</sub>+Brine system for efficient numerical simulations of CO<sub>2</sub> flows. Over the years several theoretical studies of CO<sub>2</sub>+Brine system have been published (Barta and Bradley, 1985; Bowers and Helgeson, 1983; Cramer, 1982; Drummond, 1981; Duan et al., 1992, 1995; Duan and Sun, 2003; Enick and Klara, 1990; Harvey and Prausnitz, 1989; King et al., 1992; Li and Nghiem, 1986; Masoudi et al., 2004; Malinin and Kurovskaya, 1975; Malinin and Savelyeva, 1972; Patel et al., 2001; Nesbitt, 1984; Rumph et al., 1994; Shyu et al., 1997; Soreide and Whitson, 1992; Sorensen et al., 2002; Spycher et al.,

2003; Spycher and Reed, 1988; Zuo and Guo, 1991). These investigations cover elevated temperatures and pressures mostly relevant to the study of hydrothermal systems and fluid inclusions. Like any other phase equilibrium calculations, all the techniques proposed in these investigations require iterations for some property measurements (like vapor/liquid phase volume, fugacity etc.) in order to obtain desired convergence which might not be a big issue for phase equilibrium computations itself, is really cumbersome for numerical flow simulations, however. Spycher et al., (2003) presented an approach to compute mutual solubilities of pure H<sub>2</sub>O and CO<sub>2</sub> in a temperature and pressure most relevant to the geologic sequestration of CO<sub>2</sub>. Later they (Spycher and Pruess, 2005; Spycher and Pruess, 2010) extended their models for moderately saline solutions up to 6M NaCl and for temperature and pressure range 12-300° C, 1-600 bar respectively. The techniques cannot be considered fully non-iterative, unless solving cubic EoS for obtaining CO<sub>2</sub> density (vapor, liquid or supercritical) through built-in function is ignored. In addition, computations of activity coefficients of CO<sub>2</sub> in mole fraction basis are not straight forward. One possible way to avoid solving cubic EoS in non-iterative manner is applying direct techniques like, classical Cardano's method, Nickalls approach (1993), and so forth. However, experiences say that in many cases these direct techniques mislead in finding actual roots, especially of cubic EoS's. Moreover, selection of roots as vapor or liquid volume should be concerned. Another possible way of getting rid of root finding is to obtain an appropriate explicit volumetric correlation or EoS of CO<sub>2</sub> as a function of pressure and temperature. In literature there are numbers of EoS's among which some are generalized (Gottschalk, 2007; Wei and Sados, 2000) or plainly for CO<sub>2</sub> (Diamond and Akinfiev, 2003; Span and Wagner, 1994; Yuanhui et al., 2007), however, none of them are volume explicit so far. Therefore we have shown such type of EoS as an essential part of the proposed algorithm for phase equilibrium and density calculations of CO<sub>2</sub>+brine system.

## **CALCULATIONS PROCEDURES**

The theories and methodologies involved in calculations are discussed in order.

### **Solubility calculations of CO<sub>2</sub> in aqueous phase**

From thermodynamics relations chemical potential of CO<sub>2</sub> in aqueous phase and that in vapor phase can be shown as

$$\begin{aligned}\mu_{\text{CO}_2}^{\text{V}} &= \mu_{\text{CO}_2}^{\text{V}}(0) + RT \ln f_{\text{CO}_2} \\ &= \mu_{\text{CO}_2}^{\text{V}}(0) + RT \ln y_{\text{CO}_2} P + RT \ln \phi_{\text{CO}_2}\end{aligned}\quad (1)$$

where, fugacity  $f = Py\phi$

$$\begin{aligned}\mu_{\text{CO}_2}^{\text{L}} &= \mu_{\text{CO}_2}^{\text{L}}(0) + RT \ln a_{\text{CO}_2} \\ &= \mu_{\text{CO}_2}^{\text{L}}(0) + RT \ln m_{\text{CO}_2} + RT \ln \gamma_{\text{CO}_2}\end{aligned}\quad (2)$$

where, activity  $a = m\gamma$ (molal basis)

As we know at equilibrium,  $\mu_{\text{CO}_2}^{\text{L}} = \mu_{\text{CO}_2}^{\text{V}}$ , from Eqs. (1) and (2) it can be written

$$\ln \frac{y_{\text{CO}_2} P}{m_{\text{CO}_2}} = \frac{\mu_{\text{CO}_2}^{\text{L}}(0) - \mu_{\text{CO}_2}^{\text{V}}(0)}{RT} - \ln \phi_{\text{CO}_2} + \ln \gamma_{\text{CO}_2}\quad (3)$$

In Eq. 3, reference number  $\mu_{\text{CO}_2}^{\text{V}}(0)$  is set to zero. The fugacity coefficient of CO<sub>2</sub> in the vapor phase of CO<sub>2</sub>+H<sub>2</sub>O mixtures changes very negligible from that in pure CO<sub>2</sub> (Duan et al., 1992) and therefore  $\phi_{\text{CO}_2}$  can be calculated from any suitable EoS for pure CO<sub>2</sub>. Our proposed empirical EoS is of the following form

$$V_r = y_0 + \sum_{i=1}^3 a_i e^{-b_i P_r} + c(T_r - T_{r0}) / P_r\quad (4)$$

Here  $V_r$  is the reduced volume related with  $V_r = \frac{V}{V_c}$ .

$V_c$  is not exactly critical volume but defined as

$$V_c = \frac{RT_c}{P_c}. \text{ This EoS has only 8 parameters } (y_0, a_1,$$

$b_1, a_2, b_2, a_3, b_3, c)$  which have to be estimated by the regression of volumetric data of CO<sub>2</sub> within certain temperature and pressure range. For our calculations, parameters that we have predicted are given in Table 1. These parameters have been predicted by the regression of CO<sub>2</sub> volumes within the range 20 – 40 °C and 1 – 400 bar extracted from MIT Carbon Capture and Sequestration Technologies (MIT-CCST)

(<http://sequestration.mit.edu/tools/index.html>). We have used open source SciPy optimization package ([http://www.scipy.org/doc/api\\_docs/SciPy.optimize.minpack.html](http://www.scipy.org/doc/api_docs/SciPy.optimize.minpack.html)) for data regression process.

Finally  $\ln \phi_{\text{CO}_2}$  is computed from the equation (Duan et al., 1992)

$$\begin{aligned}\ln \phi &= Z - 1 - \ln Z + \frac{a_1 + a_2 / T_r^2 + a_3 / T_r^3}{V_r} + \frac{a_4 + a_5 / T_r^2 + a_6 / T_r^3}{2V_r^2} \\ &\quad + \frac{a_7 + a_8 / T_r^2 + a_9 / T_r^3}{4V_r^4} + \frac{a_{10} + a_{11} / T_r^2 + a_{12} / T_r^3}{5V_r^5} + \frac{a_{13}}{2T_r^3 a_{15}} \\ &\quad \times \left[ a_{14} + 1 - (a_{14} + 1 + \frac{a_{15}}{V_r^2}) \times \exp\left(-\frac{a_{15}}{V_r^2}\right) \right]\end{aligned}\quad (5)$$

**Table 1.** Parameters for Eqn. 1 [P in bar, T in K, V in m<sup>3</sup>/mol, supercritical volume 94x10<sup>-6</sup> m<sup>3</sup>/mol].

parameters	subcritical condition	supercritical condition
y <sub>0</sub>	-766.2884	0.1272
a <sub>1</sub>	29.3030	0.0734
b <sub>1</sub>	21.9128	0.5304215
a <sub>2</sub>	8.5773	4.3925x10 <sup>-3</sup>
b <sub>2</sub>	5.3415	44.8821
a <sub>3</sub>	767.7692	5.9221
b <sub>3</sub>	0.0130	4.6914
c	11.7854x10 <sup>-10</sup>	0.7745

Where compressibility factor,

$$Z = \frac{PV_r}{T_r} = 1 + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3 + a_4 + a_5/T_r^2 + a_6/T_r^3}{V_r} + \frac{a_7 + a_8/T_r^2 + a_9/T_r^3 + a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{V_r^2} + \frac{a_{13}}{T_r^3 V_r^2} \left( a_{14} + \frac{a_{15}}{V_r^2} \right) \exp\left( -\frac{a_{15}}{V_r^2} \right) \quad (6)$$

Parameters of Eqs. 5 and 6 are obtained from Duan and Sun (2003). For the sake of calculations of solubility of CO<sub>2</sub> in aqueous phase, mole fraction of CO<sub>2</sub> in vapor phase has been approximated as

$$y_{CO_2} = (P - P_{H_2O}) / P \quad (7)$$

Water saturation pressure  $P_{H_2O}$  is calculated from DIPPR correlations (Daubert and Danner, 1992).

$$P_{H_2O} = \exp\left[ A_1 + A_2 / T + A_3 \ln T + A_4 T^{A_5} \right] \quad (8)$$

This measured  $y_{CO_2}$  will be corrected in later subsection. In order to calculate  $\gamma_{CO_2}$  following functional relations have been used

$$\ln \gamma_{CO_2} = 2(\lambda_{CO_2-Na} m_{Na} + \lambda_{CO_2-Cl} m_{Cl}) + \zeta_{CO_2-Na-Cl} m_{Na} m_{Cl} \quad (9)$$

Values of interaction parameters  $\lambda$ ,  $\zeta$  are taken from Duan and Sun (2003). Substituting Eq. 8 in Eq. 3 reduces to

$$\ln \frac{y_{CO_2} P}{m_{CO_2}} = \frac{\mu_{CO_2}^l(0)}{RT} - \ln \varphi_{CO_2} + 2(\lambda_{CO_2-Na} m_{Na} + \lambda_{CO_2-Cl} m_{Cl}) + \zeta_{CO_2-Na-Cl} m_{Na} m_{Cl} \quad (10)$$

Here the term

$$\frac{\mu_{CO_2}^l(0)}{RT} = c_1 + c_2 T + c_3 / T + c_4 T^2 + c_5 / (630 - T) + c_6 P + c_7 P \ln T + c_8 P / T + c_9 P / (630 - T)^2 + c_{11} T \ln P \quad (11)$$

The same parametric values for  $\lambda$ 's in Eq. 10 reported in Duan and Sun (2003) are used for our calculations. Now every term in right hand sides of Eq. 9 are known, therefore, solubility of CO<sub>2</sub> ( $m_{CO_2}$ ) in molal basis can be computed. This molal CO<sub>2</sub> is converted to mole/mass fraction basis in following manner (Pruess, 2005)

$$x_{CO_2} = m_{CO_2} / (1000 / 18.06 + m + m_{CO_2}) \quad (12)$$

$$X_{CO_2} = m_{CO_2} \times 44.01 / (1000 + m \times 58.44 + m_{CO_2} \times 44.01) \quad (13)$$

### Solubility calculations of H<sub>2</sub>O in CO<sub>2</sub> phase

Spycher and Pruess (2005) developed following equation for  $y_{H_2O}$

$$y_{H_2O} = \frac{(1 - B) 55.508}{(1 / A - B)(v m_{NaCl} + 55.508) + v m_{NaCl} B} \quad (14)$$

$$y_{CO_2} = 1 - y_{H_2O} \quad (15)$$

where

$$A = \frac{K_{H_2O}^0}{\varphi_{H_2O} P} \exp\left( \frac{(P - P_0) \bar{V}_{H_2O}}{RT} \right) \quad (16)$$

and

$$B = \frac{\varphi_{CO_2} P}{55.508 \gamma_{CO_2} K_{CO_2(v)}^0} \exp\left( -\frac{(P - P_0) \bar{V}_{CO_2}}{RT} \right) \quad (17)$$

In Eq. 14, to calculate  $\varphi_{H_2O}$  we have used fugacity expression of H<sub>2</sub>O in CO<sub>2</sub> given by King et al., (1992) where they applied modified form of Redlich-Kwong EoS (1949). For the mixing rules we have assumed  $y_{H_2O} = 0$ , which is very reasonable as discussed earlier. This nullifies all the complexities of the application of cubic or any volume implicit EoS to calculate  $\varphi_{H_2O}$  in iterative manner.

Equilibrium constants  $K_{H_2O}^0$ ,  $K_{CO_2(v)}^0$  and  $K_{CO_2(l)}^0$  are found from the references Spycher and Pruess (2003), and Spycher and Pruess (2010). It is very necessary to note that, at subcritical temperatures and pressures  $K_{CO_2(v)}^0$  has to be replaced by  $K_{CO_2(l)}^0$  if the conditions (1) T < 31.2 °C, and (2)  $V_{CO_2} < 94$  cm<sup>3</sup>/mol are simultaneously met. With necessary

input of NaCl molality ( $m_{NaCl}$ ), and from previous steps taking  $\varphi_{CO_2}$  and  $\gamma_{CO_2}$ , all the terms of right hand side in Eq. (14) are known and therefore mole fraction of H<sub>2</sub>O in CO<sub>2</sub> rich phase  $y_{H_2O}$  can be calculated in a straight forward way.

### **Density calculations**

#### ***Density of H<sub>2</sub>O+CO<sub>2</sub>***

Densities of H<sub>2</sub>O+CO<sub>2</sub> (CO<sub>2</sub> saturated water density) have been measured from very simple correlations developed by Hebach et al., (2004). For above critical density of CO<sub>2</sub> they have presented

$$\rho_{H_2O+CO_2} = l_0 + l_1P + l_2T + l_3P^2 + l_4T^2 \quad (18)$$

and for lower than the critical density with respect to the CO<sub>2</sub> phase the expression is,

$$\rho_{H_2O+CO_2} = g_0 + g_1P + g_2T + g_3P^2 + g_4T^2 + g_5PT + g_6P^3 + g_7T^2P + g_8TP^2 \quad (19)$$

#### ***Density of H<sub>2</sub>O+NaCl***

To determine brine (H<sub>2</sub>O+NaCl) density the correlation published by Anderson et al., (1992) has been implemented. Their correlation can be expressed as (in terms of molar volume)

$$\ln(V_{sat}) = V_0 + V_1\tau^{0.325} + 2V_2\tau^{0.8915} + 3V_3\tau^{0.825} + 4V_4\tau + 5V_5\tau^2 + 6V_6\tau^3 + 7V_7\tau^4 + 8V_8\tau^5 \quad (20)$$

here

$$\tau = 1 - T/T_c(b)$$

$$V_0 = 4.0208 + 3.30x_{NaCl}$$

$$V_1 = -1.9286$$

$$V_2 = -34.214$$

$$V_3 = 20.1$$

$$V_4 = 15.45 - 4.7x_{NaCl}$$

$$V_5 = -1.2059$$

$$V_6 = .63339$$

$$V_7 = 0.0$$

$$V_8 = .47437$$

Finally the volume of compressed fluid is determined by

$$V_{H_2O+NaCl} = V_{sat} [1 + C(P - P_{sat}(b))] \quad (21)$$

where

$$C = \frac{-1.14e^{-6}}{\tau^{1.25} - 5.6x_{NaCl} + 0.005}$$

The unknowns of Eqs. 19 and 20 are  $x_{NaCl}$ ,  $T_c(b)$ , and  $P_{sat}(b)$ . These represent mole fraction of NaCl, critical temperature, and saturated vapor pressure of brine solution, respectively. For any molality ( $m$ ) of NaCl it can be written,

$$x_{NaCl} = m / [1000 / 18.016 + m] \quad (22)$$

and

$$X_{NaCl} = m \times 58.448 / [1000 + m \times 58.448] \quad (23)$$

Battistelli et al., (1997) showed a cubic equation of  $X_{NaCl}$  in terms of  $T_c(b)$  which requires iterations in order to obtain correct  $T_c(b)$ . However experimental data (Sourirajan and Kennedy, 1962; Tanger and Pitzer, 1989; Bischoff and Pitzer, 1989) shows, approximately up to 995 °K,  $T_c(b)$  varies linearly with  $X_{NaCl}$ . Therefore we have used our own linear correlation of the form

$$T_c(b) = 975X_{NaCl} + 373.15 \quad (24)$$

$P_{sat}(b)$  remains same as  $P_{H_2O}$  around up to 405 °K according to the figure ( $P_{sat}(b)$  vs. T) reported by Battistelli et al., (1997). Hence we have used Eq. 8 for  $P_{sat}(b)$ .

#### ***Density of H<sub>2</sub>O+NaCl+CO<sub>2</sub>***

Pruess (2005) showed the following correlation for predicting the density of aqueous phase with dissolved CO<sub>2</sub>

$$\frac{1}{\rho_{aq}} = \frac{1 - X_{CO_2}}{\rho_{H_2O+NaCl}} + \frac{X_{CO_2}}{\rho_{CO_2}} \quad (25)$$

In this equation all quantities on the right hand side are known from previous calculations, and therefore we can easily calculate  $\rho_{aq}$ .

### **RESULTS**

First we will show feasibility tests of our presented EoS (Eq. 4) for CO<sub>2</sub>. Figures 1 and 2 show the comparisons of calculated CO<sub>2</sub> volumes with respect to the data obtained from MIT-CCST (MIT Carbon Capture and Sequestration technology). As seen in Figures 1 and 2, it is clear that our EoS can calculate CO<sub>2</sub> volumes with acceptable accuracy. For any particular data point we have observed deviation is less than 2%. This EoS performs more accurately if the parameters are estimated from isothermal volumetric data ( $T$  and  $T_r$  are constant). In this case, the number of parameters will be reduced to 7.

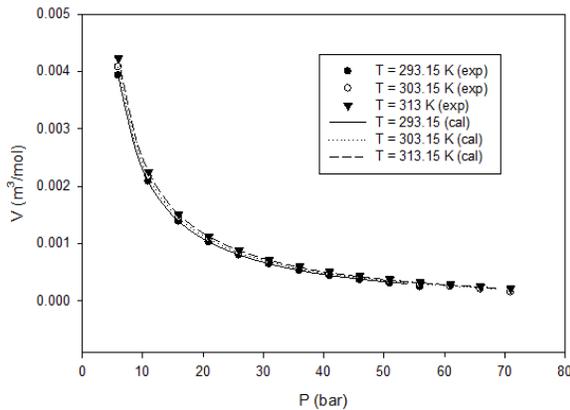
Comparisons of literature isothermal volumetric data and our reproduced values are shown in Appendix A.

These results show average absolute error 0.38% for subcritical region) and 0.0935% for supercritical region).

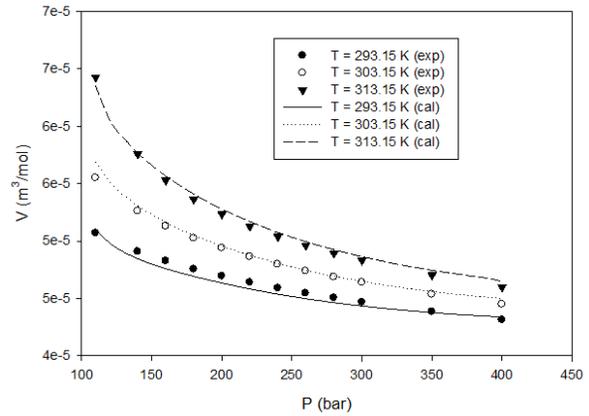
Numerous sources of solubility data of CO<sub>2</sub> in brine are available. However data at low temperatures and high pressures are scant. The data sources are addressed comprehensively in several review works and others (Diamond and Akinfiyev, 2003; Duan and Sun 2003; Kim, 2007; Li and Duan, 2007; Kiepe et al., 2002; Spycher et al., 2003; Spycher and Pruess, 2005; Spycher and Pruess, 2010; Yuanhui et al., 2007). Measured solubility data following our calculations schemes are shown in figures 3 and 4 against experimental values. Our discussed procedures reproduce experimental data close to or within experimental uncertainty. In many cases the experimental data themselves vary among the references at the same temperature and pressure (can be seen in figures 4 and 5). No literature data were found for comparing H<sub>2</sub>O solubility in CO<sub>2</sub> rich phase for saline CO<sub>2</sub>+H<sub>2</sub>O solutions. Therefore figures 5 and 6 show comparisons between calculated and experimental values (for pure CO<sub>2</sub>+H<sub>2</sub>O solutions) along with only predicted values at different salinity levels.

Since we have also presented a slightly different approach of computing brine density, comparisons of literature (Potter and Brown, 1977) and calculated data are also shown in figure 7. In this regard overall deviation is less than 1%.

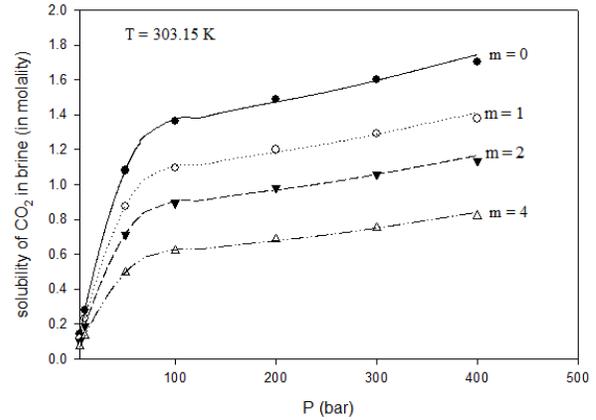
Now we will show how our proposed scheme will save huge computational expenses (cost per CPU time or memory). First we will show comparisons



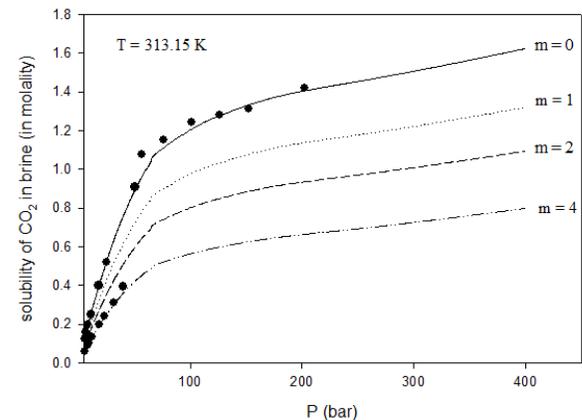
**Fig 1.** Comparison of calculated (by new EoS) CO<sub>2</sub> volume vs. data extracted from MIT-CSST at different temperatures (subcritical condition).



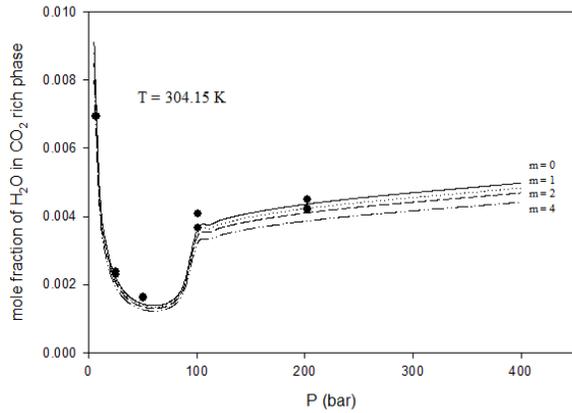
**Fig 2.** Comparison of calculated (by new EoS) CO<sub>2</sub> volume vs. data extracted from MIT-CSST at different temperatures (liquid and supercritical condition).



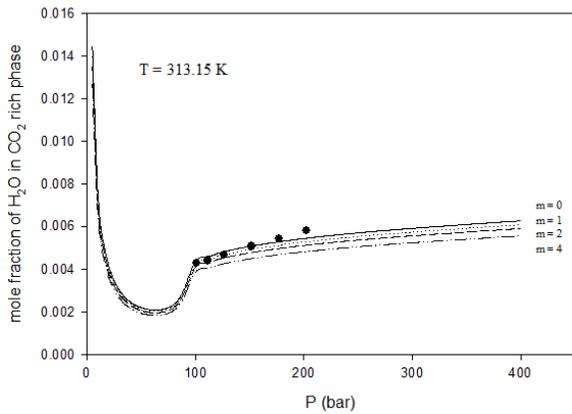
**Fig 3.** CO<sub>2</sub> solubility in brine at different pressures (symbols represent literature data from Ref 17; lines represent calculated values).



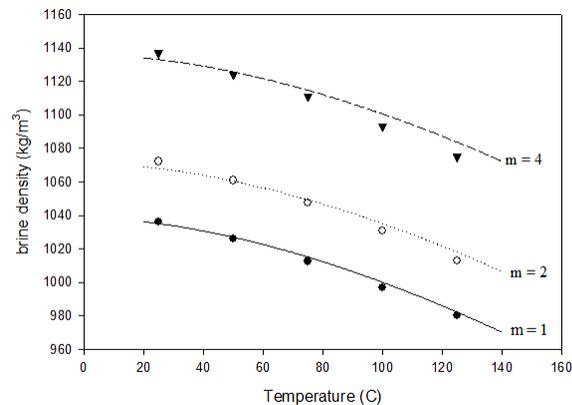
**Fig 4.** CO<sub>2</sub> solubility in brine at different pressures ((symbols represent literature data from Kim, 2007; Rumph et al., 1994; Spycher and Pruess, 2003), lines represent calculated values)).



**Fig 5.** H<sub>2</sub>O solubility in CO<sub>2</sub> rich phase at different pressures (symbols represent literature data from Spycher and Pruess, 2003 for  $m = 0$ ; lines represent calculated values).



**Fig 6.** H<sub>2</sub>O solubility in CO<sub>2</sub> rich phase at different pressures (symbols represent literature data from Spycher and Pruess, 2003 for  $m = 0$ ; lines represent calculated values).



**Fig 7.** Brine densities at different temperatures ((symbols represent literature data from Li and Duan, 2007; lines represent calculated values)).

of computational time of CO<sub>2</sub>+Brine phase equilibrium calculations following the algorithm that we have proposed using our EoS of CO<sub>2</sub> versus others EoS's which are frequently used. In this vein we have chosen Span and Wagner (S-P) (1994), Duan et al. (D et al.) (1992), and Redlich-Kwong (R-K) (1949) EoS's for comparisons. In order to provide concrete example of how our scheme will save a significant amount of computational costs, we have integrated these phase equilibrium and density calculations with the numerical simulation of CO<sub>2</sub> flows in geologic reservoir. This simulation shows how CO<sub>2</sub> plume convects down in saline aquifers over the time period (Lu and Lichtner, 2007). We are developing this in-house simulator and will be released under open access in near future (Carlson and Islam, 2011).

Table 2 shows the comparisons of execution times. Our proposed EoS performs 2.0 to 3.9 times faster phase equilibrium calculation on a notebook of average configuration (like, 3 GB Ram, Dual-core CPU T4500 @ 2.3 GHz). In a fairly high configuration lab machine (like, 11.57 GB Ram and i7-920 @ 2.67 GHz processor), this calculation is 1.1 to 3.4 times faster than others. However, the same calculation makes substantial execution time difference after combining with a reservoir simulator which may involve millions of cell grid calculations and a number of time steps. For a single time step calculation, other volume implicit EoS's make calculation 4.5 to 700.0 times slower with respect to our volume explicit EoS in a Notebook, and in lab machine these timing differences are 7.0 to 900.0 times. As the time stepping is increased in the simulator, these differences become more significant meaning our EoS may perform faster computations by 1000 times.

## CONCLUSION

The algorithm mentioned does not involve any iteration or loop in the complete calculations process, while at the same time accuracy is not compromised. This will provide very helpful tools for designing complex reservoir simulators for which computational timing is extremely important. Our proposed volume explicit EoS for CO<sub>2</sub> is very simple and is comprised of less numbers of parameters compared to others found in literature. Upon estimating parameters, this EoS can reproduce CO<sub>2</sub> volume for given temperature and pressure within very reasonable deviation compared to the datum obtained from other sources. Integrating this scheme with numerical simulator of CO<sub>2</sub> flows can make calculations more than 1000 times faster and therefore will contribute to save huge computations costs.

**Table 2.** Comparisons of execution time

computation time (CPU time in s)																
calculation of phase equilibrium only								after integrating with Simulator								
Notebook*				Lab workstation**				Notebook*				Lab workstation**				
our EoS	S-W	D et al.	R-K	our EoS	S-W	D et al.	R-K	Time steps	our EoS	S-W	D et al.	R-K	our EoS	S-W	D et al.	R-K
0.015	0.059	0.047	0.031	0.0099	0.034	0.012	0.011	1	2.1	1402.9	94.3	9.6	1.1	941.9	15.5	7.1
								120	200.5	162981.1	12201.9	1317.7	102.0	102452.2	1844.4	797.3

\*3 GB Ram, Dual-core CPU T4500 @ 2.3 GHz  
 \*\*11.57 GB, i7-920 CPU @ 2.67 GHz

**Notations:**

- $l$  = liquid phase
- $m$  = molality (mole NaCl per 1000 kg H<sub>2</sub>O)
- $P$  = pressure (bar)
- $P_0$  = reference pressure (1 bar)
- $P_c$  = critical pressure (73.88 bar)
- $P_r$  = reduced pressure ( $P/P_c$ )
- $R$  = universal gas constant (83.14472 bar.cm<sup>3</sup>/mol/K)
- $T$  = temperature (K)
- $T_c$  = critical temperature (304.2 K)
- $T_r$  = reduced temperature ( $T/T_c$ )
- $T_{r0}$  = reference reduced temperature (303.15 K)
- $V$  = vapor phase
- $V$  = volume (cm<sup>3</sup>/mol)
- $V_c$  = critical volume of CO<sub>2</sub>
- $\bar{V}_{H_2O}$  = molar volume of liquid H<sub>2</sub>O (18.1 cm<sup>3</sup>/mol)
- $\bar{V}_{CO_2}$  = molar volume of liquid CO<sub>2</sub> (32.6 cm<sup>3</sup>/mol)
- $x$  = mole fraction in aqueous (H<sub>2</sub>O rich) phase
- $X$  = mass fraction in aqueous (H<sub>2</sub>O rich) phase
- $y$  = mole fraction in vapor (CO<sub>2</sub> rich) phase
- $Y$  = mass fraction in (CO<sub>2</sub> rich) vapor phase
- $\phi$  = fugacity coefficient
- $\rho_{H_2O+CO_2}$  = CO<sub>2</sub> saturated water density (mol/cm<sup>3</sup>)
- $\rho_{H_2O+NaCl}$  = brine density (mol/cm<sup>3</sup>)
- $\nu$  = stoichimetric number (2 for NaCl)
- $\mu$  = chemical potential
- $\mu_{CO_2}^l(0)$  = standard chemical potential of CO<sub>2</sub> in liquid phase in ideal solution of unit molality

- $\mu_{CO_2}^v(0)$  = standard chemical potential of CO<sub>2</sub> in vapor phase in ideal gas when P = 1 bar
- $A_1, A_2, A_3, A_4, A_5$  = constants for DIPPR correlation
- $l_0, l_1, l_3, l_4$  = coefficients of the Eqn 17 taken from Hebach *et al.* (2004)
- $g_0, g_1, g_2, g_3, g_4, g_5, g_6, g_7, g_8$  = coefficients of the equation of 18 taken from Hebach *et al.* (2004).
- aq = aqueous
- Eqn = Equation

**Subscripts**

- sat = saturated
- exp = experimental
- cal = calculated

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**APPENDIX**

Table A1 shows comparative study between literature and calculated CO<sub>2</sub> volumes.

**Table A1:** Comparison of CO<sub>2</sub> volumes extracted from MIT-CSST and the data calculated by our EoS (T = 303.15 K)

P [bar]	V <sub>exp</sub> (MIT-CSST) [m <sup>3</sup> /mol]	V <sub>cal</sub> [m <sup>3</sup> /mol]	average absolute error (AAE*) (%)	Parameters of Eq. 4
5.0000 10.0000 15.0000 20.0000 25.0000 30.0000 35.0000 40.0000 45.0000 50.0000 55.0000 60.0000 65.0000 70.0000	4.9178e-3 2.3961e-3 1.5541e-3 1.1319e-3 8.7742e-4 7.0661e-4 5.8345e-4 4.8982e-4 4.1558e-4 3.5454e-4 3.0250e-4 2.5625e-4 2.1243e-4 1.6348e-4	4.9177e-3 2.3965e-3 1.5526e-3 1.1342e-3 8.7764e-4 7.0497e-4 5.8206e-4 4.8993e-4 4.1706e-4 3.5629e-4 3.0312e-4 2.5473e-4 2.0934e-4 1.6584e-4	0.385	y <sub>0</sub> = -1.2278e+3 a <sub>1</sub> = 3.4274e+1 b <sub>1</sub> = 26.3569 a <sub>2</sub> = 1.0498e+1 b <sub>2</sub> = 6.8620 a <sub>3</sub> = 1.2299e+3 b <sub>3</sub> = 1.4153e-3 c = 0.0
80.0000 90.0000 100.0000 110.0000 120.0000 130.0000 140.0000 150.0000 160.0000 170.0000 180.0000 190.0000 200.0000 210.0000 220.0000 230.0000 240.0000 250.0000 260.0000 270.0000 280.0000 290.0000 300.0000 310.0000 320.0000 330.0000 340.0000 350.0000	6.2664e-5 5.9069e-5 5.6983e-5 5.5500e-5 5.4346e-5 5.3402e-5 5.2601e-5 5.1907e-5 5.1293e-5 5.0744e-5 5.0246e-5 4.9791e-5 4.9373e-5 4.8985e-5 4.8624e-5 4.8286e-5 4.7969e-5 4.7669e-5 4.7386e-5 4.7117e-5 4.6862e-5 4.6618e-5 4.6385e-5 4.6162e-5 4.5949e-5 4.5744e-5 4.5546e-5 4.5356e-5	6.2585e-5 5.9230e-5 5.6990e-5 5.5415e-5 5.4244e-5 5.3323e-5 5.2560e-5 5.1903e-5 5.1320e-5 5.0790e-5 5.0302e-5 4.9848e-5 4.9424e-5 4.9026e-5 4.8652e-5 4.8299e-5 4.7967e-5 4.7653e-5 4.7356e-5 4.7077e-5 4.6812e-5 4.6563e-5 4.6327e-5 4.6105e-5 4.5895e-5 4.5696e-5 4.5509e-5 4.5332e-5	0.0935	y <sub>0</sub> = 0.12354036 a <sub>1</sub> = 4.7964 b <sub>1</sub> = 0.00571466 a <sub>2</sub> = 0.3245 b <sub>2</sub> = 0.6075 a <sub>3</sub> = 1.33485463 b <sub>3</sub> = 3.9744 c = 0.0

360.0000	4.5172e-5	4.5165e-5		
370.0000	4.4995e-5	4.5007e-5		
380.0000	4.4824e-5	4.4858e-5		
390.0000	4.4658e-5	4.4717e-5		
400.0000	4.4498e-5	4.4584e-5		

$$AAE = \sum_i^n \frac{\frac{V_{\text{exp}} - V_{\text{cal}}}{V_{\text{exp}}} \times 100}{N} ; N = \sum n_i$$