

ESTIMATION OF MUTUAL SOLUBILITY OF CO₂-H₂O IN SALINE AQUIFER SYSTEMS USING EPC-SAFT EQUATION OF STATE

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Abstract

A primary assessment of mutual solubility of CO₂ and water for estimated max and min temperatures and pressures of the prospective reservoir formations of Aurora; Cook (at >2650 m depth) and Johansen (at >2700 m depth) have been done using ePC-SAFT equation of state. Mole fraction of CO₂ in H₂O ranges from 0.025 to 0.027, and H₂O in CO₂ from 0.016 to 0.023 over pressure-temperature ranges of 265 – 283 bar and 95 – 110 °C. The potential for drying out effects (H₂O to CO₂) is significant, and there would be risk of salt precipitation in the near well area.

Keywords: Carbon Storage; mutual solubility; ePC-SAFT; Thermodynamics; Aurora

1. Introduction

An accurate determination of the distribution of components among different fluid and solid phases is crucial for efficiency and risk assessment in Carbon Capture and Storage (CCS) projects. An important step in quantification is modelling of different physical phenomena specific to a given reservoir/site. Among these, CO₂ concentration in water and water content of CO₂ have a superior priority, as saline aquifers are by far the most common type of repository, and evaporation of water into CO₂ stream causes salt precipitation and permeability impairment. However, a system such as H₂O-CO₂-Salt represents a complex fluid type due to highly non-ideal intermolecular interactions, such as association (hydrogen bonding), polarity, ionic bonds, and chain forming reactions. From a thermodynamic modelling perspective, it is not trivial to estimate the exact location of the phase boundaries and components distribution of such a complex system, by using standard engineering equations-of-state of the Van der Waals type (Peng-Robinson, Soave-Redlich-Kwong). Densities of the dense phase is especially challenging. To account for the non-ideal interactions, a good alternative is incorporating a predictive thermodynamic model that considers additional interactions (forces) between molecules: The Statistical Association Fluid Theory (SAFT). [1,2]

SAFT is a promising framework built on a reference term, which – unlike Van der Waals equations – can capture chain length (molecular shape) and molecular association [3]. Because of its accuracy and predictive capabilities, we used the ePC-SAFT [4–6] version to predict phase behaviour of H₂O-CO₂-Salt. This is at present the most advanced and accurate predictive tool for quantification of salt precipitation, and thus essential input to risk evaluations related to clogging.

2. Reservoir setting and data

The Norwegian Longship full value-chain CCS project [7] has selected deeply buried saline aquifers just offshore West Norway as suitable storage reservoirs for CO₂. The Johansen and Cook storage formations are siliciclastic, highly porous (20–30 %) Jurassic sandstones at burial depths in the order of 2.6-2.7 km below the sea floor [8]. The site has been studied extensively in the last decade [8–12]; however, there were no well data (P, T, porosity, permeability, mineralogy, fluid chemistry etc.) available from the storage license until 2020, when a CO₂ storage exploration well was drilled: 31/5-7 EOS [13]. Equinor and their Northern Lights Team, has made a data repository available [14].

Estimates of pressure (P), temperature (T) and salinity vary in previous studies and according to parameters for projections from analogue data (e.g. from Warren & Smalley, 1995[15]), and different studied locations. In [8,10,11,15] ranges are: P: 200-350 bar, T: 70-120 C and salinity 20 000 – 100 000 ppm. With new data, we now have proper input values for both the upper (Cook) and the lower (Johansen) reservoirs, and we applied formation water with TDS of 73000 - 73500 ppm, and P, T max/min scenarios of 95/110 °C, 265-283 bar [14].

2. Theory and model

The Perturbed Chain Statistical Association Fluid Theory (PC-SAFT) treats molecules as a chain composed of (m) spherical segments of equal sizes, bonded tangentially together and interacting via an intermolecular potential, *i.e.* Lennard-Jones (LJ), square-well (SW) etc. SAFT-type equations-of-states are usually formulated in terms of the residual Helmholtz energy. Considering the various types of molecular interactions we have taken into account in this work, the residual Helmholtz energy is defined as:

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} + a^{ionic} \quad (1)$$

Where \tilde{a}^{res} is the difference between the total Helmholtz energy per mole for the real gas or liquid and the ideal gas Helmholtz energy per mole at the same temperature and density. The superscripts refer to terms accounting for the hard-chain, dispersion, association, and ionic interactions, respectively. All other thermodynamic properties can be estimated through derivatives of the residual Helmholtz free energy. The fugacity coefficient, ϕ , of the components can be calculated with:

$$\ln \phi_i = \tilde{a}^{res} + \left(\frac{\partial \tilde{a}^{res}}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} - \sum_{j=1} x_j \left(\frac{\partial \tilde{a}^{res}}{\partial x_j} \right)_{T, \rho, x_{k \neq j}} + Z - 1 - \ln Z \quad (2)$$

where x_i is the mole fraction of component i , T is temperature, ρ is density, and Z is the compressibility factor and calculated with

$$Z = 1 + \rho \left(\frac{\partial \tilde{a}^{res}}{\partial \rho} \right)_{T, x} \quad (3)$$

The derivatives of the residual Helmholtz energy with respect to density can be calculated both numerically and analytically (here we used analytical derivatives). However, we generally recommend analytical derivation for the residual Helmholtz energy with respect to compositions, as we noticed that derivatives with respect to compositions are highly sensitive. The analytical derivation for hard chain and dispersion contribution of the free Helmholtz energy can be found in [16–18], for association contribution in [19], and for ionic contribution in [20].

The model requires three parameters for each compound, namely: m , the number of segments, σ , the segment diameter, and ε , the segment energy. For associative molecules, two additional parameters are needed, the association volume, κ^{AB} , and the well depth of the association energy, ε^{AB} .

We developed the model based on the following considerations:

- It is assumed that the association term can capture the polarity contribution of the molecules.
- The ePC-SAFT considers the hydrogen bonding through cross-association between unlike sites (i.e., O–H).
- The model for water molecules is based on the two-site single segment model proposed by [6], in which two associating sites of type (H) and type (O) represent the proton-donor sites and electron lone pairs, respectively. Two sites of the same type (i.e., O–O or H–H) do not associate.
- CO₂ is not considered as an associative molecule.
- Dispersion interaction is not considered between ions [6].
- Since the model is initially benchmarked for the CO₂-H₂O-NaCl system, we assumed total salinity as NaCl (i.e. TDS in formation water samples).

PC-SAFT parameters for water, Na⁺, and Cl⁻ are taken from [6]. PC-SAFT parameters for CO₂ are taken from

[17]. PC-SAFT parameters for all the components are reported in Table 1. Binary interaction parameters reported in [20] for the H₂O-CO₂-NaCl system is used.

Table 1. ePC-SAFT parameters for H₂O, CO₂, and ions

	m	σ (Å)	ε/k (K)	κ_{AB}	$\varepsilon_{AB}/k(K)$
H ₂ O	1.0953	2.8898	365.956	0.034868	2515.671
CO ₂	2.0729	2.7852	169.21	0	0
Na ⁺	1	1.6262	119.806	0	0
Cl ⁻	1	3.5991	359.660	0	0

Given a pressure P , a temperature T , and a mixture with global composition z , multi-phase flash calculations (vapour-liquid (V-L)) were performed to compute the phase fraction and the distribution of the components.

To perform multiphase flash calculations, the Rachford-Rice equation [21] is modified to account for the solid phase as follows:

$$\sum_{i=1}^{N_c} \frac{(K_i - 1)z_i}{1 + F_G(K_i - 1)} = 0 \quad (4)$$

Where N_c is the number of components, F_G is gas phase molar fraction and K_i is the equilibrium constant of component i . K_i is defined as:

$$K_i = \frac{y_i}{x_i} \quad (5)$$

$$x_i = \frac{z_i}{1 + F_G(K_i - 1)} \quad (6)$$

$$y_i = \frac{z_i K_i}{1 + F_G(K_i - 1)} \quad (7)$$

x_i is composition of component i in aqueous phase and y_i is composition of component i in gas phase.

More details of phase equilibria calculations can be found in our previous works [20,22].

3. Results and discussions

3.1 Model verification

The electrolyte and association contribution of the developed model are benchmarked for associative binary systems reported in [1] and water-salt systems reported in [6].

3.1.1 Association term

To validate the association contribution, we considered two systems. The first one is a Benzene-1-Propanol system. Benzene is a non-associating molecules and 1-propanol is an associating molecule. Figure 1.A shows isothermal vapor-liquid equilibria of this binary, self-associating mixture in which both compounds are below their critical point.

The second system is a mixture with two associating substances, Methanol and 1-Octanol. The results of isobaric vapor-liquid equilibria of this system is shown in Figure 1B.

The results confirm the ability of the model to simulate the phase behavior of systems containing associating molecules. We got the same results as [23] and matched the experimental data from [24,25].

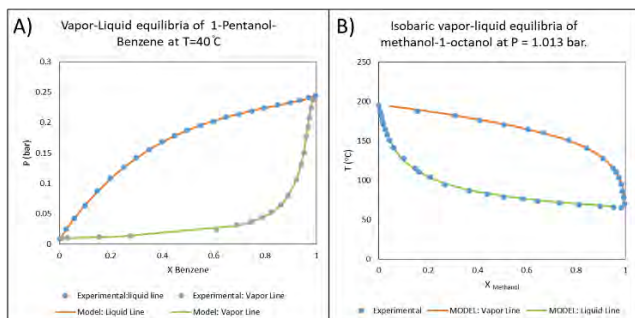


Figure 1: Vapor-liquid equilibria of: A) a system which contains one associating substance[24], and B) a system with two associating substances[24].

3.1.2 Ionic term

To validate the ionic contribution to Helmholtz energy, we considered two aqueous solutions containing monovalent ions (NaCl) and the bivalent ion (Na₂SO₄). The vapor pressure of aqueous solutions are calculated at different temperatures. The results show the ability of the model to cover the phase behavior of electrolyte solutions (Figure 2). We got the same results as [6] and matched the experimental data from [26,27].

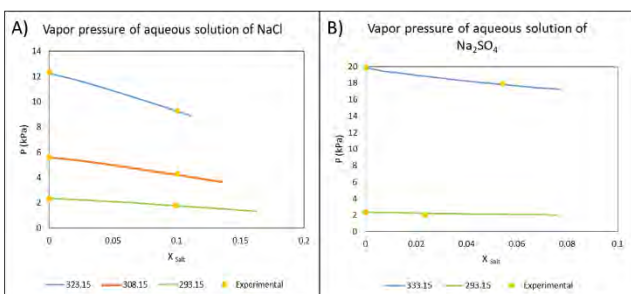


Figure 2: Vapor pressures of aqueous solutions of NaCl [26] and Na₂SO₄ [27] at different temperatures.

3.2 Mutual solubility

Figure 3 shows the mutual solubility of CO₂ and water in the CO₂-H₂O-NaCl system for 73,000 ppm salinity and CO₂ to brine ratio of 1:10 over a wide range of pressure

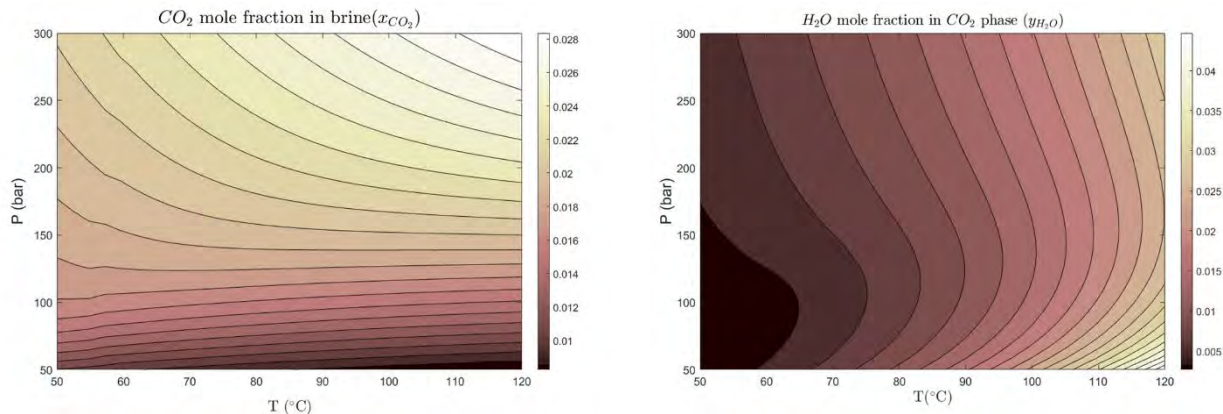


Figure 3: Mutual solubility of CO₂ in brine with 73,000 ppm NaCl and H₂O in CO₂ at varying reservoir conditions.

and temperature. The details of the mutual solubility for a combination of the expected max and min temperatures and pressures reported for the prospective reservoir formations of Aurora; Cook and Johansen, are reported in Table 2. Mole fraction of CO₂ in H₂O ranges from 0.025 to 0.027, and H₂O in CO₂ form 0.016 to 0.023 over pressure-temperature ranges of 265 – 283 bar and 95 – 110 °C.

Table 2: Mutual solubility of CO₂ and water for estimated max and min temperatures and pressures of the Johansen Fm. at >2700 m depth, and the Cook Fm. at >2650 m depth.

	T(°C)	P(bar)	x_{CO_2}	y_{H_2O}
Fluid 1	95	272	0.0258	0.0166
	110	272	0.0272	0.0231
	95	283	0.0261	0.0169
	110	283	0.0276	0.0234
Fluid 2	95	265	0.0255	0.0164
	110	265	0.0269	0.0229
	95	270	0.0257	0.0166
	110	270	0.0271	0.0230

4. Conclusion and recommendation

The PC-SAFT model set up presented here proves valid for estimating mutual solubility for CO₂-NaCl-H₂O systems, analogous to storage reservoir conditions. The estimated solubility for CO₂ in water (0.0255 – 0.0276 mol CO₂/H₂O) are in the same order of magnitude as in previous studies of the Aurora reservoirs. However, the potential for drying out effects (H₂O to CO₂) is significant, and there would be risk of salt precipitation in the near well area.

To have a better risk assessment a thorough simulation including sensitivity analysis on different salts and ions would have to be applied.

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