Monte Carlo Simulations of H₂O-CaCl₂ and H₂O-CaCl₂-CO₂ Mixtures

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Monte Carlo simulations were performed to obtain the phase behavior of binary H₂O-CaCl₂ and ternary H₂O-CaCl₂-CO₂ mixtures over a range of conditions. The solubility of CO₂ in brines plays a key role in determining the amount that can be trapped *via* geological carbon storage. Isobaric-isothermal and Gibbs ensemble Monte Carlo simulations with several fixed-point charge force field models were used for the calculations of liquid densities and vapor pressures for the binary, and compositions of both phases for the ternary system. We used the SPC and SPC/E models for water; the Åqvist, Deblein et al., and Smith-Dang parameterizations for CaCl₂; and the EPM2, Murthy et al., and TraPPE models for CO₂. While none of the model combinations were able to reproduce all the properties of interest, we found that some combinations produce accurate descriptions of individual properties. For the binary system, liquid densities are well represented by the SPC/E and Åqvist model combination, and vapor pressures are best described by the SPC and Åqvist model combination. For CO₂ solubility in aqueous CaCl₂, the combination of SPC, Smith-Dang, and TraPPE models gives the best predictions, but all the models studied show good predictive capabilities, given that no intermolecular potential parameters were optimized in the present study. These results are broadly consistent with previous calculations for the H₂O-NaCl-CO₂ system; CaCl₂ is found to have a stronger salting-out effect than NaCl at the same molality.

Keywords: Monte Carlo Simulation, Vapor-Liquid Equilibrium, Gas Solubility, Aqueous Electrolytes

1 Introduction

The geological sequestration of CO₂ has drawn increasing attention in recent years as a way to reduce greenhouse gas emissions and mitigate climate change.¹ Since aqueous brines are widely present in geological formations, the estimation of thermodynamic and phase equilibrium properties of CO₂ in such systems is crucial to the design of CO₂ sequestration processes.

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Experimental data are often not available at conditions of interest for geological carbon storage. Computer simulations with predictive molecular-based force field models can provide useful information to interpolate and extrapolate from limited experimental information.

Most prior studies of CO₂ solubilities in aqueous brines have been performed for the H₂O-NaCl-CO₂ system. For example, the properties of aqueous NaCl solutions and CO₂ solubility in H₂O-NaCl systems have been studied by experiments,^{2,3} thermodynamic models,^{4,5} and simulations.⁶⁻⁸ Phillips et al.² conducted experimental measurements of density and vapor pressures of NaCl solutions at a range of temperatures and pressures. Rumpf and Maurer³ measured the solubility of CO₂ in aqueous solutions of NaCl. Economou et al.⁴ studied the vapor-liquid equilibria of water with NaCl and other alkali halides salts at elevated pressures and temperatures using the associated perturbed-anisotropic-chain theory. Tan et al.⁵ extended statistical associating fluid theory to the modeling of ternary H₂O-NaCl-CO₂ mixtures. In general, temperature- and pressure-dependent interaction parameters have to be introduced in these models, which limits their applicability and predictive power. Recently, Orozco et al.⁶ performed a comprehensive study of thermodynamic and transport properties for the binary H₂O-NaCl mixture by simulation. In this work, the liquid density, vapor pressure, interfacial tension, and viscosity of aqueous NaCl solutions were studied for several nonpolarizable force fields. For the ternary H₂O-NaCl-CO₂ mixture, Vorholz et al.⁷ studied CO₂ solubility by Gibbs ensemble Monte Carlo simulation. Molecular dynamics simulations were also performed by Liu et al.⁸ for this ternary system to obtain the CO₂ solubility as well as the vapor-liquid surface tension.

In contrast to the relative abundance of thermodynamic models and molecular simulations for NaCl systems, there have been few experimental or simulation studies for CO₂ in aqueous solutions of alkaline-earth halides at conditions relevant for geological reservoirs.⁹ Because brines in saline aquifers contain alkali-earth ions, studying the solubility of CO₂ in alkaline-earth halide salt solutions is important for accurately modeling the long-term fate of CO₂ in such formations. A key motivation for the present study was the recent availability of solubility data over wide ranges of temperature and pressure for CO₂ in aqueous CaCl₂ solutions from Ref. 9. Prior to that study, there existed some elevated-pressure CO₂ solubility data, but they were restricted to lower temperatures.^{10,11} The goal of the present work is to evaluate the performance of H₂O, ion, and CO₂ force field model combinations with respect to CO₂ solubilities in CaCl₂ solutions at reservoir conditions. Because good models of electrolyte solutions are important for predicting CO₂ solubility, we also study the binary H₂O-CaCl₂ mixture. Experimental measurements of the liquid density and vapor pressure of this binary system exist over wide ranges of temperature and pressure.^{12,13} To the best of our knowledge, no prior simulation work has been performed on vapor-liquid equilibria for the system H₂O-CaCl₂ or H₂O-CaCl₂-CO₂.

This paper is organized as follows. Force field parameters for the molecular models studied are given in section 2.1. The details of the Gibbs ensemble and isothermal-isobaric Monte Carlo simulations performed are given in section 2.2. Results for densities and vapor pressures of the binary H₂O-CaCl₂ system are given in sections 3.1 and 3.2, respectively. Results for compositions of both phases for the ternary H₂O-CaCl₂-CO₂ system are given in section 3.3 and the summary and conclusions presented in section 4.

2 Methods

2.1 Force Field Parameters

The quality of atomistic simulation predictions depends strongly on the force field models selected to describe the interactions between molecules. Force fields used in this study are all rigid fixed-point charge models taken from the literature. Water was modeled by the SPC¹⁴ and SPC/E¹⁵ intermolecular potentials, which have parameters obtained by fitting structural and thermodynamic properties of the liquid at ambient conditions. **Although other water models exist such as TIP4P/2005,¹⁶ which admittedly gives excellent predictions for densities, water and ion models cannot be mixed and matched because water-ion interaction force field parameters are specific to each particular water force field.¹⁷** Thus, the SPC and SPC/E models were selected for the present work because they are computationally efficient and because there exist validated force field models for ions that are compatible with them. Three potential models were considered for CaCl₂: a model by Åqvist¹⁸ (in the following referred to as the “A” model), a model by Deublein et al.¹⁹ (“DRVH” model), and a model by Smith and Dang²⁰ (“SD” model). The Ca²⁺ parameters of the A model were obtained from the hydration free energy, **while the Cl⁻ parameters of the A model were taken from the SD model, as did by Gavryushov and Linse;²¹** the parameters of the DRVH model were adjusted to reproduce the liquid density at 293.15 K and 1 bar; and the parameters of the SD model were derived to reproduce binding enthalpies of ion-water clusters in the gas phase, solvation enthalpies, and solution structures. Three CO₂ models were also tested: a model by Harris and Yung²² (in the following referred to as the EPM2 model), a model by Murthy et al.²³ (“MSM” model), and a model by Potoff and Siepmann (TraPPE model). The force field parameters for H₂O, CaCl₂, and CO₂ are listed in Table 1.

The intermolecular potentials consist of Lennard-Jones (LJ) and Coulomb interactions. The interaction energy between molecule i and molecule j with m and n interaction sites, respectively, is calculated as the sum of the Lennard-Jones and Coulomb interactions:

$$u_{ij} = \sum_a^m \sum_b^n \left(\frac{1}{4\pi\epsilon_0} \frac{q_i^a q_j^b}{r_{ij}^{ab}} + 4\epsilon_{ij}^{ab} \left[\left(\frac{\sigma_{ij}^{ab}}{r_{ij}^{ab}} \right)^{12} - \left(\frac{\sigma_{ij}^{ab}}{r_{ij}^{ab}} \right)^6 \right] \right) \quad (1)$$

where ϵ_0 is the dielectric constant of the vacuum, q_i^a is the charge on site a of molecule i , r_{ij}^{ab} is the distance between sites a and b , and σ_{ij}^{ab} and ϵ_{ij}^{ab} are Lennard-Jones parameters between sites a and b on molecules i and j , respectively. The Lorentz-Berthelot combining rules were used without adjustment, in order to examine the predictive capabilities of the models and to be consistent with prior studies of aqueous electrolytes.^{6,7} The combining rules are as follows:

$$\sigma_{ij}^{ab} = \frac{1}{2} (\sigma_i^a + \sigma_j^b) \quad (2)$$

$$\epsilon_{ij}^{ab} = \sqrt{\epsilon_i^a \epsilon_j^b} \quad (3)$$

Table 1: Geometry data and potential parameters of the molecular models.

Model	Atom	σ (Å)	$\epsilon/k_B(K)$	q(e)	Geometry
SPC	O	3.166	78.197	-0.82	$r_{OH}=1.00$ Å
	H	...	...	0.41	$\theta_{H-O-H}=109.47^\circ$
SPC/E	O	3.166	78.197	-0.8476	$r_{OH}=1.00$ Å
	H	...	...	+0.4238	$\theta_{H-O-H}=109.47^\circ$
A	Ca	2.361	226.45	+2	...
	Cl	4.401	50.322	-1	...
DRVH	Ca	2.58	200	+2	...
	Cl	4.41	200	-1	...
SD	Ca	2.895	50.322	+2	...
	Cl	4.401	50.322	-1	...
EPM2	C	2.76	28.13	+0.65	$r_{CO}=1.15$ Å
	O	3.03	80.51	-0.326	...
MSM	C	2.79	29.00	+0.60	$r_{CO}=1.16$ Å
	O	3.01	83.10	-0.298	...
TraPPE	C	2.80	27.00	+0.70	$r_{CO}=1.16$ Å
	O	3.05	79.00	-0.350	...

2.2 Monte Carlo Simulations

The vapor pressure of the H_2O - $CaCl_2$ binary system was obtained by the Gibbs ensemble technique at constant volume (GEMC- NVT).^{24,25} The pressure of the vapor phase is reported as the vapor pressure of the mixture since the pressure of the liquid phase is subject to large fluctuations. Liquid densities of the H_2O - $CaCl_2$ binary mixture were obtained in the isothermal-isobaric (NPT) ensemble. Gibbs ensemble Monte Carlo simulations at constant pressure and temperature (GEMC- NPT) were used to calculate the solubility of CO_2 in $CaCl_2$ solution. All the simulations were conducted by the Cassandra suite of Monte Carlo codes.²⁶

For the GEMC- NVT calculations of the $CaCl_2$ system, between 500-550 water molecules and 1-50 $CaCl_2$ molecules were used in the runs at two temperatures, $T = 373$ K and 473 K. For simulations at 373 K, the lowest number of $CaCl_2$ molecules corresponds to molality of 0.8 mol/kg and the highest number corresponds to molality of 5 mol/kg. For simulations at 473 K, the lowest molality is $m = 0.8$ mol/kg and the highest is $m = 4$ mol/kg. Finite-size effects were tested by doubling the system size, and the results were within the statistical uncertainties of the base system size, which suggests that finite-size effects were small. For isothermal-isobaric ensemble simulations, between 490-510 water molecules and 1-60 $CaCl_2$ molecules were used at two temperatures, $T = 373$ K and 473 K, and a single pressure, $P = 7.2$ MPa. The molalities of interest are $m = 0.9$, 4, and 6 mol/kg. The GEMC- NPT simulations used between 250-350 water molecules, 1-25 $CaCl_2$ molecules, and 150 CO_2 molecules for runs at $T = 374$ and 424 K; $P = 1$ -40 MPa; and $m = 1$, 3, and 5 mol/kg.

Typical runs for all three types of MC simulations consisted of 250×10^6 Monte Carlo steps for equilibration, then another 250×10^6 Monte Carlo steps for production, and they

required between 25 and 140 CPU hours on four 2.6 GHz Sandybridge processors. Ewald summation was used to handle the Coulombic interactions, and the number of wave vectors was chosen to achieve a relative accuracy of 10^{-4} in the electrostatic energy. The cutoff distance of LJ and Coulombic interactions was 8 Å, and analytic tail corrections were applied for the LJ potential. The Monte Carlo moves used for the GEMC-*NVT* simulations included center of mass translations (constituting a fraction of 0.59 of total moves), rotations (0.25), volume changes (0.01), and transfer of species between the two boxes (0.15). The Monte Carlo moves for the isobaric-isothermal simulations were center of mass translations (0.58), rotations (0.40), and volume changes (0.02). The Monte Carlo moves for the GEMC-*NPT* simulations are center of mass translations (0.60), rotations (0.25), volume changes (0.005), and transfer of species between the two boxes (0.145). The maximum translational, rotational, and volume change moves were adjusted to achieve 50% acceptance rate. The transfer probabilities of Ca^{2+} and Cl^- ions were set to zero since no salt is present in the vapor phase. This is not an artificial constraint; molecular dynamics simulations at comparable conditions demonstrate that there is no salt present in the vapor phase, even when ions are allowed to move between phases.⁶ Statistical uncertainties of the properties of interest were obtained from block averages.²⁷

3 Results

Numerical results and associated statistical uncertainties for vapor pressures and liquid densities of the binary H_2O - CaCl_2 system and gas solubilities of the ternary CO_2 - H_2O - CaCl_2 system are listed in tabular form in the Supplementary Material. We confirmed that the simulation runs were at homogeneous solution conditions (i.e. no crystals formed in the system) by calculating the pair-correlation functions between positive and negative ions at the highest considered pressure and concentration; these are also shown in the Supplementary Material.

3.1 Binary H_2O - CaCl_2 System

3.1.1 Densities

Figure 1 shows the liquid densities of the binary mixture as a function of molality at $T = 373$ and 473 K and at $P = 7.2$ MPa. All six model combinations follow the experimental trend of mixture density increasing with CaCl_2 molality. However, all models studied underestimate the densities, and the predictions become worse at high molalities. At low molalities where water is the dominant species, the combinations that include the SPC/E model agree better with the experimental data because the SPC/E model has better pure water liquid density predictions than the SPC model.²⁸ SPC/E+A gives the best density predictions in this range of molalities out of all the combinations of models. Out of the model combinations that include the SPC water model, SPC+A gives the best predictions. Thus, the A salt model best represents the effect of salt on density at $T = 373$ and 473 K, and $P = 7.2$ MPa. The performance of the models used here is comparable to that of similar models for the H_2O - NaCl system.⁶

Figure 1: Liquid densities ρ (kg/m^3) versus molality m ($\text{mol CaCl}_2 / \text{kg H}_2\text{O}$) at $P = 7.2$ MPa for the binary $\text{H}_2\text{O-CaCl}_2$ system. Left and right figures correspond to $T = 373$ and 473 K, respectively. Experimental data are from Ref. 13.

3.1.2 Vapor Pressures

Figure 2 shows the vapor pressures as a function of the CaCl_2 concentration at $T = 373$ and 473 K. At $T = 373$ K, the model combinations with the SPC water model better describe the experimental vapor pressures than the ones with SPC/E because the pure water vapor pressure at this temperature is better predicted by the SPC model than the SPC/E model.²⁸ SPC+A and SPC+SD give comparable results; they match the slope of the experimental data better than other model combinations. Vapor pressures predicted from SPC+DRVH models, which appear to decrease linearly as a function of concentration, do not capture the curvature in the experimental trend and have a higher slope.

At $T = 473$ K, all six model combinations show larger deviations from the experimental vapor pressures than at $T = 373$ K. Yet, the model combinations that use SPC are still more accurate in terms of relative error: the combinations with SPC as the water model overpredict the vapor pressures of the mixture by factors of 1-2 while the combinations with SPC/E as the water model underpredict by factors of 2-3. The SPC+DRVH model also displays an incorrect slope at this temperature as in the case of $T = 373$ K. Thus, the SPC+A and SPC+SD combinations best describe the experimental data for the vapor pressures at $T = 373$ K and $T = 473$ K, with SPC+A slightly outperforming SPC+SD at $m = 3$ and 4 mol/kg at $T = 473$ K. Because the vapor pressures of the model combinations with SPC/E are too low, the SPC model was used for subsequent simulations of the ternary $\text{H}_2\text{O-CaCl}_2\text{-CO}_2$ system.

Figure 2: Vapor pressures, P^{sat} (MPa), for the binary $\text{H}_2\text{O}-\text{CaCl}_2$ system at $T = 373 \text{ K}$ (left) and $T = 473 \text{ K}$ (right), *versus* molality m (mol CaCl_2 / kg H_2O). Experimental data are from Ref. 12 for 373 K and Ref. 29 for 473 K. Symbols and lines are as for Figure 1.

Replotting the data of Figure 2 as the ratio of the pressure at a given molality, P^{sat} , over the vapor pressure of pure water (i.e. $m = 0 \text{ mol/kg}$) for the corresponding model, P^o , removes the effect of the differences in pure water vapor pressure predictions. The vapor pressures of pure water were obtained by performing GEMC- NVT simulations for the SPC and SPC/E water models. For 373 K, the values are 0.1245 ± 0.0034 and $0.0426 \pm 0.0011 \text{ MPa}$, respectively, which agree with literature values.²⁸ Figure 3 shows the vapor pressure ratios as a function of the CaCl_2 concentration at $T = 373 \text{ K}$. Similar results were obtained for $T = 473 \text{ K}$ and listed in Supplementary Material. The P^{sat}/P^o predictions by the SPC+SRVH and SPC/E+DRVH model combinations are inadequate; the trends drop too sharply compared to the experimental data. SPC+A and SPC+SD underestimate the ratio P^{sat}/P^o at lower molalities, then overestimate the ratio P^{sat}/P^o at higher molalities. SPC/E+A and SPC/E+SD follow the curvature of the experimental data best out of the six model combinations, slightly overpredicting the ratio P^{sat}/P^o at all concentrations.

Figure 3: Vapor pressure ratios P^{sat}/P^o for the binary $\text{H}_2\text{O}-\text{CaCl}_2$ system at $T = 373 \text{ K}$ *versus* molality m (mol CaCl_2 / kg H_2O). Experimental data are from Ref. 12. The error bars have been omitted for clarity. Symbols and lines are as for Figure 1.

3.2 Ternary $\text{H}_2\text{O}-\text{CaCl}_2-\text{CO}_2$ System

Simulations for the ternary $\text{H}_2\text{O}-\text{CaCl}_2-\text{CO}_2$ system were performed using SPC as the water model because the pure water vapor pressure predicted by the SPC/E model is too low. The CO_2 solubilities obtained from simulations are expressed as salt-free mole fractions of dissolved gas (x') in order to make the results directly comparable to the measurements of Ref. 9:

$$x' = \frac{n_g}{n_g + n_w} \quad (4)$$

where n_g is the number of CO_2 molecules in the liquid phase and n_w is the number of H_2O molecules in the liquid phase. Since salt is not present in the gas phase, the mole fraction of CO_2 in the gas phase (y) obtained from simulation is reported without conversion. The solubility of CO_2 in the liquid phase and mole fraction of CO_2 in the gas phase at CaCl_2 concentrations of 1 mol/kg and 5 mol/kg and $T = 375$ and 424 K are shown in Figures 4 and 5.

Figure 4: Solubility of CO_2 in CaCl_2 aqueous solutions (x') with molality of 1 mol/kg (top) and 5 mol/kg (bottom) at $T = 375$ K and mole fraction of CO_2 in the gas phase (y). Experimental data are from Ref. 9 for the $\text{H}_2\text{O}-\text{CaCl}_2-\text{CO}_2$ system and Ref. 30 and 31 for the $\text{CO}_2 - \text{H}_2\text{O}$ system.

As shown in Figures 4 and 5, all the model combinations predict the salting-out effect at both temperatures when compared to the solubility of CO_2 in pure water.³⁰ As the salt concentration increases, the CO_2 solubility decreases while the CO_2 composition in the gas phase increases. Despite some deviation from experimental data, all the model combinations give reasonable estimates for the CO_2 compositions in both liquid and gas phases. This is particularly satisfactory given that no adjustments have been made to any of the pure component intermolecular potential or cross-interaction parameters, thus making the calculations purely predictive.

At $T = 375$ K and $m = 1$ mol/kg, the DRVH+TraPPE combination gives accurate prediction of CO_2 solubility at low pressure but slightly overestimates the solubility at high pressure. A+TraPPE and SD+TraPPE give accurate estimation of CO_2 solubilities at the three examined pressures, while the other model combinations (except the DRVH+TraPPE model) underestimate the solubilities at all pressures. As the salt concentration increases to 5 mol/kg, CO_2 solubilities decrease, which leads to an increase of CO_2 mole fraction in the gas phase. At $T = 375$ K and $m = 5$ mol/kg, DRVH+EPM2, DRVH+MSM, and DRVH+TraPPE give better

prediction of CO₂ solubilities, while other model combinations tend to underestimate the CO₂ solubilities.

Figure 5: Solubility of CO₂ in CaCl₂ aqueous solutions (x') with molality of 1 mol/kg (top) and 5 mol/kg (bottom) at $T = 424$ K and mole fraction of CO₂ in the gas phase (y). Experimental data are from Ref. 9 for the H₂O-CaCl₂-CO₂ system and Ref. 30 and 31 for the CO₂ – H₂O system. Symbols and lines are as for Figure 4.

At $T = 424$ K and $m = 1$ mol/kg, A+TraPPE and SD+TraPPE give the best predictions of CO₂ solubility. At $T = 424$ K and $m = 5$ mol/kg, DRVH+TraPPE and SD+TraPPE overestimate the solubility of CO₂, while other model combinations underestimate it. Again, SD+TraPPE model is considered to give the best estimation of CO₂ solubilities at this condition. Therefore, we conclude that at $T = 424$ K, SD+TraPPE is the best model combination. It is worth noting that the combinations with the MSM model estimate higher mole fractions of CO₂ in the gas phase at $m = 5$ mol/kg and $P = 5$ MPa compared to the combinations with the A and SD salt models. Similar to the system at $T = 375$ K, the concentration of CO₂ in the gas phase increases with CaCl₂ concentration

It is also worth noting that the salting-out effect is greater in the H₂O-CaCl₂-CO₂ system than the H₂O-NaCl-CO₂ system,⁷ when compared at the same molality m . The stronger salting-out effect in the H₂O-CaCl₂-CO₂ system results in higher mole fractions of CO₂ in the gas phase

compared to the H_2O - NaCl - CO_2 system.⁷ Thus, systems with divalent cations appear to have greater salting-out effect and higher vapor pressures than systems with monovalent ions, as expected from the higher ionic strength at a given molality. This also agrees with the findings of Ref. 9, in which the $m = 1$ mol/kg CaCl_2 solution has bubble pressures that are 20-30% higher than the $m = 1$ mol/kg NaCl - KCl mixed brine.

4 Conclusions

Monte Carlo simulations using several fixed-point charge force field models for H_2O , CaCl_2 , and CO_2 were carried out at various temperatures, pressures, and salt concentrations to test the performance of these model combinations with respect to liquid densities and vapor pressures of the H_2O - CaCl_2 system as well as the solubilities of CO_2 in CaCl_2 solutions. Although none of the studied model combinations are found to simultaneously describe all of the properties adequately, some combinations matched experimental data of individual properties well. They are summarized as follows: (1) SPC/E+A for liquid densities of the H_2O - CaCl_2 system, (2) SPC+A for vapor pressures of the H_2O - CaCl_2 system, (3) SPC/E+A for vapor pressure ratios of the H_2O - CaCl_2 system, and (4) SPC+SD+TraPPE for CO_2 solubility in CaCl_2 aqueous solutions. For the CO_2 solubilities in CaCl_2 solutions, despite minor deviations from the experimental data, all the models studied show good predictive capabilities, given that no intermolecular potential parameters were optimized in the present study.

While nonpolarizable fixed-point charge water and salt force field models give reasonable estimations for properties of the binary H_2O - CaCl_2 and ternary H_2O - CaCl_2 - CO_2 system, they have the disadvantage of being unable to properly describe both highly polar and non-polar environments, resulting in deficiencies in predictions of properties of one of the phases, even after optimization of the cross-interaction parameters.⁶ Polarizable water and salt models will be tested in future studies to determine improved force field model combinations for the H_2O - CaCl_2 and H_2O - CaCl_2 - CO_2 systems. **Recently, it was shown that the polarization of CaCl_2 can be effectively described by the electronic continuum correction (ECC).³² The CaCl_2 force field developed by Kohagen et al.^{33,34} using the ECC approach will also be tested.**

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