Thermodynamic and dynamic investigation for CO_2 storage in deep saline aquifers

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Abstract: Thermodynamic and dynamic investigations are needed to study the sequestration capacity, CO_2 leakage, and environmental impacts. The results of the phase equilibrium and densities for CO_2-sequestration related subsystems obtained from the proposed thermodynamic model on the basis of statistical associating fluid theory equation of state were summarized. Based on the equilibrium thermodynamics, preliminary kinetics results were also illustrated with chemical potential gradient as the driving force. The proposed thermodynamic model is promising to represent phase equilibrium and thermodynamic properties for CO_2-sequestration related systems, i.e. CO_2-(H_2S)-H_2O-ions (such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}), and the implementation of thermodynamic model into kinetics model to adjust the non-ideality of species is vital because of the high pressure for the investigation of the sequestration process.

Keywords: Carbon sequestration, CO_2 storage, Thermodynamics, Dynamics, CO_2 diffusion

1. Introduction

Storage of CO_2 in deep saline aquifers is one way to limit the buildup of greenhouse gases in the atmosphere. Large-scale injection of CO_2 into saline aquifers will induce a variety of coupled physical and chemical processes including multiphase fluid flow, solute transport, and chemical reactions between fluids and formation minerals. Thermodynamic and dynamic investigations are needed to study the sequestration capacity, CO_2 leakage, and environmental impacts. Co-injection of CO_2 and H_2S (from flue gases and natural gas fields) may substantially reduce the capture and sequestration costs, and the effect of H_2S on bot h thermodynamic and dynamic models is also needed.

In thermodynamics, experimental solubility data for the CO_2 in water and aqueous NaCl solution and for the H_2S in water and aqueous NaCl solutions have been determined in a wide temperature and pressure range[1, 2]. However, only few experiments are for CO_2 solubility in brines[3]. For more complicated system, there is no available experimental data. Density is also essential to reservoir/aquifer simulation applications. The dissolution of CO_2 in aqueous solutions under most reservoir, aquifer, or deep-ocean conditions results in an increase in the density of the solution, which can induce a natural convection[3-5]. Meanwhile, the properties of the H_2O-rich phase are also strongly dependent on de nsity, which varies greatly with temperature, pressure, CO_2 concentration and salinity[6]. However, the experimental data of density for the related system are much less than those of the solubility data[7, 8].

Meanwhile, thermodynamic models have been proposed to represent the CO_2 or H_2S solubility in H_2O or aqueous NaCl solutions. The models proposed by Spycher et al.[9] and Duan et al.[2] for CO_2+H_2O and CO_2+H_2O+salt are examples of a γ-ϕ approach, where an equation of state (EOS) is used to describe the non-ideality in the CO_2-rich phase and Henry's law or an activity model is used to describe the non-ideality in the H_2O-rich phase. The inherent disadvantage of this approach is that it does not allow for estimating the density of the H_2O-rich phase. This is not an issue in a ϕ-ϕ approach, where an EOS is used for both phases. The ϕ-ϕ approach has been applied to the CO_2+H_2O+NaCl[1], H_2S+H_2O[10-14]

systems. However, to the best of our knowledge, the ϕ-ϕ approach has never been used to describe the phase equilibrium and density for other or more complicated systems.

Dynamic models were investigated on the basis of the available thermodynamic models, and sometimes the effect of ions on the CO_2 solubility is neglected[15]. Moreover, the empirical models with the concentration difference as the driving force were used to represent the dynamic process[3], such as gas dissolution, diffusion, mineral dissolution and precipitation. All these assumptions will bring uncertainty of the simulation results. It is crucial to develop a both reliable thermodynamic model and theory-based dynamic (kinetics) model in order to provide a reliable prediction for CO_2 storage in deep saline aquifers.

We have been working on the related studies for several years and obtained promising results[8, 16-21]. Thermodynamic study is on the basis of statistical associating fluid theory (SAFT) EOS, and preliminary kinetics investigation is based on t he non-equilibrium thermodynamics with chemical potential gradient as driving force. In this work, our work on the thermodynamic and dynamic models is summarized, and then perspective is given.

2. Modeling

The thermodynamic properties are represented using SAFT EOS in which the dimensionless residual Helmholtz energy is defined as:

$$\tilde{a}^{res} = \tilde{a}^{seg} + \tilde{a}^{assoc} + \tilde{a}^{chain} + \tilde{a}^{ion} \tag{1}$$

where the superscripts refer to terms accounting for the residual, segment, association, chain, and ionic interactions, respectively. The model was proposed as SAFT1-RPM first, and then improved to SAFT2. The detailed description for both SAFT1-RPM and SAFT2 was in references[8, 16-20].

In model, each component is modeled as one kind of segments with parameters, i.e. segment number m, segment volume v^{oo}, segment energy u/K, and the reduced range of the potential well λ. For molecule with association interactions, there are two additional parameters, i.e. the well depth of the association site-site potential ε, and the parameter related to the volume available for bonding κ. For ions, there is one additional parameter, effective diameter d. The mixing rules are followed those in our previous work[8, 16-19, 20].

To describe the CO_2 diffusion in water or brine, non-equilibrium thermodynamic model was used in which the chemical potential gradient was used as the driving force with the following equation:

$$\frac{\partial f_i(x,t)}{\partial t} = D_{eff} \frac{\partial^2 f_i(x,t)}{\partial x^2} \tag{2}$$

where x is the position in m, t is the time in s, f is the fugacity of a component that is calculated with SAFT EOS, and D_{eff} is the effective diffusion constant that is a combination of a molecule diffusion and natural convection. The detail description was in reference[21].

3. Results and perspective

To represent properties of CO_2-(H_2S)-H_2O-ions (such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}) up to high pressures, research has been carried out for several years for different subsystems.

3.1. Phase equilibrium and properties for CO_2-H_2O-NaCl system

Phase equilibrium and thermodynamic properties of CO_2-H_2O and CO_2-H_2O-NaCl system are very important for the CO_2 sequestration, and then they were investigated firstly with the SAFT1-PRM model[8] in which CO_2 was modeled as a molecule with three association sites, two sites of type O and one site of type C. H_2O was modeled as a molecule with four association sites, two sites of type O and two sites of type H. The salt was modeled as a molecule composed of two charged, but non-associating, spherical segments, of which one represents the cation and one represents the anion. For the CO_2-H_2O system, only one type of cross association was assigned, i.e., between site of type O in CO_2 and site of type H in H_2O. Using temperature-dependent parameters, SAFT1-RPM is found to represent the density and equilibrium data for the CO_2-H_2O system, including the minimum H_2O concentration in the CO_2-rich phase in the composition (y)- pressure (P) diagram, as shown in Fig. 1 (a) at 308.15 K. For CO_2-H_2O-NaCl system, an additional binary interaction constant was used, the same for both CO_2-Na^+ and CO_2-Cl^- pairs, which was needed to correct the short-range interactions. SAFT1-RPM is also found to represent the equilibrium and density data for the CO_2-H_2O-NaCl system. As shown in Fig. 1 (b), the CO_2 solubility decreases with increasing salt concentration (molality, m, mol/kgH_2O), salt-out effect, and the model captures not only the pressure effect on the CO_2 solubility but also the salting-out effect.
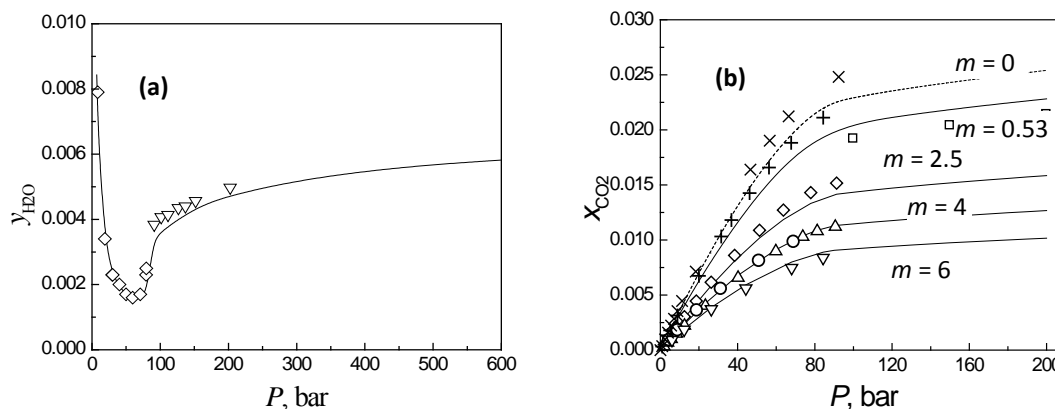

Fig. 1. (a) Mole fractions of H_2O in CO_2-rich phase (y_{H2O}) for CO_2-H_2O at 308.15 K at different pressures (P). Experimental data[22-24]; —, calculated. (b) Mole fractions of CO_2 in H_2O-rich phase (x_{CO2}) for CO_2-H_2O-NaCl at 313.15 K, different pressures (P), and salt concentration (molality, m). Experimental data[23, 25-27] : —, calculated (m = 0.5292, 2.5, 4.0 and 5.999). ⋯; calculated (m = 0).

3.2. CO_2 diffusion in brines

Numerous investigations on the mass transfer of CO_2 in high-pressure water or brines have been pursued to simulate the CO_2 geological and ocean disposal processes. It has been showed that the dissolution of CO_2 in brines increases the density, and then induces the density-driven natural convection, which then significantly accelerates the diffusion of CO_2 in the brine. Yang and Gu[3] investigated experimentally the CO_2 dissolution in brine at elevated pressures and described the mass transfer of CO_2 in brine using a modified diffusion equation with an effective diffusion coefficient. The effective diffusion coefficients are two orders of magnitude larger than the molecular diffusivity of CO_2 in water, which implies that the density-driven natural convection greatly accelerates the mass transfer of CO_2 in brines.

Since the salinity of brines is low for the experimental data of Yang and Gu[3], the main components are Na^+ and Cl^-, it is reasonable to assume that the brine is the aqueous solution of NaCl[21]. Based on t his assumption, the CO_2 equilibrium concentration was calculated with SAFT1-RPM and compared with those measured experimentally with good agreement, as shown in Fig. 2 (a). Moreover, the mass transfer of CO_2 in brines was investigated further by chemical potential gradient model based on non-equilibrium thermodynamics[21]. Fig. 2 (b) illustrates the CO_2 concentration distribution at 300.15 K calculated with the non-equilibrium thermodynamics and those obtained from the modified Fick's second law. The difference in the concentration distribution reveals the importance to combine the thermodynamic model with kinetics model.
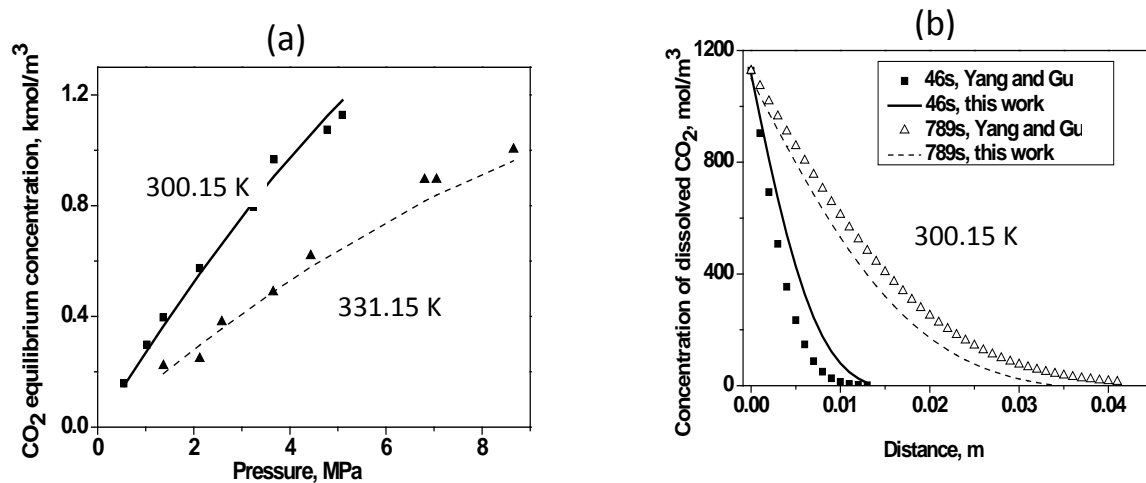

Fig. 2. (a): Equilibrium concentration of CO_2 in brine, symbols: experimental data[3], curves: prediction. (b): CO_2 concentration distribution. Curves: calculation with chemical potential gradient as driving force. Symbols: calculation with concentration difference as driving force[3].

3.3. *Properties for aqueous electrolyte solutions*

Properties of brines are different from different sources, and it is not always reasonable to assume it be aqueous NaCl solution when the effect of other ions is considerable. Generally, the components in brines include Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}. Meanwhile, ions of Li^+, Br^-, I^-, NO_3^-, HCO_3^-, and SO_4^{2-} play important roles in other industries. Thus, the properties of such aqueous electrolyte solutions were studied. In SAFT1-RPM, except the diameter, the parameters for electrolytes are ion-based. Later, the ion-based SAFT EOS was proposed and called ion-based SAFT2[19, 20].

To represent the properties of aqueous single-salt solutions in the temperature, pressure, and concentration ranges of 298.15 to 473.15 K, 1.013 to 1000 bar, and 0 to 6 mol/kgH_2O in ionic strength, respectively, the short-range interaction between cation and anion was needed to capture the effect of pressure on the properties of electrolyte solutions. A set of parameters at 298.15 K for 5 c ations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and 7 a nions (Cl^-, Br^-, I^-, NO_3^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}) was obtained from the fitting of the experimental mean ionic activity coefficients and liquid densities of 26 aqueous single-salt solutions. An additional set of ion-specific coefficients used in the temperature-dependent parameter expressions for 5 cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and 5 anions (Cl^-, Br^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}) was obtained from the fitting of the experimental mean ionic activity coefficients and liquid densities of 15 aqueous single-salt solutions at low pressures and temperatures up to 473.15 K.

For the properties of aqueous multiple-salt solutions at ambient and elevated temperatures and pressures, the short-range interactions between two different cations were allowed to obtain better representations of the solution properties. The adjustable parameter used in the mixing rule for the segment energy was fitted to the experimental osmotic coefficients of two-salt solutions containing one common anion at various temperatures and low pressures. The predictions of the osmotic coefficients, densities, and activity coefficients of multiple-salt solutions including brine/seawater are found to agree with experimental data. Fig. 3 illustrates the comparison of the density calculated with model and reference data[28] for aqueous NaCl solutions and experimental data for brines[29].
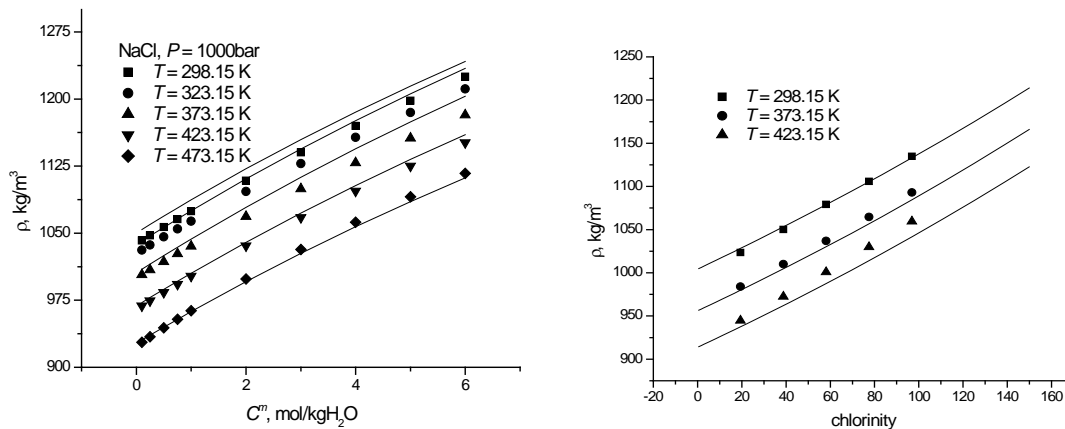

Fig. 3. Density (ρ) for aqueous NaCl solutions and brines. Symbols: experimental data[28, 29]; —, calculation.

3.4. Phase equilibrium for H_2S-H_2O system

CO_2 capture is a former step of CO_2 sequestration. Research reveals that the cost for CO_2 capture is two thirds of the totally cost for CO_2 capture and storage. How to cut the cost for CO_2 capture is one of the main barriers. Generally, H_2S is another main component in flue gases and natural gas fields, the co-injection of H_2S and CO_2 will substantially reduce the capture and sequestration costs, while it will also affect the sequestration capacity and the sequestration process (from solubility to transfer to reaction with rocks). This leads to the significance of the study of the thermodynamics and kinetics for H_2S-CO_2 related sequestration systems.

Thus, the phase equilibrium of the binary system of H_2S-H_2O was represented using ion-based SAFT2[14] in which H_2S was modelled as a molecule with four association sites, i.e., two sites of type S and one site of type H, and sites of the same type did not associate with each other. The parameters of H_2S were fitted to its vapor pressure and saturated liquid density. Cross association between the association site H in H_2S and the site O in H_2O was allowed, and two temperature-dependent parameters were used to describe this cross association. A temperature-dependent binary interaction parameter was used to correct the cross dispersive energy for this binary system. Cross parameters were fitted to mole fractions both in H_2S-rich/vapor and H_2O rich phases[30]. The model is found to represent the phase equilibria from 273 to 630 K and at pressure up to 200 bar[14]. Fig. 4 shows the equilibrium compositions. At 310.93 and 366.48 K, the vapor phase changes to H_2S-rich liquid phase when the pressure increases up to a certain value, while at higher temperatures of 422.04K and 477.49K, no H_2S-rich liquid phase exists in the investigated pressure range. This observation is represented with the model.
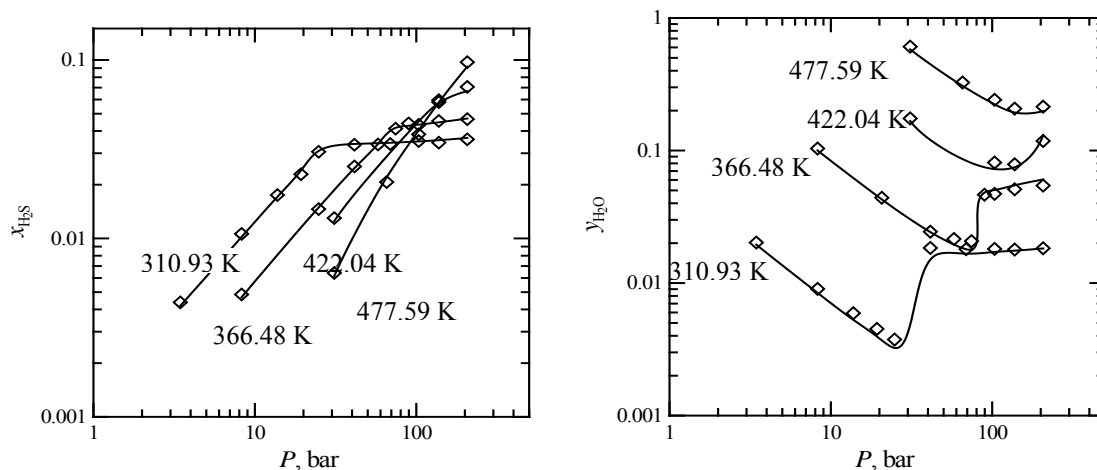
Fig. 4. Mole fractions of H_2S in H_2O-rich phase (x_{H2S}) and mole fractions of H_2O in H_2S-rich/vapor phase (y_{H2O}) for H_2S-H_2O system. ◇: experimental data[14]; —, calculation.

3.5. Perspectives

To represent properties of CO_2-(H_2S)-H_2O-ions (such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}), the phase equilibrium and thermodynamic properties for CO_2-H_2S, H_2S-H_2O-NaCl, H_2S-brines, CO_2-brines system are needed to investigated further. In kinetics, the preliminary result reveals the importance of the combination of thermodynamic model with mass transfer model. While the improvement itself relates both the thermodynamic model and the description of the CO_2 sequestration process of solubility, dissolution, transfer, and reaction with rocks. The implementation of the thermodynamic model into the process model to provide reliable long-term prediction pertaining to geochemical carbon sequestration, such as sequestration capacity, CO_2 leakage, and environmental impacts, is another main part of the further work.

4. Conclusions

Storage of CO_2 in deep saline aquifers is one way to limit the buildup of greenhouse gases in the atmosphere, and the co-injection of CO_2 and H_2S may substantially reduce the capture and sequestration costs, and the effect of H_2S on both thermodynamic and dynamic models is also needed to study the sequestration capacity, CO_2 leakage, and environmental impacts. Based on SAFT EOS, the phase equilibrium and densities for H_2S-CO_2-sequestration related subsystems have been investigated and summarized. Meanwhile, using non-equilibrium thermodynamics in which the chemical potential difference as the driving force, preliminary kinetics results were illustrated. The proposed thermodynamic model is promising to represent phase equilibrium and thermodynamic properties for CO_2-sequestration related systems, i.e. CO_2-(H_2S)-H_2O-ions (such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}), and it is necessary to implement the reliable thermodynamic model into kinetics model to adjust the non-ideality of species because of the high pressure to investigate the sequestration process.

Acknowledgment

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