Modeling of CO₂ Solubility in Single and Mixed Electrolyte Solutions

Using Statistical Associating Fluid Theory

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Statistical associating fluid theory (SAFT) is used to model CO₂ solubilities in single and mixed electrolyte solutions. The proposed SAFT model implements an improved mean spherical approximation in the primitive model to represent the electrostatic interactions between ions, using a parameter K to correct the excess energies (“KMSA” for short). With the KMSA formalism, the proposed model is able to describe accurately mean ionic activity coefficients and liquid densities of electrolyte solutions including Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, Br⁻ and SO₄²⁻ from 298.15 K to 473.15 K using mostly temperature independent parameters, with sole exception being the volume of anions. CO₂ is modeled as a non-associating molecule, and temperature-dependent CO₂ – H₂O and CO₂ – Ion cross interactions are used to obtain CO₂ solubilities in H₂O and in single ion electrolyte solutions. Without any additional fitting parameters, CO₂ solubilities in mixed electrolyte solutions and synthetic brines are predicted, in good agreement with experimental measurements.

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1. Introduction

Carbon dioxide (CO₂) is the primary green house gas contributing to the global warming (Solomon *et al.* 2009). The geologic sequestration of CO₂ in underground formations, primarily in saline aquifers, is a promising approach for the reduction of CO₂ emissions (IPCC, 2005). Understanding the behavior of CO₂ in electrolyte solutions and brines is of great importance to the design of a CO₂ geologic sequestration project. At the temperature and pressure conditions of geological CO₂ storage, thermodynamic properties of CO₂ – H₂O and CO₂ – H₂O – electrolytes mixtures are quite complex and modeling of such systems is extremely challenging.

CO₂ solubility in H₂O or aqueous electrolyte solutions is one of the most important factors determining the fate of CO₂ in geological formations. Numerous experimental measurements have been used to obtain solubility data for CO₂ in H₂O and aqueous electrolytes. Previous studies of CO₂ solubility in H₂O include those by Wiebe and Gaddy (1940, 1941), Takenouchi and Kennedy (1964), Yan *et al.* (2011) and Capobianco *et al.* (2013). The solubility of CO₂ in aqueous NaCl solutions at elevated temperatures and pressures has also been widely investigated. Some recent experimental measurements include those by Kiepe *et al.* (2002), Bando *et al.* (2003), Hou *et al.* (2013) and Zhao *et al.* (2015a). Measurements of CO₂ solubility in other electrolyte solutions and aqueous brines are, however, relatively scarce. Tong *et al.* (2013) reported the solubility of CO₂ in aqueous solutions of CaCl₂ and MgCl₂ at pressures up to 40 MPa. Zhao *et al.* (2015b) measured CO₂ solubility in high temperature aqueous CaCl₂, MgCl₂, Na₂SO₄ and KCl solutions. Liu *et al.* (2011a) studied the CO₂ solubility in mixed NaCl + KCl + CaCl₂ solutions. Recently, Zhao *et al.* (2015c) studied the CO₂ solubility in natural and synthetic formation brines, and concluded that the CO₂ solubility in synthetic formation brines may be represented by that in mixed NaCl + CaCl₂ solutions.

In addition to experimental studies, molecular simulation has become a useful alternative to study thermophysical properties, especially the solubility, for CO₂ bearing electrolyte solutions. CO₂ solubilities in salt-free H₂O, and in aqueous NaCl or CaCl₂ solutions were obtained by Monte Carlo (Destigneville *et al.* 1996; Liu *et al.* 2011b; Orozco *et al.* 2014; Evaline *et al.* 2015) and molecular dynamics (Rivera *et al.* 2002; Liu *et al.* 2013) simulations, and the performances of various force field models were evaluated. Transport properties, such as diffusivities, were also studied using molecular dynamics simulations (Moultos *et al.* 2014).

Experimental determination of solubility and thermodynamic properties of CO₂ bearing solutions is expensive and time consuming, while simulations also require large-scale computing resources and accurate force fields. Thus, it is highly desirable to develop thermodynamic models that can provide reliable correlations (or even predictions) for these properties. There has been much prior work on modeling electrolyte solutions and the corresponding CO₂ solubility. In general, thermodynamic models can be divided into two main categories: activity coefficient correlations and equations of state (EoS). Perhaps the most popular activity coefficient model is by Pitzer (Pitzer, 1973; 1991), which gives quite accurate correlations for activity coefficients of many electrolyte solutions. Activity coefficient models have also been used to calculate CO₂ solubility in aqueous NaCl solutions. Akinfiev and Diamond (2010) developed a thermodynamic model that is based on the Pitzer's activity coefficient model for the ternary CO₂– H₂O – NaCl system. The CO₂ solubility calculated by this model is in excellent agreement with experimental measurement with a relative deviation of 1.6%. The Pitzer model (and any other activity coefficient model) is based on excess free energy and the calculation of volumetric properties requires an additional model. Therefore, Akinfiev and Diamond (2010) had to combine the Pitzer activity coefficient model with an EoS to calculate vapor-liquid equilibrium properties, such as gas solubility. Moreover, the Pitzer model, due to its empirical nature, has a large number of parameters. Consequently, a lot of high quality experimental data (302 data points) were used to adjust the Pitzer parameters in the Akinfiev and Diamond model (2010), which makes the model impractical to study CO₂ solubility in mixed solutions or brines. Helgeson *et al.* (1974, 1981, 1988) proposed a series of thermodynamic models to calculate the activity coefficient, partial molar volume and other important properties of aqueous electrolyte solutions. The models by Helgeson are generally an extension of Debye-Huckel law and widely used in geochemistry.

EoS can also be used to study CO₂ - H₂O - electrolyte systems. With an EoS, phase equilibria data, such as CO₂ solubilities, and PVT properties can be calculated in a self-consistent way. Due to the presence of hydrogen bonding and Coulombic interactions in electrolyte solutions, classical cubic EoS, which only empirically account for the van der Waals interactions, are inadequate for these mixtures. There have been efforts to improve the performance of cubic EoS by introducing additional energy correction terms; the most successful such modification is the cubic plus association (CPA) EoS (Kontogeorgis *et al.* 2006a, 2006b). Tan *et al.* (2013) developed the electrolyte-CPA EoS to calculate the CO₂ solubility in aqueous NaCl solution, and the effect of SO₂ on the CO₂ solubility. Courtial *et al.* (2014) applied the electrolyte-CPA EoS to system containing

CH₄, CO₂, H₂O and NaCl, and the phase behavior of the system was well represented under a wide range of temperature and pressure conditions. Recently, Maribo-Mogensen *et al.* (2015) proposed an improved electrolyte-CPA EoS for mixed solvent electrolyte solutions using a self-consistent model for the solvent static permittivity.

Statistical associating fluid theory (SAFT), which is a perturbation theory based EoS, has been successfully applied to the modeling of complex fluids including aqueous electrolytes, polymer systems, liquid crystals, biomaterials and ionic liquid (Tan *et al.* 2008) since it was first proposed about 25 years ago (Chapman *et al.* 1989). There are many different SAFT models for H₂O and aqueous electrolyte solutions available in the literature. Cameretti *et al.* (2005) proposed the ePC-SAFT equation of state, which is a combination of Perturbed Chain-SAFT (PC-SAFT, Gross and Sadowski, 2001) and Debye-Hückel term, to calculate properties of aqueous electrolyte solutions (Held *et al.* 2008, 2012). The ePC-SAFT EoS was implemented to model CO₂ solubility in NaCl solution, and good description of solubilities was achieved with temperature dependent CO₂ - H₂O and CO₂ - ion interaction parameters (Tan *et al.* 2013). Diamantonis and Economou (2012) used both the PC-SAFT and the truncated PC-Polar SAFT (tPC-PSAFT) equations of state to study the vapor-liquid equilibria properties of CO₂ - H₂O mixture. Rozmus *et al.* (2013) developed the ePPC-SAFT EoS for 20 alkali halides salt solutions and studied the activity coefficient, density, vapor pressure and gas (CO₂ and CH₄) solubility of salt solutions.

The statistical associating fluid theory for potentials of variable range (SAFT-VRE, Gil-Villegas *et al.*, 1997) was used to model aqueous electrolyte solutions by Galindo *et al.* (1999). Recently, the SAFT-VRE EoS was improved by incorporating the effects of temperature, density and composition on the dielectric constant of solution (Schreckbenberg *et al.* 2014). The improved SAFT-VRE EoS gives good description of properties of both aqueous salt solutions and H₂O – alkanol – salt mixtures. The SAFT-VRE model is capable to predict CO₂ solubilities in aqueous NaCl solution at 323 K without introducing any fitting parameter for the CO₂ – ion cross interactions. However, the representations of CO₂ solubility at other temperatures and in other salt solution or brine were not investigated.

Tan *et al.* (2005) proposed the SAFT1-RPM EoS, which combined the statistical associating fluid theory with mean spherical approximation in the restricted primitive model (RPM). Model parameters of SAFT1-RPM EoS were assigned to salts instead of ions, which make the model difficult to apply to mixed salt solutions. The SAFT1-RPM model was used to study the phase equilibria and densities of CO₂ - H₂O and CO₂ - H₂O - NaCl systems (Ji *et al.*, 2005), but

temperature dependent cross interaction parameters were found to be necessary to correlate the CO₂ solubility.

The ion-based SAFT EoS for aqueous electrolyte solutions, namely SAFT2, was proposed by Tan *et al.* (2006), and it was used to describe single and mixed salt solutions at temperatures and pressures up to 473 K and 1000 bar (Ji and Adidharma, 2007; 2008). Later, Ji and Zhu (2012, 2013) extended the SAFT2 EoS to calculate phase compositions and densities of quaternary H₂S – CO₂ – H₂O – NaCl system, while the ternary CO₂ – H₂O – NaCl system was also well represented using temperature dependent parameters for ions and CO₂ – ion interactions.

Sun and Dubessy (2010, 2012) studied the VLE and PVTx properties of binary CO₂ - H₂O and ternary CO₂ – H₂O – NaCl systems using a Lennard-Jones (LJ) reference SAFT EoS. The SAFT-LJ model provides good representation of CO₂ solubility in salt-free H₂O from 323 to 623 K with a relative deviation to experimental data within 6%. For the ternary CO₂ – H₂O – NaCl system, the SAFT-LJ EoS was coupled with the mean spherical approximation in the restricted primitive model (MSA-RPM) to handle the ion-ion interactions, and the model yields satisfactory calculation of CO₂ solubility (AAD within 3%) and PVT properties over a wide range of temperatures and pressures up to 573 K and 1000 bar. It is noticed that the SAFT-LJ EoS uses a large number of temperature dependent parameters to adjust ion - H₂O, ion - CO₂ and H₂O - CO₂ interactions.

CO₂, H₂O and electrolytes are small molecules with relatively simple molecular structures, and the behavior of the CO₂ – H₂O – electrolyte system is primarily affected by the intermolecular interactions instead of molecular structure. The properties of CO₂ bearing electrolyte solutions are dominated by the long-range Coulomb interactions of ions. An accurate presentation of ion-ion interactions is of great importance to the modeling of CO₂ – H₂O – electrolyte systems. Most of the SAFT-type EoS handle the ion-ion interactions in the primitive model, in which the solvent is treated as a dielectric continuum. The contribution to free energy from the electrostatic interactions is generally approximated by the Debye-Hückel (DH) theory, in which ions are considered as point charges neglecting the excluded volume, or by the integral equation theory such as MSA, in which the ions are treated as charged hard spheres. Maribo-Mogensen *et al.* (2012) have shown that the performance of DH and MSA is similar (MSA reduces to the DH at infinite dilution), and either approach could be adopted in an EoS. This is arguably the reason that all the above mentioned SAFT-like equations of state, which used DH theory or MSA, behave somewhat similar for the modeling of CO₂ solubility in electrolyte solutions. The MSA theory has been extensively used to

study aqueous electrolyte solutions and model the CO₂ sequestration process in brines (Friedman and Dale, 1977; Balashov *et al.*, 2013; Hnedkovsky, L., 2005; Sharygin, 2006).

Recently, Jiang and Adidharma (2015) proposed a modification to the mean spherical approximation in the primitive model, which uses a density-dependent parameter K to correct the excess internal and Helmholtz energies (“KMSA” for short), for a better representation of the ion – ion interactions. By introducing a density dependent parameter K , the representation of excess free energy by MSA is significantly improved, and the KMSA was found to be in agreement with Monte Carlo simulation results, while remaining numerically simple.

In the present work, SAFT2 EoS is coupled with the KMSA to study CO₂ solubility in single and mixed electrolyte solutions, and also in synthetic brines. Instead of using multiple temperature or pressure dependent parameters to achieve accurate correlation of experimental solubility data, we try to explore the predictive capacity of the proposed SAFT2-KMSA model, especially for systems containing multiple electrolytes. With the SAFT2-KMSA model, we study a range of aqueous electrolyte solutions including Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, Br⁻ and SO₄²⁻ from 298.15 to 473.15 K. The CO₂ solubilities in aqueous NaCl, KCl, CaCl₂, MgCl₂, and Na₂SO₄ solutions were calculated. Without any adjustment of parameters for ion-ion interactions, CO₂ solubilities in mixed electrolyte solutions and brines are predicted. To our knowledge, CO₂ solubilities in mixed electrolyte solutions and synthetic brines were not previously studied by any advanced EoS in a predictive manner.

2. Thermodynamic Model

The statistical associating fluid theory is defined in terms of the dimensionless residual Helmholtz energy ($\tilde{a}^{res}$),

$$\tilde{a}^{res} = \tilde{a}^{hs} + \tilde{a}^{disp} + \tilde{a}^{chain} + \tilde{a}^{assoc} + \tilde{a}^{ion} \quad (1)$$

where the superscripts on the right-hand side refer to contributions to free energy from hard sphere, dispersion, chain, association and ion interactions. The SAFT2 model used in this work was originally developed by Adidharma and Radosz (1998), and Tan *et al.* (2006); the detailed expressions for the hard-sphere, dispersion, chain and association terms, and the calculation of thermodynamic properties from the residual Helmholtz energy can be found in the appendix.

H₂O is modeled as an associating molecule with 4 association sites, and the model parameters for H₂O were taken from literature (Tan *et al.* 2006). The model parameters for nonelectrolyte associating components are: number of segment (m), segment volume (v), segment energy for square-well potential (u), width of square-well potential (λ), association energy (ε) and association site volume (κ). Model parameters for nonelectrolyte pure components are obtained by fitting saturated liquid density and vapor pressure of pure fluid. Diamantonis and Economou (2012) have concluded that the self-association of CO₂ has negligible effect on the modeling of binary CO₂ - H₂O system, however the cross association (or solvation) between CO₂ and H₂O may strongly affect the CO₂ solubilities in H₂O. There are two choices for modeling CO₂: a simple non-associating molecule with a binary interaction parameter (k_{ij}) for CO₂ - H₂O dispersive interaction that accounts for the solvation effect, or an associating molecule having explicit cross association with H₂O. It was found that even with the explicit cross association between CO₂ and H₂O, a binary interaction parameter is still necessary to have good representations of VLE properties for CO₂ - H₂O mixture. Therefore, in order to reduce the number of parameters, CO₂ is treated as a non-associating molecule, but the energy for CO₂ - H₂O dispersive interaction is adjusted to the CO₂ solubility data in H₂O (Wiebe and Gaddy 1941; Nakayama *et al.* 1987; King *et al.* 1992; Valtz *et al.* 2004; Yan *et al.* 2011) using a binary interaction parameter k_{ij} according to the expression:

$$u_{ij} = \sqrt{u_i u_j} (1 - k_{ij}) \quad (2)$$

It was found that k_{ij} are also needed for cross interaction between CO₂ and ions in order to represent CO₂ solubility in aqueous electrolyte solutions. Details of these binary interaction parameters will be discussed in Section 3.2.

Ions are considered to be fully dissociated in aqueous solution, and they are modeled as spherical segments ($m = 1$) without association. The electrostatic interactions between ions are handled through the KMSA in the primitive model (Jiang and Adidharma, 2015). A parameter K is introduced into the original MSA formalism to correct the dimensionless excess internal energy ($\tilde{u}^{ion}$),

$$\tilde{u}^{ion} = -\frac{e^2}{4\pi\epsilon_0 k_B T \sum_i \rho_i} \left\{ \Gamma \sum_i \frac{\rho_i z_i^2}{1 + K\Gamma d_i} + \frac{\pi}{2\Delta} \Omega P_n^2 \right\} \quad (3)$$

where Γ is the shielding parameter and the summation runs over all the ions. d_i is the effective ion diameter (hydrated diameter) and ρ_i is the number density of ion i . The calculations of parameters

P_n , Ω , Γ and Δ are the same as the original MSA formalism. The dimensionless excess Helmholtz energy for the ion term is calculated as,

$$\tilde{a}^{ion} = \tilde{u}^{ion} + \frac{\Gamma^3}{3\pi \sum_i \rho_i} \quad (4)$$

The universal parameter K is given by the expression:

$$K = 1 - 0.5786 \times \eta + 0.4825 \times \eta^2 \quad (5)$$

where η is the packing fraction of ions ($\eta = \frac{\rho}{6} \sum_i r_i d_i^3$). The parameter K was obtained by fitting excess internal and Helmholtz energy for an equal-sized, type 1:1 charged hard sphere system at reduced temperature of 0.594, which corresponds to an aqueous solution at room temperature with an ion size of 0.425 Å. The KMSA has been proved to give accurate representation of excess energies for electrolyte system with size- and charge-asymmetry at different temperatures (Jiang and Adidharma, 2015).

3. Parameterization and Results

The model parameters for CO₂ were obtained by fitting the saturated liquid densities and vapor pressure of pure fluid, while ion parameters were regressed to the activity coefficients and liquid densities of aqueous NaCl, KCl, CaCl₂, MgCl₂, Na₂SO₄, K₂SO₄, NaBr and KBr solutions from 298.15 to 473.15 K. Model parameters for pure components are listed in Table 1. H₂O parameters were taken from (Tan *et al.* 2006), while CO₂ parameters were obtained in this work. The width of square well potential (λ) is made dimensionless using the segment diameter.

In order to have transferrable model parameters, we obtained ion parameters by simultaneously fitting activity coefficients and liquid densities data of aqueous NaCl, KCl, CaCl₂, MgCl₂, Na₂SO₄, K₂SO₄, NaBr and KBr solutions from 298.15 to 473.15 K. For a satisfactory representation of activity coefficients over a wide temperature range, the segment volume parameter (v) of anions (Cl⁻, SO₄²⁻ and Br⁻) were made temperature dependent using a third order polynomial,

$$v = b_0 + b_1 \times (T - 298.15) + b_2 \times (T - 298.15)^2 \quad (6)$$

while the remaining of the ion parameters are constant. The coefficients (b_0 , b_1 , and b_2) in Eq. 6 are given in Table 2. The total number of model parameters is significantly reduced compared to previous SAFT models (Ji and Adidharma, 2007, 2008; Sun and Dubessy, 2012; Jiang and Adidharma, 2012) in which all the ion parameters were made to be temperature dependent. The new SAFT model requires fewer adjustable parameters for ions, which indicates the KMSA is a better approach to handle ion – ion interactions than the original MSA. With the parameters in Tables 1 and 2, the activity coefficients and liquid densities of single aqueous electrolyte solutions are calculated, and the average absolute deviation (AAD%) between experimental data and model calculations are listed in Table 3. In addition to the properties of single aqueous solutions, H₂O activities and osmotic coefficients of mixed NaCl + Na₂SO₄ and NaCl + MgCl₂ solutions are predicted.

Table 1. Model parameters for CO₂ and ions.*

Species	m	v (cm ³ /mol)	u/k_B (K)	λ/σ	d (Å)
H ₂ O	1.0	9.8307	311.959	1.5369	-
CO ₂	1.922	7.593	167.188	1.565	-
Na ⁺	1.0	0.200	2036.454	1.659	4.235
K ⁺	1.0	0.205	2422.713	1.978	4.689
Ca ²⁺	1.0	0.334	1489.515	2.210	4.455
Mg ²⁺	1.0	0.203	1086.357	2.016	5.011
Cl ⁻	1.0	Eq. 6	2447.784	1.973	5.429
SO ₄ ²⁻	1.0	Eq. 6	1695.242	1.435	3.516
Br ⁻	1.0	Eq. 6	2262.856	2.135	5.788

* Parameters for H₂O were taken from Tan *et al.* (2006). For H₂O, it is $\varepsilon/k_B = 1481.41$ K and $\kappa = 0.04682$.

Table 2. Coefficients (b_0 , b_1 , and b_2) in Eq. 6.

ions	b_0 (cm ³ /mol)	b_1 (cm ³ /mol/K)	b_2 (cm ³ /mol/K ²)
Cl ⁻	7.631	0.01175	-5.8×10 ⁻⁴
SO ₄ ²⁻	12.718	0.03991	-2.85×10 ⁻⁴
Br ⁻	7.170	0.02024	-2.6×10 ⁻⁴

CO₂ solubilities in single electrolyte solutions are calculated with temperature dependent binary interaction parameter (k_{ij}) for dispersive cross interactions of CO₂ - H₂O and CO₂ - ions,

$$k_{ij} = c_0 + c_1 T \quad (7)$$

with coefficients (c_0 and c_1) listed in Table 4. The k_{ij} were adjusted to the CO₂ solubility data (Wiebe and Gaddy 1941; Nakayama *et al.* 1987; King *et al.* 1992; Valtz *et al.* 2004; Yan *et al.* 2011; Hou *et al.* 2013; Zhao *et al.* 2015b) in H₂O and single-electrolyte solutions, including NaCl, KCl, CaCl₂, MgCl₂ and Na₂SO₄. It is worthy to mention that in the fitting process, all k_{ij} for CO₂-ions interactions were simultaneously adjusted to solubility data in these single-electrolyte solutions in order to have transferrable parameters that can be easily extended to mixed electrolyte solutions and brines. With coefficients listed in Table 4, CO₂ solubilities in NaCl + KCl, KCl + CaCl₂, NaCl + CaCl₂, NaCl + KCl + CaCl₂ solutions and synthetic brines are predicted.

Table 3. % AADs* for activity coefficients (γ) and densities (ρ) of aqueous solutions at 298.15 K – 473.15 K.

Salt	Maximum molality (mol/kg)	AAD% (γ)	AAD% (ρ)	Data source
NaCl	6.0	1.87	0.61	Pitzer <i>et al.</i> 1984.
KCl	5.0	1.93	0.23	Marques <i>et al.</i> 2006; Pabalan and Pitzer, 1988.
CaCl ₂	5.0	1.89	0.46	Holmes <i>et al.</i> 1994; Oakes <i>et al.</i> 1995.
MgCl ₂	3.0	2.31	1.49	Holmes and Mesmer, 1996; Wang <i>et al.</i> 1998.
Na ₂ SO ₄	3.0	2.03	1.11	Phutela and Pitzer, 1986; Holmes and Mesmer, 1986.
K ₂ SO ₄	2.5	2.62	1.14	Holmes and Mesmer, 1986; Palmer <i>et al.</i> 2002.
NaBr	5.0	2.02	1.67	Holmes and Mesmer, 1998; Archer, 1991.
KBr	5.0	2.46	1.78	Holmes and Mesmer, 1998; Abdulagatov and Azizov, 2006.

$$* \text{AAD}(g) = 1 / N \sum_{i=1}^N \left| (g_i^{cal} - g_i^{exp}) / g_i^{exp} \right| \quad \text{AAD}(r) = 1 / N \sum_{i=1}^N \left| (r_i^{cal} - r_i^{exp}) / r_i^{exp} \right|$$

Table 4. Coefficients (c_0 and c_1) in Eq. 7

	$c_0 (-)$	$c_1 (K^{-1})$
CO ₂ - H ₂ O	0.0977	2.61×10^{-4}
CO ₂ - Na ⁺	0.2047	-4.79×10^{-5}
CO ₂ - K ⁺	-0.3970	-1.81×10^{-5}
CO ₂ - Ca ²⁺	-0.0011	1.21×10^{-4}
CO ₂ - Mg ²⁺	-0.0183	1.26×10^{-3}
CO ₂ - Cl ⁻	-0.0249	9.31×10^{-6}
CO ₂ - SO ₄ ²⁻	0.2072	7.17×10^{-4}

4. Discussion

4.1 Aqueous Solution Properties

The model parameters for pure components and ions are given in Table 1. For CO₂, the calculated saturated liquid densities and vapor pressures from 220 to 290 K are in close agreement with experimental data (NIST, 2015) with relative deviations of 1.6% and 1.5%, respectively. Since the temperatures and pressures of interest in this work are generally well above the critical point of CO₂, the performance of this set of parameters with respect to the prediction of density in supercritical region was also tested and a good agreement with experiment data (NIST, 2015) was obtained. The details of these calculations can be found in the supporting information.

Figures 1 and 2 show activity coefficients of aqueous NaCl and K₂SO₄ solutions calculated using the proposed SAFT2-KMSA model. The calculated activity coefficients are in good agreement with experimental data (Pitzer *et al.* 1984; Holmes and Mesmer, 1986), and the effects of temperature and salt concentration on activity coefficients are well correlated by the proposed SAFT2-KMSA model. Calculations with similar accuracy were obtained for other electrolyte solutions, and are not shown here. Figure 3 shows the calculated liquid densities for CaCl₂ solutions, and again excellent agreement between calculation and experimental data (Oakes *et al.* 1995) is observed. Similar representations of liquid densities were also found for other electrolyte solutions and are not shown here.

Figure 1. Activity coefficient of aqueous NaCl solution from 298.5 to 473.15 K. Symbols are experimental data (Pitzer *et al.* 1984) and lines are SAFT2-KMSA calculations.

Figure 2. Activity coefficient of aqueous K_2SO_4 solution from 298.5 to 473.15 K. Symbols are experimental data (Holmes and Mesmer, 1986) and lines are SAFT2-KMSA calculations.

Figure 3. Liquid density of aqueous CaCl_2 solution from 298.5 to 473.15 K. Symbols are experimental data (Oakes *et al.* 1995) and lines are SAFT2-KMSA calculations.

One of the advantages of the proposed SAFT2-KMSA model is that the model parameters are assigned to ions instead of salts, which make the model very convenient to extend to mixed electrolyte solutions. To test the transferability of ion parameters, two mixed salt solutions are studied without using any fitting parameters for ion-ion interactions. Figure 4 shows the activity of H_2O in $\text{NaCl} + \text{Na}_2\text{SO}_4$ solutions. At different $\text{NaCl}/\text{Na}_2\text{SO}_4$ concentration ratios, our model accurately predicts the H_2O activities, and suggests that H_2O activities of this mixed salt solution are not sensitive to the temperature, which is consistent with the experimental data (Marliacy *et al.* 2003). Osmotic coefficients of aqueous $\text{NaCl} + \text{MgCl}_2$ solutions are predicted and shown in Figure 5. In general, the prediction of osmotic coefficients by the model is reasonable, although larger deviations can be found at high salt concentrations. It is noticed that the calculation of osmotic coefficients can be improved by introducing a binary interaction parameter between Na^+ and Mg^{2+} , as shown by Ji and Adidharma (2008). However, our goal is to explore the predictive power of the model rather than having a perfect correlation of experimental data (Wang *et al.* 1997), hence such binary interaction parameter is not used in the current model.

Figure 4. Activity of H₂O in mixed NaCl(1)+Na₂SO₄(2) solutions. Symbols are experimental data (Marliacy *et al.* 2003) and lines are SAFT2-KMSA calculations.

Figure 5. Osmotic coefficient (ϕ) of mixed NaCl + MgCl₂ solutions with the ionic strength (I) of NaCl equals to that of MgCl₂. Symbols are experimental data (Wang *et al.* 1997) and lines are SAFT2-KMSA calculations.

4.2 CO₂ Solubilities in H₂O and Single Electrolyte Solutions

The binary interaction parameters (k_{ij}) given by Eq. 7 with coefficients listed in Table 4 are used in Eq. 2 to calculate the cross interactions for CO₂ - H₂O and CO₂ - ion dispersion interactions. The k_{ij} for CO₂ - H₂O dispersion is fitted to CO₂ solubility data (Wiebe and Gaddy 1941; Nakayama *et al.* 1987; King *et al.* 1992; Valtz *et al.* 2004; Yan *et al.* 2011) in salt-free H₂O from 298 to 413 K, and the k_{ij} for CO₂ - ion dispersion interactions are fitted to CO₂ solubility data (Hou *et al.* 2013; Zhao *et al.* 2015b) in 5 aqueous solutions, including NaCl, KCl, CaCl₂, MgCl₂ and Na₂SO₄.

Equilibrium phase compositions of the binary CO₂ - H₂O mixture at 298, 323 and 413 K are calculated and shown in Figure 6. For the H₂O rich phase, the model calculation is satisfactory compared to the experimental data (Wiebe and Gaddy 1941; Nakayama *et al.* 1987; King *et al.* 1992; Valtz *et al.* 2004; Yan *et al.* 2011). At 298 K, the binary mixture exhibits VLE at low pressures, while the system exhibits liquid-liquid equilibria (LLE) at pressures higher than 6 MPa. The proposed SAFT2-KMSA model successfully captures the transition from VLE to LLE, as seen from the dramatic change of slope for the pressure-composition curve. For the CO₂ rich phase, the calculation agrees well with experimental data at low pressures, while the representation of phase compositions at the LLE region is less accurate. Since H₂O is a strongly polar component whose properties significantly differ from those of CO₂, a CO₂ - H₂O cross interaction parameter optimized to the H₂O rich phase compositions is generally inadequate for calculations of CO₂ rich phase properties, and this has been previously observed by Diamantonis and Economou (2012) with PC-SAFT EoS and Dufal *et al.* (2015) with SAFT-VR Mie EoS. Orozco *et al.* (2014) conducted molecular simulation for CO₂ - H₂O mixture, and suggested that one may need to consider the effect of polarizability in order to accurately represent the equilibrium compositions for both phases. Such effort is beyond the scope of this work and is under investigation. It is worthy to mention that although the cross interaction parameters are adjusted to CO₂ solubility data around or under 40 MPa, the proposed SAFT2-KMSA model can be extended to high-pressure range. Comparing with the model proposed by Duan and Sun (2003) that gives excellent correlation for CO₂ solubility in H₂O under wide range of temperature and pressure conditions, our model gives reasonable prediction for the solubility up to 2000 bar.

Figure 7 shows equilibrium phase compositions for the ternary CO₂ - H₂O - NaCl mixture. The experimental CO₂ solubility data in 2.5 mol/kg NaCl aqueous solution at 323 K and 423 K are used to tune the temperature dependent binary interaction parameter, while the CO₂ solubilities in 4.0

mol/kg NaCl solutions are calculated in a predictive manner. The CO₂ solubilities in aqueous NaCl solution calculated or predicted from the SAFT2-KMSA model agree with the experimental data (Hou *et al.* 2013), and the effect of pressure on the CO₂ solubility is accurately predicted. The SAFT2-KMSA model successfully captures the “salting-out” effect of NaCl on CO₂ solubility. For the vapor phase, the calculated phase compositions are close to experimental measurement, although the CO₂ mole fraction is overestimated by the model.

Figure 6. CO₂ solubility in salt-free H₂O rich phase (left) and H₂O solubility in CO₂ rich phase (right) at 298, 323 and 413 K. Symbols are experimental data (Wiebe and Gaddy 1941; Nakayama *et al.* 1987; King *et al.* 1992; Valtz *et al.* 2004; Yan *et al.* 2011) and lines are SAFT2-KMSA calculations.

Figure 7. CO_2 solubility in aqueous NaCl solutions in terms of molality (left) and mole fraction of H_2O in the vapor phase (right) at 323 K and 423 K. Symbols are experimental data from Hou *et al.* (2013), solid lines are SAFT2-KMSA calculations of CO_2 solubility and vapor phase mole fraction for the ternary CO_2 - H_2O -NaCl mixture, and dashed lines are model calculations of CO_2 solubility and vapor phase mole fraction for the salt-free binary CO_2 - H_2O mixture.

Figure 8 shows CO_2 solubilities in CaCl_2 solutions at 323 K, 423 K, and 150 bar. At 323 K, the calculated CO_2 solubilities are in excellent agreement with experimental data (Zhao *et al.* 2015b). At 423 K, the representation of solubilities at high salt concentration is satisfactory, while the CO_2 solubilities at low salt concentration are underestimated. Similar representation of CO_2 solubilities in aqueous KCl, MgCl_2 , Na_2SO_4 solutions were also found; these results are not shown here but given as supporting information.

Figure 8. CO₂ solubilities in aqueous CaCl₂ solutions at 323 K, 423 K and 15 MPa. Symbols are experimental data (Zhao *et al.* 2015b) and lines are SAFT2-KMSA calculations.

4.3 CO₂ Solubilities in Mixed Electrolyte Solutions and Brines

The proposed model can be conveniently applied to mixed electrolyte solutions and brines without additional parameters to fit. Figure 9 shows the CO₂ solubilities in mixed NaCl + CaCl₂ solutions. The concentrations of NaCl and CaCl₂ are 1.0601 mol/kg and 0.2172 mol/kg, respectively, resulting in an ionic strength of 1.712 mol/kg. As shown in Figure 9, CO₂ solubilities predicted by the model generally agree well with experimental data although minor underestimation of solubilities can be observed at 423 K. Again, no additional adjustable parameters are needed for this mixed electrolyte solution. Figure 10 shows the CO₂ solubilities in NaCl + KCl and KCl + CaCl₂ solutions at 318 K. The mixed solutions have total salt concentrations of 10 wt% and a 1:1 salt concentration ratio. The model underestimates the CO₂ solubilities in both solutions but the agreement between calculation results and experimental data (Liu *et al.* 2011a) is still quite reasonable. The calculation indicates that NaCl + KCl and KCl + CaCl₂ solutions with the same total salt concentration yield similar “salting-out” effect, which is consistent with experimental observation.

CO₂ solubilities in aqueous NaCl + KCl + CaCl₂ solutions are shown in Figure 11. Similar to Figure 10, a reasonable agreement with experimental data (Liu *et al.* 2011a) is demonstrated although some small underestimation of CO₂ solubilities can be found. For these complex mixed electrolyte solutions, model predictions can be improved by fitting k_{ij} between two ions to experimental CO₂ solubility data. However, since our goal is to explore the predictive ability of the proposed SAFT2-KMSA model, which turns out to be reasonable, we do not attempt to use such additional parameter.

Figure 9. CO₂ solubilities in mixed NaCl + CaCl₂ solutions with solution ionic strength $I = 1.712$ mol/kg. Symbols are experimental data (Zhao *et al.* 2015c) and lines are SAFT2-KMSA predictions.

Figure 10. CO₂ solubilities in mixed NaCl + KCl (weight ratio = 1:1) and KCl + CaCl₂ (weight ratio = 1:1) solutions with total salt concentration of 10 wt% at 318 K. Symbols are experimental data (Liu *et al.* 2011a) and lines are SAFT2-KMSA predictions.

Figure 11. CO₂ solubilities in mixed NaCl + KCl + CaCl₂ solutions at 318 K. The total salt concentrations are at 5.0, 10.0 and 14.3 wt%, respectively. The weight concentration ratio of NaCl, KCl and CaCl₂ is 1:1:1. Symbols are experimental data (Liu *et al.* 2011a) and lines are SAFT2-KMSA predictions.

The performance of the SAFT2-KMSA model is further tested by considering CO₂ solubilities in synthetic brines. We studied two sets of synthetic brines, namely A and B, whose CO₂ solubilities were recently measured by Zhao *et al.* (2015c). These synthetic brines contain 7 salt species including NaCl, KCl, CaCl₂, MgCl₂, Na₂SO₄, NaBr and SrCl₂, and the ionic strength are 1.712 mol/kg and 4.984 mol/kg, respectively. The chemical compositions of these brines are given as supporting information. Since the concentration of SrCl₂ is very low in both brines (0.002 mol/kg and 0.008 mol/kg, respectively) and Sr²⁺ is not included in the parameter estimation, the effect of SrCl₂ on CO₂ solubility is neglected. In addition, the binary interaction parameter between CO₂ and Br⁻ is assumed to be 0.0.

Figure 12 shows the CO₂ solubility in synthetic brine A ($I=1.712$ mol/kg). Despite some minor underestimation at 423 K, the solubilities predicted by the model are in close agreement with experimental data (Zhao *et al.* 2015c). Zhao *et al.* (2015c) claimed that the mixed NaCl + CaCl₂ solution can be used as a substitute for studying CO₂ solubility in synthetic formation brine provided that the ionic strengths are the same. A comparison between Figures 9 and 12 shows that the calculated CO₂ solubilities in mixed NaCl + CaCl₂ solution are indeed very similar to those in synthetic brine A.

Figure 13 shows the CO₂ solubilities in synthetic brine B, which has a higher ionic strength ($I=4.984$ mol/kg). The proposed model underestimates the CO₂ solubility at 323 K, while excellent agreements with experimental data can be observed at higher temperatures. Again, no additional fitting parameter is used to adjust the ion – ion interactions. The satisfactory prediction of CO₂ solubilities in these complex synthetic brines suggests that the model parameters are transferrable, and the proposed SAFT2-KMSA model is predictive.

Figure 12. CO₂ solubilities in synthetic brine A ($I = 1.712$ mol/kg) at 323 K, 373 K and 423 K. Symbols are experimental data (Zhao *et al.* 2015c) and lines are SAFT2-KMSA predictions.

Figure 13. CO₂ solubility in synthetic brine B ($I = 4.984$ mol/kg) at 323 K, 373 K and 423 K. Symbols are experimental data (Zhao *et al.* 2015c) and lines are SAFT2-KMSA predictions.

5. Conclusions

The statistical associating fluid theory was used to model CO₂ solubility in H₂O, single- and mixed electrolyte solutions, and brines. The ions considered in this work included Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, Br⁻ and SO₄²⁻. The electrostatic interactions between ions were modeled with an improved mean spherical approximation formalism (KMSA), which was demonstrated to be more suitable for electrolyte systems than the original MSA. The proposed SAFT2-KMSA model was capable to correlate activity coefficients and liquid densities of electrolyte solutions over a wide range of temperature with only temperature-dependent parameters for the volume of anions. The properties of mixed electrolyte solutions, such as H₂O activity or osmotic coefficient, can be reasonably described by the model without ion – ion binary interaction parameters. The CO₂ solubilities in H₂O and single electrolyte solutions were calculated by the proposed model. Temperature dependent binary interaction parameters were used to adjust the dispersion energy for CO₂ - H₂O and CO₂ - ion interactions. The calculations of CO₂ solubilities were accurately extended to the mixed electrolyte solutions and brines without any additional fitting parameter. It was found that the proposed SAFT2-KMSA model gives satisfactory correlation for CO₂ solubility in H₂O and single electrolyte solutions, and shows great predictive power for CO₂ solubility in mixed electrolyte solutions and brines.

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Appendix

The SAFT2 EoS used in this work is expressed in terms of dimensionless residual Helmholtz energy. The reference state of the Helmholtz energy is the ideal gas. The SAFT2 EoS was first proposed by Adidharma and Radosz (1998), and further developed by Tan *et al.* (2005, 2006) to model the aqueous electrolyte solutions. The SAFT2 EoS was designed to model both homosegmented and heterosegmented molecules. To keep the general form of the SAFT2 EoS, all the terms are given in heterosegmented form, although H₂O, CO₂ and ions were modeled as homosegmented molecules in this work.

The hard-sphere contribution to dimensionless residual Helmholtz energy is given as,

$$\tilde{a}^{hs} = \frac{6}{\pi N_{Av} \rho_m} \left[\frac{(\xi_2)^3 + 3\xi_1 \xi_2 \xi_3 - 3\xi_1 \xi_2 (\xi_3)^2}{\xi_3 (1 - \xi_3)^2} - \left(\xi_0 - \frac{(\xi_2)^3}{(\xi_3)^2} \right) \ln(1 - \xi_3) \right] \quad (A1)$$

and

$$\zeta_k = \frac{\pi}{6} N_{Av} \rho_m \sum_i X_i m_i \sum_{\alpha} x_{\alpha} (\sigma_{\alpha})^k \quad (k = 0, 1, 2, 3) \quad (A2)$$

where N_{Av} is the Avogadro number, ρ_m is the molar density, X_i is the mole fraction of component i , m_i is the number of segments of component i (=H₂O, CO₂ or ions), x_{α} is the mole fraction of type α segment in component i . σ_{α} is the diameter of segment α , which is related to the segment volume (v_{α}) as,

$$\sigma_{\alpha} = \left(\frac{6}{\pi} \frac{v_{\alpha}}{N_{Av}} \right)^{1/3} \quad (A3)$$

τ is the closed packing fraction. For homosegmented molecules, component or molecule i has segments of the same type and thus σ_{α} becomes σ_i , and x_{α} is 1.0.

The dispersion term is given as,

$$\tilde{a}^{disp} = \left(\sum_i X_i m_i \right) \left(\frac{1}{k_B T} a_1^{disp} + \frac{1}{(k_B T)^2} a_2^{disp} + \tilde{a}^t \right) \quad (A4)$$

where k_B is the Boltzmann constant, and a_1^{disp} and a_2^{disp} are the first and second order perturbation terms, respectively. The first order term is given as,

$$a_1^{disp} = \sum_a \sum_b x_a x_b a_{1,ab} \quad (A5)$$

$$a_{1,ab} = -4 \frac{\rho}{\epsilon} S_{ab}^3 N_{Av} r_m \frac{0}{0} u_{ab} \left(l_{ab}^3 - 1 \right) g_{ab}^{hs} \left(S_{ab}, V_{3,eff} \right) \quad (A6)$$

The cross interaction between segments α and β is calculated by Lorentz-Berthelot combining rules with binary interaction parameter $k_{\alpha\beta}$,

$$S^{ab} = \frac{1}{2} \left(S^a + S^b \right) \quad (A7)$$

$$u^{ab} = \left(u^a u^b \right)^{0.5} \left(1 - k_{ab} \right) \quad (A8)$$

and

$$l^{ab} = \frac{1}{2} \left(l^a + l^b \right) \quad (A9)$$

$g_{ab}^{hs} \left(S_{ab}, V_{3,eff} \right)$ is the radial distribution function (RDF) of hard-sphere fluid evaluated at the contact distance and at effective reduced density $V_{3,eff}$. The hard-sphere RDF is calculated by the Carnahan-Starling equation as,

$$g_{ab}^{hs} \left(S_{ab}, V_{3,eff} \right) = \frac{1}{1 - V_{3,eff}} + \frac{3 S_a S_b}{S_a + S_b} \frac{V_{2,eff}}{(1 - V_{3,eff})^2} + 2 \frac{S_a S_b}{S_a + S_b} \frac{V_{2,eff}^2}{(1 - V_{3,eff})^3} \quad (A10)$$

$$V_{3,eff} \left(l_{ab}, Z_3 \right) = Z_3 \frac{0}{0} 1 + d \left(l_{ab}, Z_3 \right) \frac{0}{0} \quad (A11)$$

$$d \left(l_{ab}, Z_3 \right) = l_{ab}^{5.397} \left(l_{ab} - 1 \right) \left(1 - 0.59 Z_3 \right) \sum_{m=1}^6 \sum_{n=1}^6 c_{mn} \frac{Z_3^{m-1}}{l_{ab}^{n-1}} \quad (A12)$$

c_{mn} are coefficients and their values can be found elsewhere (Tan *et al.* 2006). The effective reduced variable $V_{2,eff}$ is given as,

$$V_{2,eff} = \frac{Z_2}{Z_3} V_{3,eff} \quad (A13)$$

The second order term is calculated as,

$$a_2^{disp} = \sum_a \sum_b x_a x_b a_{2,ab} \quad (A14)$$

and $a_{2,\alpha\beta}$ is calculated based on $a_{1,\alpha\beta}$,

$$a_{2,ab} = \frac{1}{2} u_{ab} K^{hs} r \frac{a_{1,ab}}{r} \quad (A15)$$

where K^{hs} is the compressibility of a hard-sphere fluid,

$$K^{hs} = \frac{Z_0(1 - Z_3)^4}{Z_0(1 - Z_3)^2 + 6Z_1Z_2(1 - Z_3) + 9Z_2^3} \quad (A16)$$

The truncation correction in Eq. A4 is given by an empirical correlation as,

$$\tilde{a}_t = \sum_{m=2}^5 \sum_{n=1}^2 D_{mn} \left(\frac{u}{k_B T} \right)^m \left(\frac{\eta}{\tau} \right)^n \quad (A17)$$

where D_{mn} are universal constants, whose values can be found in literature (Tan *et al.* 2006). u is the potential depth, which can be evaluated by the van der Waals one-fluid theory,

$$\frac{u}{k_B T} = \frac{\sum_a \sum_b x_a x_b u_{ab} / k_B T}{\sum_a \sum_b x_a x_b v_{ab}} \quad (A18)$$

$$v_{ab} = \frac{1}{2} \left(v_a^{1/3} + v_b^{1/3} \right)^3 \quad (A19)$$

Similar to the hard-sphere term, for homosegmented molecules, the summations over segments in the dispersion term are replaced by the summations over molecules.

The chain term is calculated from the RDF of square-well (SW) fluid at the contact distance,

$$\tilde{a}^{chain} = - \sum_i X_i (m_i - 1) \left[\ln \tilde{g}_i^{SW}(\sigma_{\alpha\beta}) - \ln \tilde{g}_{0,i}^{SW}(\sigma_{\alpha\beta}) \right] \quad (A20)$$

$$\ln \tilde{g}_i^{SW}(\sigma_{\alpha\beta}) = \sum_i B_{\alpha\beta,i} \ln g_{\alpha\beta}^{SW}(\sigma_{\alpha\beta}) \quad (A21)$$

where $g_{\alpha\beta}^{SW}(\sigma_{\alpha\beta})$ is the RDF of square-well segments α and β evaluated at the contact distance,

$\tilde{g}_{0,i}^{SW}(\sigma_{\alpha\beta})$ is $\tilde{g}_i^{SW}$ evaluated at zero density limit, and $B_{\alpha\beta,i}$ is the bond fraction of type $\alpha\beta$ in molecule

of component i . For homosegmented molecules, the bond fraction is 1.0 since there is only one type of bond in the molecules. The RDF of square-well fluid at the contact distance is approximated from that of hard-sphere fluid using a first order perturbation,

$$g_{ab}^{SW}(S_{ab}) = g_{ab}^{hs}(S_{ab}) + \frac{u_{ab}}{k_B T} g_{1,ab}(S_{ab}) \quad (A22)$$

where the RDF of hard-sphere fluid at the contact distance is given as,

$$g_{ab}^{hs}(S_{ab}) = \frac{1}{1 - Z_3} + \frac{3S_a S_b}{S_a + S_b} \frac{Z_2}{(1 - Z_2)^2} + 2 \frac{S_a S_b}{S_a + S_b} \frac{Z_2^2}{(1 - Z_3)^3} \quad (A23)$$

and the first perturbation order term is given as,

$$g_{1,ab}(S_{ab}) = \frac{1}{4u_{ab}} \frac{1}{\rho / 6 \times S_{ab}^3 N_A} \frac{1}{\sum_i X_i m_i} \frac{a_{1,ab}}{r} - \frac{1}{3\zeta \rho / 6 \times S_{ab}^3 N_A} \frac{1}{\sum_i X_i m_i} \frac{a_{1,ab}}{r} \quad (A24)$$

The association term is given as,

$$\tilde{a}^{assoc} = \sum_i X_i \sum_{\alpha} \left[\sum_{A_{\alpha i}} \left(\ln X^{A_{\alpha i}} - \frac{X^{A_{\alpha i}}}{2} \right) + \frac{n(\Gamma_{\alpha i})}{2} \right] \quad (A25)$$

where $n(\Gamma_{\alpha i})$ is the number of association sites on segment α in component i , and $X^{A_{\alpha i}}$ is the mole fraction of component i that is not bonded at side A of segment α . For homosegmented molecules, each molecule has same type of segment, therefore the association is considered between site A in molecule i and site B in molecule j . The summation over all segment types in Eq. A25 is not needed. Since the association term in different version of SAFT EoS is very similar, the details of the association term are not given here and can be found in literature (Adidharma and Radosz, 2001).

The ion-ion interaction is handled by the KMSA formalism in the primitive model (Jiang and Adidharma, 2015). The dimensionless excess internal energy of a charged hard-sphere fluid is corrected by a density dependent parameter K , as given by Eqs. 3 and 4 in the main text. The details of each variables used in Eqs. 3 and 4 are listed below,

$$P_n = \frac{1}{W} \sum_i \frac{r_i d_i z_i}{1 + G d_i} \quad (A26)$$

$$W = 1 + \frac{\pi}{2D} \sum_i \frac{r_i d_i^3}{1 + G d_i} \quad (\text{A27})$$

$$2G = \left\{ \frac{e^2}{\epsilon \epsilon_0 k_B T} \cdot \sum_i r_i \left[\frac{z_i - (\rho / 2D) d_i^2 P_n}{1 + G d_i} \right]^2 \right\}^{0.5} \quad (\text{A28})$$

$$D = 1 - h \quad (\text{A29})$$

$$h = \frac{\rho}{6} \sum_i \bar{a} r_i d_i^3 \quad (\text{A30})$$

where ϵ_0 is the permittivity of vacuum, ϵ is the relative permittivity, z_i is the charge magnitude of ion i . Γ is the shielding parameter, which can be obtained by numerically solving Eq. A28. d_i is the hydrated diameter and ρ_i is the number density of ion i . The excess dimensionless Helmholtz energy and the parameter K are given by Eqs. 4 and 5.

An equation of state can be constructed from the residual Helmholtz energy as,

$$\frac{P}{\rho RT} = 1 + \rho \frac{\partial \tilde{a}^{res}}{\partial \rho} \quad (\text{A31})$$

where ρ is the density of a fluid mixture, and the fugacity coefficient (ϕ_i) of component i in a mixture can be calculated as,

$$\ln \phi_i = \tilde{a}^{res} + \left(\frac{\partial \tilde{a}^{res}}{\partial x_i} \right)_{T, \rho, x_{k \neq i}} - \sum_j x_j \left(\frac{\partial \tilde{a}^{res}}{\partial x_j} \right)_{T, \rho, x_{k \neq j}} + \rho \left(\frac{\partial \tilde{a}^{res}}{\partial \rho} \right)_{T, x} - \ln Z \quad (\text{A32})$$

The activity coefficient ($\gamma_{\pm}$) of a salt solution can be expressed as,

$$g_{\pm} = \frac{\bar{a}_{\pm}^{\infty} f_{\pm}^{\infty}}{\bar{a}_{\pm} f_{\pm}^{\infty}} = \frac{\bar{a}_{\pm}^{\infty} f_{\pm}^{\infty}}{\bar{a}_{\pm} f_{\pm}^{\infty}} \quad (\text{A33})$$

where the superscript ∞ indicates the infinite dilution state, hence the standard state of ions for the calculation of activity coefficient is infinite dilution.

For the calculation of equilibrium phase compositions (x , y), the following system of nonlinear equation is solved,

$$x_i f_i^L - y_i f_i^V = 0 \quad (i = 1, \dots, N) \quad (\text{A34})$$

$$1 \quad \sum_{i=1}^N \hat{a}_i x_i = \sum_{i=1}^N \hat{a}_i y_i = 1 \quad (\text{A35})$$

2 where L indicates the liquid (or H₂O-rich) phase and V indicates the vapor (or CO₂-rich) phase.

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