Multicomponent Equations of State for Electrolytes

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Four equations of state have been implemented and evaluated for multicomponent electrolyte solutions at 298.15 K and 1 bar. The equations contain terms accounting for short-range and long-range interactions in electrolyte solutions. Short range interactions are described by one of the three equations of state, Peng-Robinson, Soave-Redlich-Kwong, or Cubic-Plus-Association (CPA). Long-range interactions are described by either the simplified mean spherical approximation (MSA) solution of the Ornstein–Zernicke equation or the simplified Debye–Hückel term. An optional Born term is added to these electrostatic terms. The resulting electrolyte equations of state were tested by determining the optimal model parameters for the multicomponent test system consisting of H_2O, Na^+, H^+, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}. To describe the thermodynamics of this multicomponent system, ion specific parameters were determined. The parameters in the equations of state were fitted to experimental data consisting of apparent molar volumes, osmotic coefficients, mean ionic activity coefficients, and solid–liquid equilibrium data. The results of the parameter fitting are presented. The ability of the equations of state to reproduce the experimental data is demonstrated. The performance of the equations of state for multi component systems is compared and analyzed in view of the various short-range and long-range terms employed.
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Introduction

Electrolyte solutions are encountered in many natural and industrial processes. In geochemistry, electrolytes influence many processes such as sea water intrusion into fresh water aquifers, the flow of the pollution front of groundwater, and the production of geothermal energy. In many processes such as desalination, wastewater treatment, extractive distillation, fractional crystallization, scale formation in pipe lines and gas scrubbing, understanding the phase equilibrium of systems containing electrolytes is crucial.[1] In biochemical industries, salt concentration is an important factor to purify protein products in protein precipitation processes.[2] In the pharmaceutical industry, it is necessary to understand the behavior of electrolytes in the human body to improve the transport of drugs in the body.[3] In oil and gas production, equilibrium of systems containing electrolytes need to be studied to avoid the formation of gas hydrates, to prevent corrosion, to avoid scaling problems, and to increase the oil recovery.

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Quantum mechanics provide powerful theoretical tools to study electrolyte solutions. While it is intellectually satisfying to derive solution properties from the fundamental theory of Chemistry—the Schrödinger equation—the technical problems involved are formidable.[4] Owing to the large amount of particles, complicated interactions among the particles and the available energy states involved in the system, different approximations have been made to simplify the procedure of solving the N-particle time-independent Schrödinger equation describing the electrolyte solution through mathematical treatment or reasonable physical assumption. Theories at different levels of accuracy lead to different solutions of the equations, both analytically and numerically. If we turn to classical mechanics and introduce some basic assumptions such as equal a priori probability, we can link the quantum mechanical level properties of the electrolyte solution with the macroscopic level thermodynamic properties (e.g. Helmholtz free energy or entropy) through statistical mechanics.[5] The theories derived from statistical mechanics include:

1. Those obtained from solving the Poisson–Boltzmann equation, such as the Debye–Hückel model,[6] and the more complete model derived by Gronwall et al.[7]

2. Those obtained from perturbation theories using Taylor expansion of Helmholtz free energy such as the Barker–Henderson–Leonard method.[8–10]

3. Those obtained from solving the Ornstein–Zernicke equation (OZ) using the integral-equation theories. Examples are the solution of the OZ equation with mean spherical approximation (MSA)[11–13] closure and with hypernetted chain closure.[14]

4. Those focusing on the fluctuation of composition in an open system (fluctuation theory), such as the Kirkwood–Buff equation.[15]

The computer simulation results of the interacting particles from the Monte Carlo method and molecular dynamics method can also be converted into macroscopic thermodynamic properties for comparison with computational results from models or real electrolyte systems.[16,17]

Since the 1920s, empirical equations have been constructed for engineering applications. Significant advances have been made in combining theoretical and empirical approaches to develop engineering models that are less rigorous and theoretical to describe electrolyte solutions. Many different engineering models, either empirical or semiempirical, have been proposed for calculating the thermodynamic properties of electrolyte solutions. There are two kinds of approaches to establish an engineering model, i.e. the excess Gibbs free energy formalism and the residual Helmholtz free energy formalism.

In the excess Gibbs free energy formalism, excess Gibbs free energy is used to derive activity coefficients and the models established through this formalism are called activity coefficient models. In 1973, Pitzer developed a very useful and successful model through extension of the Debye–Hückel (DH) theory,[18] Chen et al. developed the electrolyte NRTL activity coefficient model based on a modification of the NRTL local composition model.[19,20] Sander et al.[21] presented in 1986 an extension of the UNIQUAC model by adding a Debye–Hückel term allowing this extended UNIQUAC model to be used for electrolyte solutions. The model has since been slightly modified by Thomsen et al.[22–24] and it has proven itself applicable for calculations of vapor–liquid–liquid–solid equilibria and of thermal properties in aqueous solutions of electrolytes and nonelectrolytes.

There are some disadvantages of using models formulated through the excess free Gibbs energy formalism. One disadvantage is that the density of the solution cannot be derived from the model itself. Also the pressure dependency of the activity coefficients cannot be calculated directly. In spite of these disadvantages, these models have been applied successfully to geochemical systems and to systems of interest in chemical industry, including multicomponent mixed-solvent electrolytes.

Equations of state (EOS) do not have these disadvantages and they can be established through the residual Helmholtz free energy formalism. However, electrolyte solutions are considerably more difficult to model than most other solutions encountered in engineering applications. Ions are charged particles and the electrostatic interactions between ions and between ions and solvents are different from the dispersive and repulsive forces taken into account by most EOS. These interactions make the electrolyte solution more nonideal than a nonelectrolyte solution even at very low concentrations. Thus, additional Helmholtz free energy terms are needed to describe these interactions in electrolyte solutions. One of the first attempts to develop an EOS for electrolyte solutions was that of Planche and Renon.[25] Several fundamental EOS for electrolyte solutions have been published since, the most notable being the equations of Jin and Donohue,[26–28] Fürst and Renon,[29,30] Wu and Prausnitz,[31] and Myers et al.[32] Significant progress in developing a series of EOS, the statistical associated fluid theory (SAFT), has been achieved since the 1980s.[33] Its strong statistical mechanics theoretical basis and the accuracy of SAFT for a number of different systems made SAFT a very popular EOS in the academic and industrial communities. Recent years SAFT has also been extended to systems containing electrolytes. Galindo and coworkers,[34] Cameretti et al.,[2] Tan et al.,[3] and Liu et al.[35] proposed their electrolyte SAFT EOS. Some details of the above mentioned electrolyte EOS are summarized in Table 1.

From Table 1, it can be seen that all EOS are composed of two types of terms: one nonelectrolyte term, which can be one of the commonly used EOS such as SRK, PR, or SAFT EOS, and one or more electrolyte terms. The electrolyte term is either the different solutions (complete, simplified implicit, and simplified explicit forms) of OZ equation with MSA closure or different kinds of Debye–Hückel terms (complete or truncated) with or without Born term.[36]

Mean ionic activity coefficients, osmotic coefficients, and densities of binary aqueous electrolyte systems are physical properties that have been used to estimate parameters for all electrolyte EOS. Mixed solvent electrolyte systems have been treated by a few authors. Ternary aqueous electrolyte systems have seldom been considered. Vapor–liquid equilibrium (VLE) calculations containing electrolytes were included by some authors, but solid–liquid equilibrium (SLE) calculations for multicomponent electrolyte systems are rarely seen in these papers.

Table 1. Different Equation of States in Literature

Author	Applications	Nonelectrolyte Term	Electrolyte Term	Pure compound Parameter	Interaction Parameter
Jin and Donohue[28–30] (1988, 1991)	1. Mean ionic activity coefficients ($\gamma_{\pm}$) of binary systems of 50 strong electrolytes 2. Vapor–liquid–equilibrium (VLE) of binary systems of four weak electrolytes 3. Solid–liquid–equilibrium (SLE) calculation for ternary, quaternary, and quinary systems	Perturbed–Anisotropic–Chain theory, PACT[28]	1. perturbation expansion term of long–range charge–charge interaction 2. perturbation expansion term of charge–molecule interaction	One adjustable ion specific parameter	None
Fürst and Renon[31] (1993)	1. Osmotic coefficients (Φ) for 28 binary aqueous alkaline and alkaline–earth halide electrolyte solutions at 25°C and 1 bar 2. The representation of experimental Φ for 30 ternary systems without mixing parameters	Modified SRK EOS	1. Simplified Implicit MSA term (primitive model, short as PM) 2. SR2 term	None	One (W_{ij} in the SR2 term, for interactions between cationanion)
Wu and Prausnitz[33] (1998)	1. Predict the solubility of methane in salt–free water and in an aqueous solution NaCl (1 and 4 molal, 125 °C, 100–600 bar) 2. Correlation results of $\gamma_{\pm}$ and water activity for aqueous solution NaCl (25 to 300 °C)	1. Peng–Robinson EOS (PR) 2. Wertheim association term of for associating compound	1. Complete Implicit MSA (PM) 2. Wertheim association term for ion association 3. Born term	One adjustable ion specific parameter	None
Myers, Sandler, and Wood[34] (2002)	1. Correlations for $\gamma_{\pm}$ for 138 aqueous binary electrolyte solutions (25 °C, 1 bar) 2. Correlations for $\gamma_{\pm}$, Φ, densities, and free energies of hydration of seven salts at 25–300 °C and 1 to 120 bar 3. The prediction of Φ for ternary systems, NaCl–LiCl–H_2O (25 °C, 1 bar) and NaCl–$CaCl_2$–H_2O (110 °C, 1.45 bar)	PR EOS with volume translation parameter	1. Simplified explicit MSA (restricted primitive model, short as RPM) 2. Born term	Three adjustable salt specific parameters	One (k_{ij} in PR EOS, for salt and water interactions, used only for salts in applications 2 and NaCl–$CaCl_2$–H_2O in application 3.)
Galindo, G–Villegas, Jackson and Burgess[36] (1999)	1. Nine strong aqueous binary electrolyte systems (vapor pressure, density) 2. One aqueous ternary electrolyte system (LiBr + Lil, vapor pressure)	SAFT–VR EOS	1. Simplified explicit MSA (RPM)	One adjustable ion specific parameter	None
Cameretti, Sadowski and Mollerup[2] (2005)	Vapor pressures and densities of 12 binary electrolyte systems in the temperature range from 5 to 60 °C	PC–SAFT EOS	1. The complete Debye–Hückel term	Two adjustable ion specific parameters	None
Tan et al.[3] (2005)	1. Six aqueous alkali halide solutions ($\gamma_{\pm}$, Φ, vapor pressure and density) at 25 °C 2. One binary system ($\gamma_{\pm}$, Φ, and density) at 25, 50 and 100°C	SAFT EOS	1. Simplified explicit MSA (RPM) and neglect the associations for ions	Four adjustable ion specific parameters	None
Liu et al.[37]	Fifteen binary aqueous alkali halide solutions ($\gamma_{\pm}$, Φ, density) at 25°C	SAFT EOS with a Lennard–Jones potential	1. The low–density expansion of the MSA closure for the nonprimitive model 2. Wertheim term for association of ions and solvent	Two salt specific parameters	None

The goal of this work is to explore the possibility of using an EOS based on ion specific parameters for multicomponent mixtures containing electrolytes and nonelectrolytes and the possibility of reproducing SLE phase diagrams with electrolyte EOS. We would like to evaluate different short-range terms and long-range terms by applying them to a chosen test system.

Model and Theory

General

When constructing EOS we use energy terms describing different interparticle forces. The energy terms are added to account for the total interparticle force. For example, molecular interactions (short-range interactions) can be described by short range terms such as conventional cubic EOS. Long-range electrostatic forces (Coulumbic force) can be taken into account by the Debye–Hückel term or MSA term. Assuming that these different interparticle forces are separable, the corresponding energy terms can be summed to obtain the total energy change.

In this article, we consider four different EOS. Short-range interactions are described by one of the three equations of state: Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), or Cubic-Plus-Association (CPA). Long-range interactions are described by either the simplified MSA terms or the simplified Debye–Hückel term. An optional Born term is added to these electrostatic terms. The terms are discussed in details below.

The nonelectrostatic terms for the electrolyte EOS

Peng–Robinson Term. The Peng–Robinson term used by Myers's et al.[32] in their electrolyte EOS is given by

$$\frac{\Delta A^{\mathrm{PR}}(T,V,\mathbf{n})}{RT} = \frac{an}{2\sqrt{2}bRT}\ln\left(\frac{V+c+(1-\sqrt{2})b}{V+c+(1+\sqrt{2})b}\right) + n\ \ln\left(\frac{V}{V+c-b}\right) \quad (1)$$

In this term, a volume translation parameter c has been introduced for the Peng–Robinson EOS to improve the density calculation. $\mathbf{n}$ is a vector of the mole number of each component of the mixture. The van der Waals one-fluid mixing rules were used in this equation [Eq. (3) below].

SRK Term. The SRK term is given by

$$\frac{\Delta A^{\mathrm{SRK}}(T,V,\mathbf{n})}{RT} = \frac{an}{RTb}\ln\left(\frac{V}{V+b}\right) + n\ \ln\left(\frac{V}{V-b}\right) \quad (2)$$

The mixing rules used here are the van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1-k_{ij}) \quad \text{and} \quad b = \sum_i x_i b_i \quad (3)$$

In Eq. (3) x_i is the mole fraction of component i in the mixture, and k_{ij} is the binary interaction parameter. In the SRK term of CPA EOS[37] a_i is calculated as $a_i = a_i^0\left(1+c_{1,i}\left(1-\sqrt{T_r}\right)\right)$ from the two nonelectrolyte pure compound parameters a_i^0 and $c_{1,i}$. In SRK + DH EOS, a_i for the nonelectrolyte pure compound i, is calculated from its critical property T_c, P_c, and ω.

Association Term. Many polar substances forming hydrogen bonds are of importance to industrial applications. Examples are water, alcohols, amines, acids, and phenols. Species forming hydrogen bonds often exhibit unusual thermodynamic behavior due to association. For systems containing associating compounds, conventional models like cubic EOS (SRK and PR) are often insufficient, especially for multicomponent and multiphase equilibrium. In most electrolyte systems of industrial interest, water is the main solvent and main component. To develop a good EOS for electrolytes, the first requirement is that the EOS describes the phase behavior of water accurately. The SAFT type EOS can fulfill this requirement, for hydrogen-bonding can be accounted for by the Wertheim association term[38,39] in the SAFT model. This term has the following form:

$$\frac{\Delta A^{\mathrm{assoc}}}{RT} = \sum_i n_i \sum_{A_i}\left(\ln X_{A_i} + \frac{1-X_{A_i}}{2}\right) \quad (4)$$

X_{A_i} is the mole fraction of the molecule i not bonded at site A and is defined as:

$$X_{A_i} = \left(1+\rho\sum_j\sum_{B_j} x_j X_{B_j}\Delta^{A_iB_j}\right)^{-1} \quad (5)$$

X_{A_i} is calculated by solving Eq. (5). ρ is the molar density of the mixture.

The association strength parameter is defined as:

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j} \quad (6)$$

where $\Delta^{A_iB_j}$ is the association strength between two association sites A and B belonging to two different molecules i and j, where $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are the association energy and volume of interaction between site A of the molecule i and site B of the molecule j, respectively. The expression $g(\rho)$ is the radial distribution function. Kontogeorgis et al.[40] suggested the following simplified hard-sphere radial distribution function:

$$g(\rho) = \frac{1}{1-1.9y}, \qquad \text{where } y = \frac{b}{4V}. \quad (7)$$

The CPA EOS using Eq. (7) is denoted as simplified CPA. It is the simplified CPA that has been used in this work. Only the self-association of water is considered in this work.

The electrostatic terms of the electrolyte EOS

MSA Term. The additional Helmholtz free energy change due to the electrostatic interaction between ions can be calculated through solution of the OZ equation with mean spherical approximation (MSA) closure. Blum[11] and Blum and Hoye[12] derived the MSA term for the primitive model (PM) in which the solvent is considered as a dielectric continuum and obtained an analytical expression for excess thermodynamic properties including the Helmholtz free energy, activity coefficients, chemical potentials, and osmotic coefficients. It can be shown that the MSA term for the activity coefficients in dilute solution yield values closely analogous to those obtained from DH theory.[13,41]

The expression of the complete implicit MSA term for PM yields an equation set of three coupled implicit equations. The complete MSA term requires solving the implicit screening parameter Γ before it can be used to calculate other thermodynamic properties, i.e. a complicated set of equations that must be solved by an iterative method. The complete MSA term was used by Wu and Prausnitz in their electrolyte EOS.[31] This complete term was not adopted in this work.

Simplified Implicit MSA Term. The analytic results of MSA have been modified and developed to other empirical but widely applicable models by many other researchers. Planche and Renon[25] took into account the short-range forces between neutral solvent molecules in order to get a primitive representation of electrolyte solution. By using the formalism of Blum, they solved the OZ equation and obtained analytical solutions.

This approach was extended and simplified by Fürst and Renon[29] to develop a new equation of state for electrolyte solutions from the Helmholtz free energy containing a nonelectrolyte part and an electrolyte part. In this work, we have implemented their simplified MSA term for PM. The Helmholtz free energy expression for this term is given in Eq. (8).

$$\Delta A_{\mathrm{im}}^{\mathrm{sMSA}}(T,V,\mathbf{n}) = -\frac{e^2 N_A}{4\pi\varepsilon_0\varepsilon}\left(\Gamma\sum_i \frac{n_i z_i^2}{1+\Gamma\sigma_i}\right) + \frac{V\Gamma^3}{3\pi}kT \quad (8)$$

where

$$4\Gamma^2 = \frac{e^2 N_A^2}{\varepsilon_0\varepsilon RT}\sum_i \frac{n_i}{V}\left[\frac{z_i}{1+\Gamma\sigma_i}\right]^2 \quad (9)$$

Γ is the MSA screening parameters. e is the elementary electronic charge, k is the Boltzmann's constant, ε is the relative permittivity of the medium, ε_0 is the vacuum permittivity, z_i is the valence of ionic species i, σ_i is the diameter of ionic species, and T is the absolute temperature. It can be seen that an explicit expression of Γ can not be obtained from Eq. (9). The above simplified implicit MSA term can be reduced to the below simplified explicit MSA term of the RPM used by Myers et al.[32] using a common ion size assumption.

Simplified Explicit MSA Term. Two simplified and explicit MSA terms have been shown to be simple and accurate[42]. One of the simplifications is based on a linear mixing rule for a common effective ion size. The average ion diameter σ can be calculated through various mixing rules and here the conventional linear mixing rule $\sigma = \sum_{\mathrm{ions}} n_i\sigma_i / \sum_{\mathrm{ions}} n_i$ has been adopted. If all ions are assumed to have the same diameter σ (RPM) and combined with the electroneutrality condition, the implicit equation set of the complete MSA reduces to the following explicit expression of the MSA screening parameter:

$$\Gamma = \frac{1}{2\sigma}\left[\sqrt{1+2\sigma\kappa}-1\right] \quad \text{and} \quad \kappa = \left(\frac{e^2 N_A^2}{\varepsilon\varepsilon_0 RTV}\sum_{\mathrm{ions}} n_i Z_i^2\right)^{1/2} \quad (10)$$

κ is the Debye screening length ($\Gamma \to \kappa/2$ at infinite dilution). The expression of the Helmholtz energy from the simplified explicit MSA term turns to be the following simplified expression:

$$\Delta A_{\mathrm{ex}}^{\mathrm{sMSA}} = -\frac{2\Gamma^3 RTV}{3\pi N_A}\left\{1+\frac{3}{2}\Gamma\sigma\right\}, \quad (11)$$

This simplified explicit MSA term is used by Myers et al.[32] in their EOS for electrolytes.

Debye–Hückel Term. To investigate the MSA terms, we compare it with other terms accounting for electrostatic interaction in electrolyte solution. The below truncated DH term commonly seen in thermodynamic textbooks has been chosen for comparison with the simplified MSA terms.

$$\ln\gamma_i^{\mathrm{DH}} = -z_i^2\frac{AI^{1/2}}{1+bI^{1/2}} \quad (12)$$

where I is the molality based ionic strength, calculated as:

$$I = \frac{1}{2}\sum_{i=1}^{N} m_i z_i^2 \quad (13)$$

m_i refers to the molality of ion i.

The parameter b is considered constant equal to 1.50 (kg/mol)$^{[1/2]}$ and the exact A parameter can be calculated as

$$A = \sqrt{2\pi N_A d_0}\left(\frac{e}{\sqrt{4\pi\varepsilon_0\varepsilon kT}}\right)^3 \quad (14)$$

d_0 refers to the density of the solvent in kg/m^3.

Based on table values of the relative permittivity and density of pure water, the A parameter can be approximated in the temperature range 273.15–383.15 K according to Thomsen:[22]

$$A = 1.131 + 1.335\times10^{-3}\times(T-273.15) + 1.164\times10^{-15}\times(T-273.15)^2 \ \mathrm{kg}^{1/2}/\mathrm{mol}^{1/2} \quad (15)$$

In this work we calculate the DH A parameter from Eq. (15). This simplified DH term is independent of pressure and volume. It does not give a contribution to the volume of the solution.

Born Term. The Helmholtz free energy required to charge an ion in a medium with relative permittivity of ε is calculated by the equation proposed by Born.[36]

$$\Delta A_{\mathrm{chg}}^{\mathrm{Born}}(T,V,\mathbf{n}) = \frac{N_A e^2}{4\pi\varepsilon_0\varepsilon}\sum_{\mathrm{ions}}\frac{n_i Z_i^2}{\sigma_i} \quad (16)$$

The free energy required to discharge ions in vacuum is calculated by:

$$\Delta A_{\mathrm{dis}}^{\mathrm{Born}}(T,V,\mathbf{n}) = -\frac{N_A e^2}{4\pi\varepsilon_0}\sum_{\mathrm{ions}}\frac{n_i Z_i^2}{\sigma_i} \quad (17)$$

The Born contribution used here is the same as that in Myers et al.[32], and it provides a means to calculate solvation free energies of ions in water. The aforementioned terms have all been used to construct electrolyte EOS though different combinations.

Expression of the Electrolyte EOS

In this section, we summarize how the above terms are combined for constructing the four EOS investigated in

this paper. We aim at performing phase equilibrium calculation for complex multicomponent electrolyte solutions. Models using salt specific parameters have different sets of parameter values for the common ions contained in different salts. The salt specific parameters for cation and anion of a certain salt are set equal to the same single value. For example, the values of the attraction, covolume and the ion size parameters (a, b, and σ) of MSW EOS for Na^+ are not universal in different sodium salts according to Myers et al.[32] due to their use of salt specific parameters: The values of the attraction parameter a for Na^+ in NaCl and NaBr are 2.4611 and 3.2858 Pa m^6/mol, respectively. The same ion is mathematically treated as different species in different salts. It is possible to conduct solid–liquid phase equilibrium computations for multicomponent systems containing common ions using salt specific parameters. It requires, however, the use of a specially constructed model, like the electrolyte NRTL activity coefficient model.[20] To perform the same type of calculation with a general EOS it is necessary to use ion specific parameters. Ion specific parameters require a simultaneous regression of experimental data, if available, of all possible combination of ions and the ion specific parameters determined in this work are valid and optimized for the six ion test system studied in this article.

Myers, Sandler, and Wood Electrolyte equation of state.[32] In this work the Myers, Sandler, and Wood Electrolyte equation of state (MSW EOS) is used with ion specific parameters rather than the salt specific parameters used by Myers et al.[32] The expression for the total change in Helmholtz free energy to form the electrolyte system is:

$$A(T,V,\mathbf{n})-A^{\mathrm{IGM}}(T,V,\mathbf{n})=\Delta A^{\mathrm{PR}}+\Delta A^{\mathrm{sMSA}}_{\mathrm{ex}}+\Delta A^{\mathrm{Born}}_{\mathrm{dis}}+\Delta A^{\mathrm{Born}}_{\mathrm{chg}} \tag{18}$$

The PR EOS with volume translation parameter was used here as the short-range term. According to Myers et al.,[32] the use of a volume translation parameter c for ions have no significant effect on the properties tested. This was confirmed by our initial tests. Therefore, it was set equal to zero for all ions. In this work, the MSW EOS is used with three adjustable ion specific parameters, the attraction and covolume parameters, a and b, the ion diameter σ and one binary interaction parameter for each species pair.

Modified Myers, Sandler, and Wood Electrolyte EOS (mMSW EOS). This modified equation of state is developed simply for the purpose of comparison between the simplified explicit MSA term (11) and the simplified implicit MSA term (8). The simplified explicit MSA term in MSW EOS is replaced by the simplified implicit MSA term used in Fürst's electrolyte EOS[29,30] to construct the new modified EOS. The rest of the terms in MSW EOS remained unchanged. The modified Myers, Sandler, and Wood electrolyte EOS (mMSW EOS) can be expressed in terms of Helmholtz free energy as follows:

$$A(T,V,\mathbf{n})-A^{\mathrm{IGM}}(T,V,\mathbf{n})=\Delta A^{\mathrm{PR}}+\Delta A^{\mathrm{sMSA}}_{\mathrm{im}}+\Delta A^{\mathrm{Born}}_{\mathrm{dis}}+\Delta A^{\mathrm{Born}}_{\mathrm{chg}} \tag{19}$$

The mMSW EOS is used with the same number of adjustable parameters as the MSW EOS.

The Electrolyte CPA EOS. The CPA EOS has been applied successfully to many systems. It has been shown in the past to be a successful model for phase equilibrium calculations for binary or ternary systems containing water, hydrocarbons, alcohols, and glycols. For nonpolar (non self-associating) compounds CPA reduces to SRK. The CPA EOS is considerably simpler than SAFT and performs as well as SAFT (or even better) for systems containing water. Therefore we would like to extend the SRK based CPA equation to electrolyte systems. Wu and Prausnitz's equation of state[31] is an example of an electrolyte CPA EOS based on the PR EOS. Here we would like to test an SRK based CPA EOS. In this EOS, we just replace the nonelectrolyte term (PR EOS) in mMSW EOS (19) with CPA EOS and the rest remains unchanged. The electrolyte CPA EOS (eCPA EOS) has the following general form.

$$A(T,V,\mathbf{n})-A^{\mathrm{IGM}}(T,V,\mathbf{n})=\Delta A^{\mathrm{SRK}}+\Delta A^{\mathrm{Assoc}}+\Delta A^{\mathrm{sMSA}}_{\mathrm{im}}+\Delta A^{\mathrm{Born}}_{\mathrm{dis}}+\Delta A^{\mathrm{Born}}_{\mathrm{chg}} \tag{20}$$

The eCPA EOS does not have a volume translation parameter. To minimize the number of fitting parameters, the association term is not used for ions and only used to account for the self-association of water. The water–ion cross-association contribution can be accounted for by the hydrated diameters in the MSA term.[3] For the electrolyte systems chosen here ionic association has been neglected. Thus we are using the eCPA EOS with three adjustable ion specific parameters: the attraction and covolume parameters, a and b, the ion diameter, σ; and one binary interaction parameter per species pair.

Debye–Hückel SRK electrolyte EOS. We would like to examine whether or not the performance of an electrolyte EOS is proportional to its complexity. For this reason, a very simple EOS has been developed. It consists of two terms and the expression for Debye–Hückel SRK electrolyte EOS (SRK+DH EOS) is as follows:

$$\ln \gamma^*(T,V,\mathbf{n}) = \ln\ \gamma^{\mathrm{SRK}}(T,V,\mathbf{n}) + \ln\ \gamma^{\mathrm{sDH}}(T,\mathbf{n}) \tag{21}$$

γ^* is the mole-fraction based activity coefficient of a component in a mixture. $\ln\ \gamma^{\mathrm{sDH}}$ is the truncated, simplified Debye–Hückel term in Ref. 12. $\ln\ \gamma^{\mathrm{SRK}}$ is the activity coefficient contribution from SRK EOS. Since the DH term makes no contribution to the system volume, the volume is calculated from the SRK EOS alone. The computational speed of this EOS is much higher than that of the other three EOS.

The SRK+DH EOS has only two ion specific parameters: the attraction parameter a and the covolume parameter b. This equation also has one binary interaction parameter per species pair in SRK term.

The MSW, mMSW, and the eCPA EOS are referred to as "three-parameter EOS" in the following, due to their three ion specific parameters. All of the aforementioned EOSs are summarized in Table 2.

Water parameters

Before the determination of parameters for electrolytes, the parameters for pure water should be determined. In this way, the equations of state can accurately predict the properties of pure water in the limit of infinite dilution concentra-

Table 2. Four Different Electrolyte Equation of States Applied in This Study

Electrolyte EOS	Nonelectrolyte Term	Electrolyte Terms	Pure Compound Parameter	Interaction Parameter
MSW EOS	1. PR EOS with volume translation parameter	1. Simplified explicit MSA 2. Born term	Three adjustable ion specific parameters a, b, σ. Volume translation parameter c is not used for ions.	One (k_{ij} in PR EOS)
mMSW EOS	1. PR EOS with volume translation parameter	1. Simplified implicit MSA 2. Born term	Three adjustable ion specific parameter a, b, σ. Volume translation parameter c is not used for ions.	One (k_{ij} in PR EOS)
eCPA EOS	1. SRK EOS 2. Wertheim association term of for associating compound	1. Simplified implicit MSA 2. Born term	Three adjustable ion specific parameters a, b, σ.	One (k_{ij} in SRK EOS)
SRK+DH EOS	1. SRK EOS	1. Simplified Debye-Hückel term	Two adjustable ion specific parameters a, b in SRK EOS.	One (k_{ij} in SRK EOS)

tion of an aqueous salt solution. Myers et al.[32] provided a set of best-fit temperature dependent parameters (nine parameters) for the PR EOS with a volume translation parameter. This set of parameters results in average relative deviations (abbreviated as ARD) of 0.22 and 0.83%, respectively, for vapor pressure and liquid densities of water over wide temperature (10–374.15°C) and pressure ranges (up to 250 bar). The same set of parameters for water has also been used in the mMSW EOS. Regarding the CPA EOS, Kontogeorgis et al.[40] provided an optimal set of CPA parameters (five parameters) with a 4C association scheme for water by fitting of vapor pressure and density data in the range of the reduced temperature of water from 0.5 to 0.95 and the corresponding water vapor pressure range (personal communication with Kontogeorgis GM). The ARDs of CPA is 0.8% for vapor pressure and 0.5% for liquid densities of water.[43] The SRK EOS simply use the critical properties of water to calculate the attractive parameter a and the covolume parameter b.

The maximum density of water at about 4°C cannot be described by any of the aforementioned EOS, nor can any other state-of-the-art EOS to our knowledge. All in all, the PR EOS with volume translation parameter and the CPA EOS give reliable enough representation of pure water as a basis for aqueous electrolyte solutions. SRK EOS gives a less accurate representation of the properties of water than these two EOS.

The relative permittivity of water (dielectric constant) can be calculated by the nonprimitive model, while PM for electrolyte needs an additional equation to calculate the water relative permittivity externally. Both the DH term and the simplified MSA term from the OZ equation in this paper belong to the primitive models.

The A parameter in the DH term is correlated by a temperature dependent Eq. (15), hence, no external model for the relative permittivity of water is needed in the SRK + DH EOS.

Several empirical equations are available in the literature for calculating the permittivity of water. Fernandez et al.[44] have developed a very accurate 12-parameter model that treat the relative permittivity of pure water as a function of temperature (238–873 K) and density over a pressure range up to 1200 MPa. However, Uematsu and Franck[45] have alternatively developed a simpler 10-parameter model that is valid within 273–1273 K and pressure below 1600 MPa. For this preliminary study, we follow the approach of Myers et al.[32] and use the Uematsu and Franck[45] model to calculate the relative permittivity of water. This also makes the later comparison of different electrostatic terms easier. The Uematsu and Franck model for water relative permittivity is a function of temperature and water density. The pure water density is obtained by an approximation proposed by Myers et al.[32]:

$$d_{H_2O} \approx n_{H_2O} M_{H_2O} / V \tag{22}$$

where n_{H_2O} is the number of moles of water in the solution, M_{H_2O} is the molecular mass of water in kg/mol, and V is the system volume and not the pure water volume. This approximation simplifies the electrolyte EOS and improves calculation speed. Under this approximation, the water permittivity becomes a function of system temperature T, system volume V, and water mole number n_{H_2O}. Therefore, the contribution of partial derivatives of water relative permittivity should be included when deducing the first-order and second-order derivatives of the Helmholtz free energy with respect to T, V, and n_{H_2O}. This approach was used for all the three-parameter EOS in this work.

Thermodynamic Properties

Equations-of-state are often constructed in terms of the Helmholtz free energy. Helmholtz free energy is a function taking system temperature, volume, and composition as its natural independent variables. Experimental data of thermodynamic properties are usually measured and reported as functions of system temperature, pressure, and composition. All thermodynamic properties of a system can be derived from Helmholtz free energy by standard differentiation with respect to its independent variables.

This is accomplished by first calculating the volume V^* of a single liquid phase in the system from the pressure equation at given temperature, pressure, and composition (T, P^*, $\mathbf{n}$), as that of experimental data. The pressure equation is given by

$$P^* = f(T, V^*, \mathbf{n}) = -\left(\frac{\partial A(T, V, \mathbf{n})}{\partial V}\right)_{T,\mathbf{n}}\Bigg|_{V=V^*} \tag{23}$$

Any equation root-finding algorithm (root solver routine) such as bisection methods or Newton-Raphson method can

do the job. Then, substitute the volume V^* into different derivatives of Helmholz free energy to calculate other thermodynamic properties.

The fugacity coefficient of each component in a mixture is an important quantity for phase equilibrium calculation. The fugacity coefficient of a component in a mixture is calculated through the expression in terms of temperature, volume, and composition.

$$\hat{\varphi}_i(T,P^*,\mathbf{n}) = \frac{nRT}{PV}\exp\left(\frac{\partial A^r(T,V,\mathbf{n})}{RT\partial n_i}\right)_{T,V,n_{j\neq i}}\Bigg|_{V=V^*} \tag{24}$$

$A^r(T,V,\mathbf{n})$ is the residual Helmholtz free energy defined as the difference between the total Helmholtz free energy and the ideal gas Helmholtz free energy. It can be calculated using one of the Eqs. (18), (19), or (20).

When conducting phase equilibrium calculation for electrolyte systems, activity coefficients are usually needed. The activity coefficients are derived from fugacity coefficients. The mole-fraction-based activity coefficient of a solvent species in an electrolyte solution is defined as the ratio of the fugacity coefficient of the compound i in the solution to the fugacity coefficient of the pure compound i:

$$\gamma_i(T,P,\mathbf{n}) = \frac{\hat{\varphi}_i(T,P,\mathbf{n})}{\hat{\varphi}_i(T,P,\mathbf{n}_0)}, \quad i \neq \text{ion} \tag{25}$$

$\mathbf{n}_0$ is a vector of the mole number of each component at infinite dilution. The unsymmetric mole fraction based activity coefficient of a solute species (ion) in an electrolyte solution is defined as the ratio of the activity coefficient of the ionic compound i in the solution to the infinite dilution activity coefficient of the ionic compound i:

$$\gamma_i^*(T,P,\mathbf{n}) = \frac{\gamma_i(T,P,\mathbf{n})}{\gamma_i(T,P,\mathbf{n}_0)}, \quad i = \text{ion} \tag{26}$$

The unsymmetric mole fraction based activity coefficient of a solute species tends towards unity at infinite dilution in the pure solvent. The expression for the unsymmetric activity coefficient calculated from the fugacity coefficients is:

$$\gamma_i^*(T,P,\mathbf{n}) = \frac{\hat{\varphi}_i(T,P,\mathbf{n})}{\hat{\varphi}_i(T,P,\mathbf{n}_0)}, \quad i = \text{ion} \tag{27}$$

$\hat{\varphi}_i(T,P,\mathbf{n_0})$ is the infinite dilution fugacity coefficient for solute species.

To compare the calculated values with experimental data presented in literature, it is necessary to convert the mole-fraction-based activity coefficient to molality-based activity coefficient. The molality-based activity coefficient of component i is calculated as

$$\gamma_i^m(T,P,\mathbf{n}) = \left(\sum_{\text{solvent}} x_{\text{solvent}}\right)\gamma_i^*(T,P,\mathbf{n}) \tag{28}$$

Experimental activity coefficient data are usually presented in the form of molality based mean activity coefficients in literature. The molality based mean activity coefficient for a certain dissolved salt is defined as:

$$\gamma_\pm^m = \left[(\gamma_c^m)^{v_c}(\gamma_a^m)^{v_a}\right]^{1/v} \tag{29}$$

where and v_c and v_a are the stoichiometric coefficients of cations and anions in the salt. $v = v_c + v_a$. The subscripts c and a denote cation and anion. The superscript m stands for the molality.

The water activity is an important property of electrolyte solutions. Usually the water activity is expressed as osmotic coefficient. The osmotic coefficient is defined as follows:

$$\Phi = -\frac{n_{\text{solvent}}\ln a_{\text{solvent}}}{v n_{\text{solute}}} \tag{30}$$

n_{solvent} is the mole number of the solvent.

Volumetric properties are also important properties of electrolyte solutions. For electrolyte solutions, the apparent molar volume (abbreviated as AMV) of the salt is often measured directly. The apparent molar volume V_Φ of a salt is defined through the following equation

$$nv = n_{\text{solvent}}v^0_{\text{solvent}} + n_{\text{solute}}V_\phi \tag{31}$$

where v and v^0 are the molar volume of the solution and the molar volume of the pure solvent, respectively.

The apparent molar volume of a salt is more sensitive to model accuracy than density. Very small deviations in the calculated density against experimental data can lead to a large deviation in the predicted apparent molar volume values. Therefore, it is more difficult to fit apparent molar volumes than density. In other words, using experimental data of apparent molar volume in parameter fitting can improve the goodness of fit of density data.

Because of the electroneutrality condition, it is impossible to have two cations or anions in a binary solution. Hence, the need for ion–ion interaction parameters cannot be evaluated from water-single salt systems. This is why we also include experimental data for solid–liquid equilibrium of ternary electrolyte systems in order to evaluate whether binary interaction parameters between cation–cation and anion–anion are needed in the parameter optimization process.

The saturation index of salt can be used for evaluating the accuracy of SLE calculations. It is defined as the activity product of the salt k divided by its solubility product.

$$SI_k = \frac{\Pi_i a_i^{v_i}}{K_k}, \text{ where } a_i = x_i\gamma_i \tag{32}$$

In the later parameter optimization process, binary experimental data such as mean ionic activity coefficient, osmotic coefficient, apparent molar volumes, and binary and ternary SLE experimental data are all used.

The parameter determination for the electrolyte EOS

To determine the model parameters, an objective function was defined. This objective function is presented in Eq. (33). The parameters were determined through a weighted least squares fit. The chosen electrolyte EOS is first used for calculating the selected thermodynamic properties. Then the

Table 3. The Optimized Electrolyte EOS Parameter Values for Six Ions in the Test System Based on Apparent Molar Volume, Mean Ionic Activity Coefficient, and Osmotic Coefficient Experimental Data (The AAD and ARD Values of the Calculated Properties are also Given)

Parameters							AAD†	%ARD‡	
EOS	Ion	A (Pa m^6/mol)	B (cm^3/mol)	σ (m^{-10})	k_{ij}* (water–ion)	Salt	Apparent motor volume (cm^3/mol)	Activity coefficient	Osmotic coefficient
MSW	Na^+	0.87012	7.36070	5.08140		$CaCl_2$	0.44	/	1.78
	Ca^{2+}	0.10938	0.78196	2.46610		NaOH	0.38	1.28	1.11
	H^+	0.20929	5.68740	2.79430		Na_2SO_4	0.73	/	1.14
	Cl^-	3.57920	19.15500	5.95770	−0.56019	NaCl	0.27	0.31	0.42
	SO_4^{2-}	16.38100	30.32000	22.44100	−0.72530	HCl	0.30	0.60	0.46
	OH^-	0.29526	1.93110	8.95210	−4.21910				
mMSW	Na^+	1.31000	8.43310	15.38800		$CaCl_2$	0.48	/	2.23
	Ca^{2+}	0.04246	0.44287	5.39270		NaOH	0.35	1.67	1.31
	H^+	0.38680	6.49010	8.66720		Na_2SO_4	0.62	/	1.24
	Cl^-	3.22090	18.75200	1.81550	−0.59243	NaCl	0.45	1.31	1.15
	SO_4^{2-}	13.89000	28.73500	11.41300	−0.81505	HCl	0.83	0.40	0.27
	OH^-	0.11306	0.96579	3.05520	−6.79020				
eCPA	Na^+	0.92684	8.61080	16.04700		$CaCl_2$	0.56	/	2.16
	Ca^{2+}	0.02000	0.65312	6.13720		NaOH	0.85	1.34	1.27
	H^+	0.02000	4.16140	8.73400		Na_2SO_4	0.25	/	0.43
	Cl^-	0.72390	19.86300	0.87696	−0.82185	NaCl	0.64	1.43	1.25
	SO_4^{2-}	3.68970	32.66000	3.02240	−1.17450	HCl	0.55	0.47	0.34
	OH^-	0.02007	5.95860	0.66376	−9.50000				
SRK+DH	Na^+	0.02668	1.88010			$CaCl_2$		/	3.73
	Ca^{2+}	0.02034	2.19980			NaOH	2.15	7.80	5.16
	H^+	0.02000	2.03540			Na_2SO_4	0.68	/	1.17
	Cl^-	0.03623	1.55880		−1.00030	NaCl	2.01	1.99	1.66
	SO_4^{2-}	0.11775	2.07130		−1.05010	HCl	2.03	0.62	0.36
	OH^-	0.02000	0.40576		−2.48120				

*In the column of water–ion interaction parameters, the interaction parameter values are presented according to the corresponding ion in the ion column.

†Average absolute deviation is fined by following equation: $\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left(\left|x_i^{\text{experiment}} - x_i^{\text{calculated}}\right|\right)$.

‡Average relative deviation is fined by following equation: $\mathrm{ARD}\% = \frac{1}{N}\sum_{i=1}^{N}\left(\left|\frac{x_i^{\text{experiment}} - x_i^{\text{calculated}}}{x_i^{\text{experiment}}}\right|\right) \times 100\%$.

sum of the squares of the residuals (i.e. difference between the calculated results and the corresponding values of experimental data) is calculated.

$$f = \sum_{j=1}^{2}\sum_{i=1}^{N_j}\left(w_j\frac{x_{ij}^{\exp} - x_{ij}^{\mathrm{cal}}}{x_{ij}^{\exp}}\right)^2 + \sum_{i=1}^{N_{\mathrm{AMV}}}\left[w_{\mathrm{AMV}}(V_{\phi,i}^{\exp} - V_{\phi,i}^{\mathrm{cal}})\right]^2 + \sum_{i=1}^{N_{\mathrm{SLE}}}[w_{\mathrm{SLE}}\ln(SI_i)]^2 \quad (33)$$

where x_{ij}^{cal} and $x_{ij}^{\exp}$ are the calculated value and the corresponding experimental value of osmotic coefficient or molal mean ionic activity coefficient. V_Φ is the AMV. SI_i is the saturation index of SLE data point i. w_j is the weight for the data of type j.

The parameter optimization can be unweighted optimization (conventional equal weight optimization) or weighted optimization (put more weight on residuals of one property of interests than others) based on the requirements and experiences. The data used for the parameter estimation are all from the IVC-SEP electrolyte databank (www.ivc-sep.kt.dtu.dk/databank/help.htm).

A gradient method (Marquardt method) and a direct search method (Nelder-Mead simplex search method) for nonlinear least square minimization have been adopted. It was found that an alteration between the two optimization methods yields good results. The Marquardt method has a high convergence speed but often stops at a local minimum when the norm of the gradient becomes zero. The simplex method can help to jump out of the local minimum: it can find another point where the objective function gives a lower value than the previous local minimum, as long as the previous local minimum is not the global minimum. Therefore, the combined algorithm often finds a better minimum than when separately running any of the two methods alone.

Results and Discussion

Aqueous electrolyte solution at 25°C and 0.101325 MPa (binary and ternary systems)

The four electrolyte equations of state were tested by determining the optimal model parameters for the multi component system consisting of water, Na^+, H^+, Ca^{2+}, Cl^-, OH^-, and SO_4^{2-} ions. This multicomponent system has been chosen as the test system.

The parameter regression was performed in three stages using various amounts and types of data:

1. Stage a and stage b: (a) AMV data alone; (b) data for mean ionic activity coefficient plus osmotic coefficient ($\gamma_\pm$ + Φ data).

2. AMV data and data for mean ionic activity coefficient plus osmotic coefficient (short as AMV + $\gamma_\pm$ +Φ),

Table 4. The Optimized Electrolyte EOS Parameter Values for Six Ions in the Test System Based on Apparent Molar Volume, Mean Ionic Activity Coefficient, Osmotic Coefficient and Solid-Liquid Equilibrium Experimental Data. The AAD and ARD Values of the Calculated Properties are also Given

Parameters								AAD*	%ARD*	
EOS	Ion	a (Pa m^6/mol)	b (cm^3/mol)	σ (m^{-10})	k_{ij}^* water-ion	k_{ij}^* ion-ion	Salt	Apparent Molar Volume cm^3/mol	Activity Coefficient	Osmotic Coefficient
						Na^+, OH^-				
MSW	Na^-	1.28860	8.95430	5.21920	0.15705	1.36990	$CaCl_2$	1.63	/	4.29
	Ca^{2+}	0.52778	4.25860	5.43320	1.46570	Ca^{2+}, Cl^-	NaOH	2.20	1.67	0.92
	H^+	0.31489	8.11380	4.19940	0.53501	0.76425	Na_2SO_4	1.69	/	3.79
	Cl^-	2.32510	15.66000	3.05450	−0.81023		NaCl	1.91	3.23	1.12
	SO_4^{2-}	7.46540	22.42500	4.48380	−0.86462		HCl	0.47	1.04	0.65
	OH^-	1.29990	0.02015	4.28390	−0.87093					
						Na^+, OH^-				
mMSW	Na^-	0.61611	4.24450	3.14280	−0.96137	1.95720	$CaCl_2$	1.51	/	4.92
	Ca^{2+}	1.16000	0.02366	5.43760	−1.71680	Ca^{2+}, Cl	NaOH	1.72	1.54	0.78
	H^-	0.09110	3.24410	2.51440	−2.58990	0.26958	Na_2SO_4	2.49	/	1.38
	Cl^-	2.82900	19.96600	5.17690	−0.06265		NaCl	0.85	1.14	0.79
	SO_4^{2-}	6.42600	26.26900	4.29670	0.05702		HCl	0.36	0.92	0.68
	OH^-	0.55749	0.16348	4.57400	0.15437					
						Na^+, OH^-				
eCPA	Na^+	0.72975	9.34160	2.59090	0.44503	1.72450	$CaCl_2$	0.84	/	4.79
	Ca^{2+}	0.20587	0.02303	3.25740	3.42320	Ca^{2+}, Cl	NaOH	0.41	0.85	0.72
	H^+	0.02190	4.79750	2.78590	2.71640	1.32550	Na_2SO_4	1.06	/	3.06
	Cl^-	1.05920	19.54100	4.82610	−1.54680		NaCl	0.99	1.56	1.29
	SO_4^{2-}	2.99870	27.05000	5.11120	−1.47080		HCl	0.98	1.08	1.08
	OH^-	0.84542	0.02185	7.15380	−1.07990					
						Na^+, OH^-				
SRK+DH	Na^-	0.02225	1.37270		0.10808	1.01930	$CaCl_2$	/	/	4.76
	Ca^{2+}	0.02302	0.86771		0.27824	Ca^{2+}, Cl	NaOH	/	1.03	0.79
	H^+	0.02002	1.29900		−0.30135	0.31392	Na_2SO_4	/	/	5.86
	Cl^-	0.04277	2.17850		−0.93610		NaCl	/	2.11	0.86
	SO_4^{2-}	0.12454	2.99330		−1.01860		HCl	/	2.00	1.55
	OH^-	0.02000	0.28546		−1.09550					

*In the column of water–ion interaction parameters, the interaction parameters,the interaction parameter values are presented according to the corresponding ion in the ion column. In the column of ion–ion interaction parameters, above each value the corresponding ion pairs are given.

†Average absolute deviation is fined by following equation: $\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left(\left|x_i^{\text{experiment}} - x_i^{\text{calculated}}\right|\right)$.

‡Average relative deviation is fined by following equation: $\mathrm{ARD}\% = \frac{1}{N}\sum_{i=1}^{N}\left(\left|\frac{x_i^{\text{experiment}} - x_i^{\text{calculated}}}{x_i^{\text{experiment}}}\right|\right) \times 100\%$.

3. AMV data, data for mean ionic activity coefficient, osmotic coefficient, and binary and ternary SLE data.

In all cases, it was attempted to minimize the number of parameters required for a satisfactory prediction of the test system. This was achieved via trial and error.

Stage I: All of the above mentioned four EOS can easily represent either (a) the AMV data or (b) the mean ionic activity coefficient and the osmotic coefficient data exclusively. In the above two cases, no interaction parameters were needed for any of the three-parameter EOS. At least three interaction parameters were needed for the SRK+DH EOS.

Stage II: When any one of the three-parameter EOS is simultaneously fitted to the combined three types of data, i.e. AMV $+ \gamma_{\pm} + \Phi$, it appears to be very difficult to achieve good results without interaction parameters. It is observed that the AMV causes more difficulties for the EOS than $\gamma_{\pm} + \Phi$ during the simultaneous data fitting. The EOS can often give a better representation of the mean ionic activity coefficient and osmotic coefficient than of the AMV data. This is expected, for apparent molar volume is a rather sensitive and strict property. After dozens of careful trials, all four EOS can represent these three types of data when interaction parameters are introduced. The results of the fitted parameters and their ARDs for AMV and mean ionic activity coefficient, osmotic coefficient experimental data are presented in Table 3.

Because of its simplicity, even with interaction parameters the SRK+DH EOS cannot reproduce AMV experimental data as accurate as the other three EOS. The reason is that the DH term does not contribute to the volume. However, SRK+DH EOS is able to provide very accurate results when exclusively fitted to $\gamma_{\pm} + \Phi$ data. Therefore, in the third optimization stage, SRK+DH EOS parameters were not fitted to AMV.

Interestingly, it is observed that not all interaction parameters have the same effect on the data fitting. The anion–water interaction parameters appear to be more influential than other interaction parameters. Even though other interaction parameters such as the ion–ion or cation–water interaction parameters can improve the goodness of fit, they are not as efficient as anion–water interaction parameters. Consequently, all three anion–water interaction parameters have been chosen in the second stage for binary systems and no other interaction parameters are needed.

Generally speaking, the three-parameter EOS behave almost similarly well in describing the test systems in stage

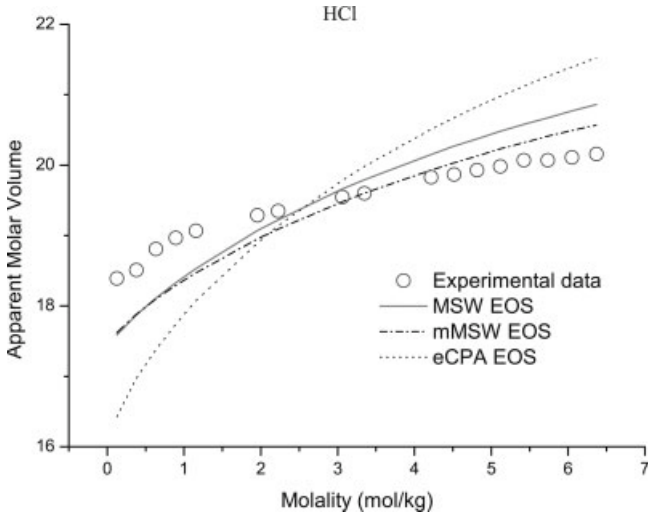

Figure 1. Apparent molar volume (cm^3/mol) of aqueous HCl at 25°C and 0.101325 MPa.

two. The EOS accurately reproduces the mean ionic activity and osmotic coefficient of all solutions over the entire range of concentration. The MSW EOS is slightly better than the mMSW EOS overall and the mMSW EOS is slightly better than the eCPA EOS. As regard to computational time, the differences are quite significant. Generally, the computational speed of eCPA is the lowest due to its Wertheim association terms and the implicit MSA term. Its computation time is approximately 4 times as much as that of MSW EOS. The computation time of mMSW EOS is approximately 2–2.5 times that of MSW EOS. The computational speed of SRK+DH EOS is highest, but the ability of reproducing AMV experimental data is the lowest of the four EOS.

Stage III: In addition to AMV + $\gamma_{\pm}$ + Φ data, binary and ternary SLE data are included in parameter determination. In this stage, the anion–water interaction parameters alone seem to be insufficient for all EOS to fulfill the task. With eight interaction parameters (six ion–water interaction parameters and two ion–ion interaction parameters) the goal could be achieved without much difficulty.

The results of the fitted parameters and their ARDs for AMV and mean ionic activity coefficient, osmotic coefficient experimental data are presented in Table 4. If a certain inaccuracy of density data or AMV can be accepted, the number of interaction parameters can be further reduced without influencing the calculation accuracy of the other three types of experimental data.

In Table 4 it can be seen that the three 3-parameter electrolyte EOS behave similarly well in reproducing AMV + $\gamma_{\pm}$ + Φ data. Generally speaking, the mMSW EOS reproduces the $\gamma_{\pm}$ + Φ data most accurately while eCPA EOS gives the best calculated results of AMV. Combining the AMV and $\gamma_{\pm}$ + Φ data, the eCPA EOS performs slightly better (Table 4). The mMSW EOS is better than MSW EOS but not as good as the eCPA EOS. The SRK+DH EOS gives excellent results. Even though it is a simple EOS, it can still correlate three types of data ($\gamma_{\pm}$ + Φ +SLE) well with fewer parameters than the other EOS. Especially with mean ionic activity coefficient and osmotic coefficient, it is as good as the three-parameter EOS. For some electrolytes, it performs even better than the three-parameter EOS, such as the osmotic coefficient of NaCl. Considering its fast computational speed and its simplicity of implementation, this simple electrolyte EOS is outstanding.

The inclusion of AMV data complicates the parameter fitting and the reproduced AMV results are not as good as other fitted properties. Fitting to AMV data helps to improve the accuracy of the calculated density significantly even when the AMV itself is poorly reproduced. This is illustrated in Figures 1 and 2: The same parameters were used for calculating the two graphs. In Figure 1, the calculated AMV data were plotted together with the experimentally measured AMV data. In Figure 2, the same data were converted to density and plotted as such. Calculated and experimental AMV data for $CaCl_2$ and NaOH solutions are presented in Figures 3 and 4.

From Figure 5–7, we can see that the calculated mean ionic activity coefficients and osmotic coefficients of the four EOS are very close to each other. The same is the case with the remaining systems not shown here.

Overall, it can be seen in Table 4 that the ARDs of the calculated mean ionic activity coefficient and osmotic coefficient are less than 1.6% in general, except for $CaCl_2$ and Na_2SO_4. In contrast, half of the average absolute deviations (AADs) of the calculated AMV are larger than 1.0 cm^3/mol. An ADD value of AMV below 0.8 cm^3/mol indicates a good fitting. It is acceptable if between 1.0 to 1.5 cm^3/mol and it is a poor fitting if larger than 1.8 cm^3/mol. All three-parameter EOS can capture the correct curvatures and trend of AMV and consequently give reasonable solution density. However, it is not recommended to use an EOS if a high precision of the AMV is required.

Of the five electrolyte solutions for which such data were available, the AMV data of aqueous NaOH and Na_2SO_4 solutions appear to be the most difficult to fit. The AADs of calculated AMV of sodium sulfate are large for all the three-pa-

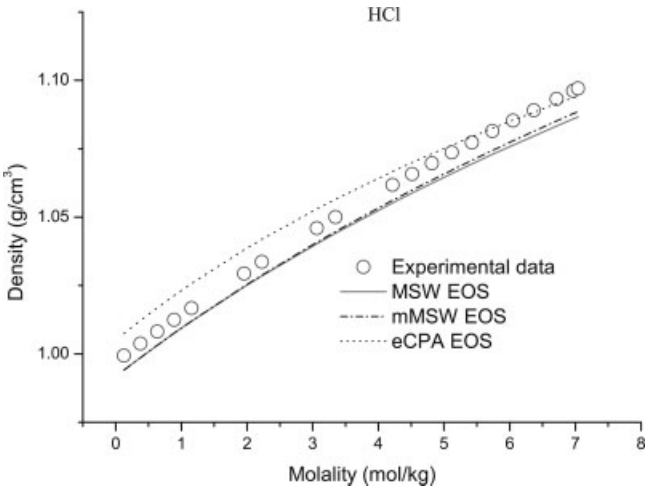

Figure 2. Density (g/cm^3) of aqueous HCl at 25°C and 0.101325 MPa. Calculated with the same set of parameters used to calculate apparent molar volume of aqueous HCl at 25°C and 0.101325 MPa in Figure 1.

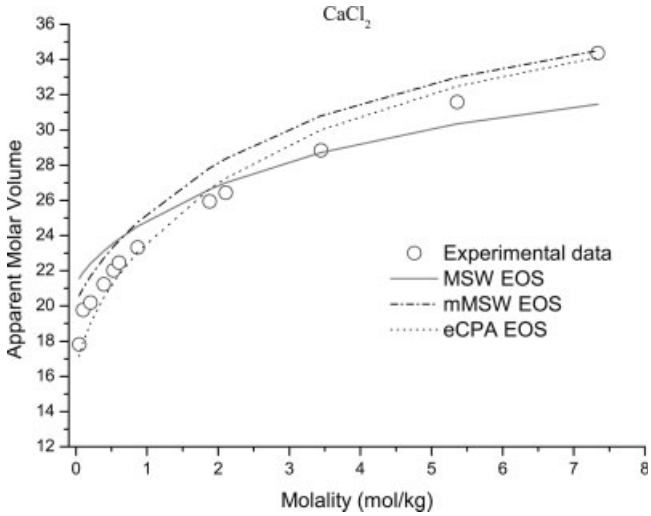

Figure 3. Apparent molar volume (cm^3/mol) of aqueous $CaCl_2$ at 25°C and 0.101325 MPa.

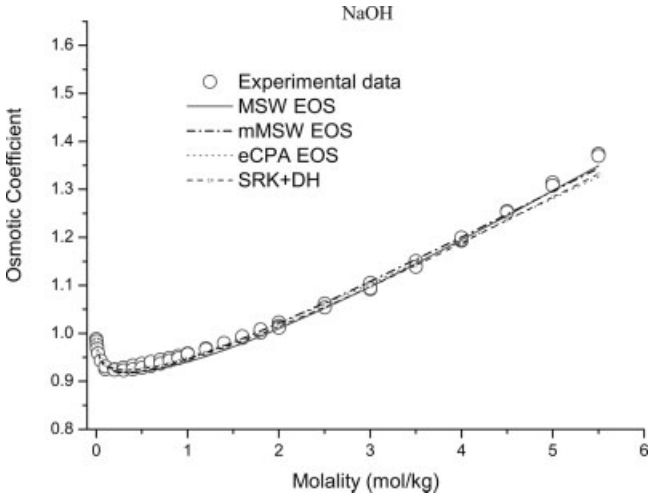

Figure 5. Osmotic coefficient of aqueous NaOH at 25°C and 0.101325 MPa.

rameter EOS. The large absolute values of the interaction parameters *kij* for OH^-–Na^+ in all of the three EOS result from fitting the AMV of sodium hydroxide. If the AMV data of the hydroxide salts are removed in the objective function, the absolute value of *kij* for the OH^-–Na^+ interaction parameter will decrease.

It was found that the interaction parameters influence the activity coefficient and osmotic coefficient most. In this context, the large interaction parameters suggest that the mixing rule may not be adaptive for the fittings of activity and osmotic coefficient in the simultaneous fitting. Using a better mixing rule might result in reduced numerical values of the interaction parameters.

Comparing the ARDs of the calculated mean ionic activity coefficient and osmotic coefficient data (Table 4) and the graphical results, we find that the osmotic coefficients of the various solutions are calculated with great accuracy except for sodium sulfate (Figure 7). The solubility of sodium sulfate is approximately 2 molal at room temperature. When the concentration is higher than 2 molal, the aqueous sodium sulfate solution becomes super-saturated. Figure 7 shows that the ability of electrolyte EOS to represent osmotic coefficient over the super-saturated concentration range (2–5 molal).

$CaCl_2$ solutions have the highest ARDs of the mean ionic activity coefficient and osmotic coefficient of the test systems. It is probably caused by the unique, concave curvature of the osmotic coefficient curve of calcium chloride solution at high concentration (Figure 6). The largest deviation occurs at concentrations higher than 7 molal where the curve starts to bend down when concentration increases. In this concentration range, complex formation starts in $CaCl_2$ solutions[46] and the properties of the solution are changed. SLE data also contribute to the large ARDs of calcium chloride solutions. To obtain accurate predictions of SLE data, the osmotic coefficients at saturation concentration have to be accurately fitted. Therefore, the calculated osmotic coefficient curves are forced to pass the point of

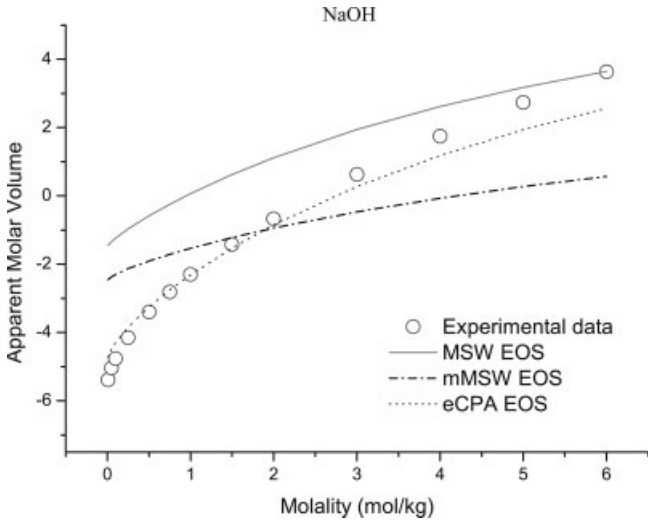

Figure 4. Apparent molar volume (cm^3/mol) of aqueous NaOH at 25°C and 0.101325 MPa.

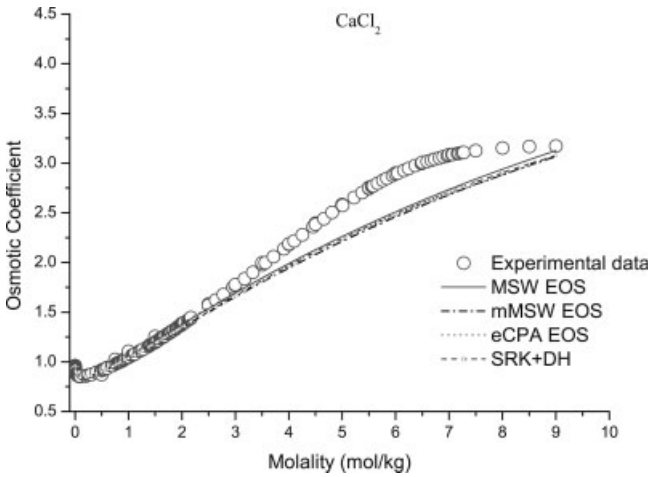

Figure 6. Osmotic coefficient of aqueous $CaCl_2$ at 25°C and 0.101325 MPa.

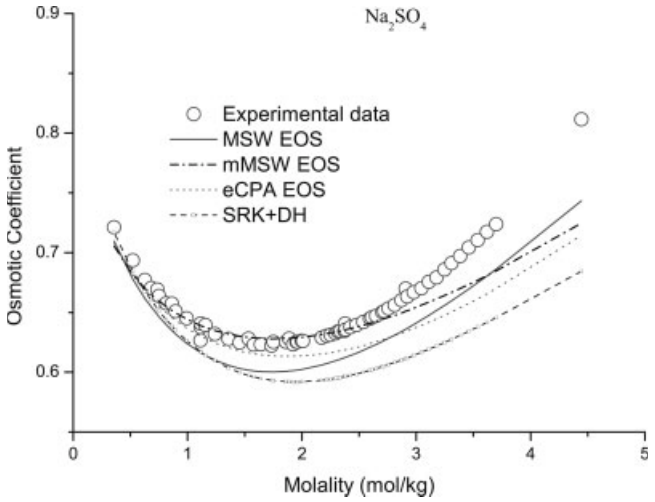

Figure 7. Osmotic coefficient of aqueous Na_2SO_4 at 25°C and 0.101325 MPa.

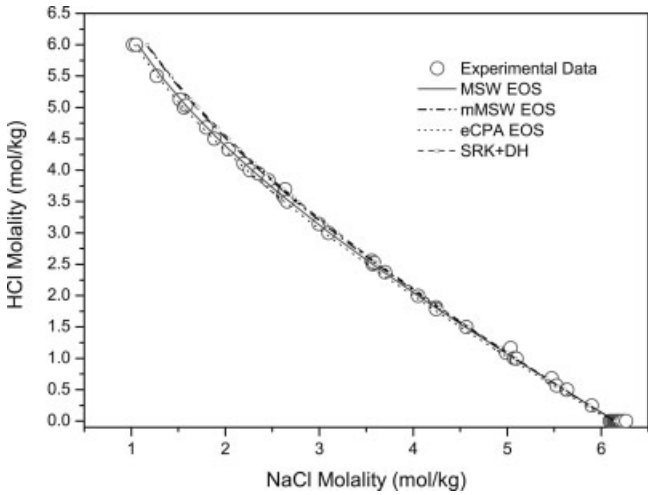

Figure 9. Phase diagram for the ternary aqueous system NaCl and HCl at 25°C and 0.101325 MPa

the osmotic coefficient at saturation concentration (last point in the osmotic coefficient plots) and sacrifice the goodness of fit of the data points from 3 to 9 molal.

The solubilities of $CaCl_2$, $Ca(OH)_2$, Na_2SO_4, NaCl, and $CaSO_4$ at 25°C are all very well reproduced, see the solubility at saturation concentration on the axes of the SLE plots in Figure 8–17. Most SLE data of ternary systems are accurately reproduced, such as the aqueous Na_2SO_4–NaCl, NaCl–HCl, NaOH–NaCl, NaCl–$CaCl_2$,$CaSO_4$–$CaCl_2$, $Ca(OH)_2$–$CaCl_2$. For ternary systems containing electrolytes whose mean ionic activity coefficient and osmotic coefficient data of binary system are poorly fitted (such as calcium chloride and sodium sulfate) or containing electrolytes of low solubility, whose mean ionic activity coefficient and osmotic coefficient data are unavailable in the literature due to the difficulties of measurement (such as calcium sulfate and calcium hydroxide), these ternary SLE data are not very well reproduced. Aqueous Na_2SO_4–$CaSO_4$ and $CaCl_2$–HCl belong to these ternary systems (Figures 13 and 14). Generally speaking all four EOS reproduce the ternary SLE data satisfactorily. For some difficult ternary systems, the three-parameter EOS performs slightly better than the SRK+DH EOS. In most cases, the calculated saturation curves overlap with each other and the difference is hardly perceptible.

Conclusion

1. The EOS for electrolytes considered in this work can be applied to multicomponent systems using ion specific parameters. Apparent molar volume, mean ionic activity coefficient or osmotic coefficient, and solid–liquid equilibrium

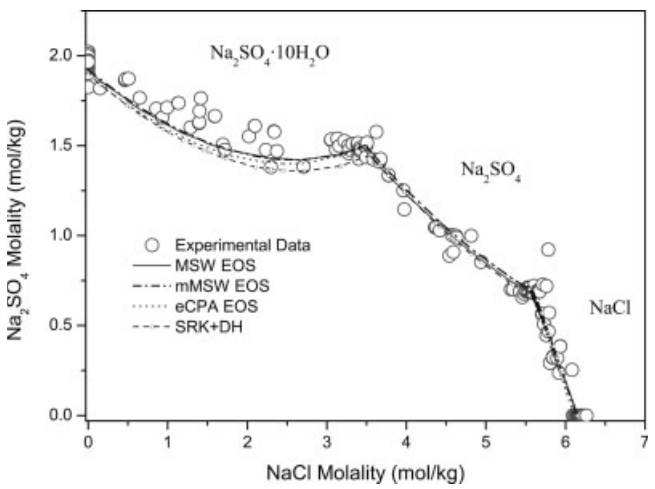

Figure 8. Phase diagram for the ternary aqueous system NaCl and Na_2SO_4 at 25°C and 0.101325 MPa.

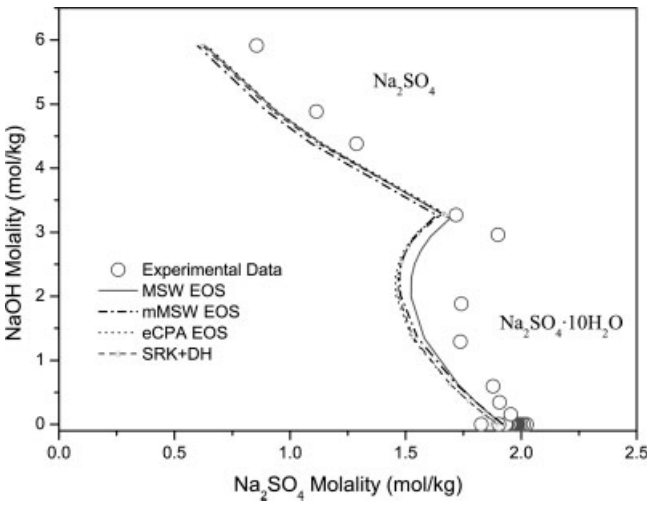

Figure 10. Phase diagram for the ternary aqueous system NaOH and Na_2SO_4 at 25°C and 0.101325 MPa.

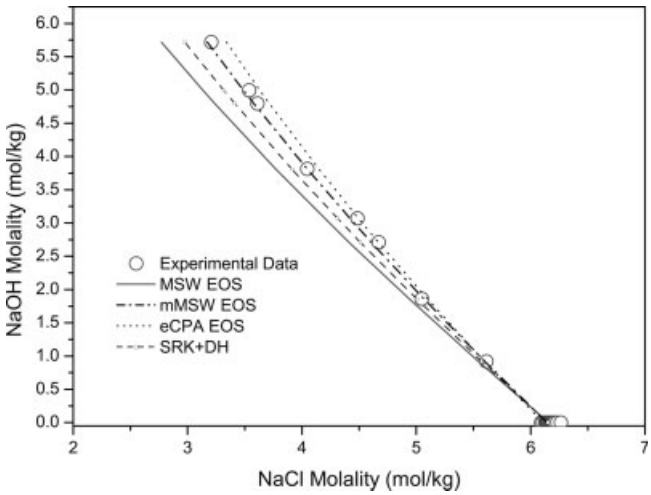

Figure 11. Phase diagram for the ternary aqueous system NaOH and NaCl at 25°C and 0.101325 MPa.

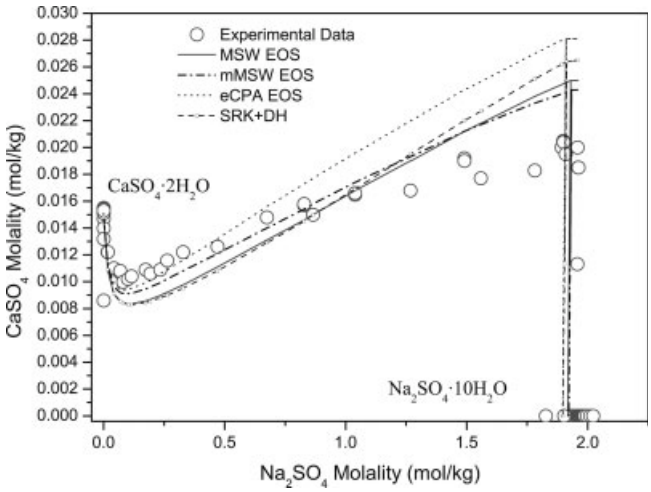

Figure 13. Phase diagram for the ternary aqueous system $CaSO_4$ and Na_2SO_4 at 25°C and 0.101325 MPa.

experimental data can be simultaneously fitted and represented with a small number of interaction parameters. The apparent molar volume of aqueous electrolyte solution is only fitted well by the EOS representing water density accurately and containing an electrostatic term contributing to the volume.

2. The interaction parameter *kij* plays an important role in simultaneous fittings of volumetric data and thermodynamic data. Especially when apparent molar volume is included in the parameter fitting, it can improve the goodness of fit of activity and osmotic coefficient significantly. When the EOS is exclusively fitted to apparent molar volume or exclusively fitted to activity and osmotic coefficient data, the number of interaction parameters can be reduced even to zero.

3. There is no significant difference in the performances of complicated electrolyte terms and simple electrolyte terms according to our studies. The simplified explicit MSA term performs as well as the complicated simplified implicit MSA terms or sometimes even better. However, the simplified explicit MSA term needs only one third or one fourth of the computational time required by the implicit MSA term. The simple, truncated DH term with no parameters performs equally well in reproducing activity coefficients and osmotic coefficients as MSA terms in most cases. Apparent molar volumes are not reproduced well by SRK + DH EOS as the electrostatic term does not contribute to the volume of the solution. Considerable work load in programming can be reduced and the computational

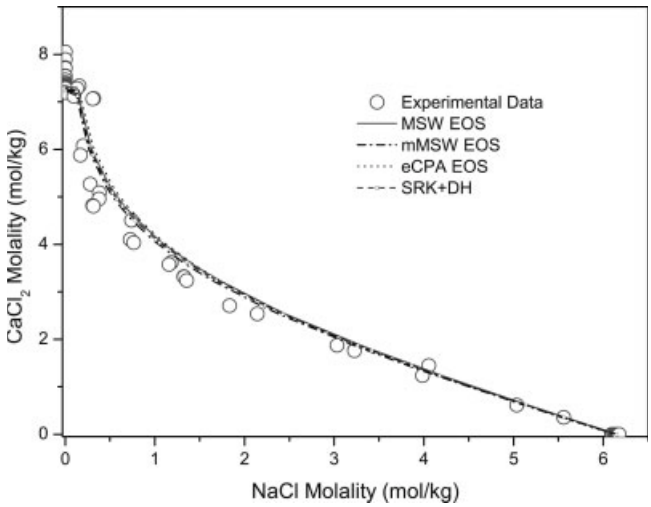

Figure 12. Phase diagram for the ternary aqueous system $CaCl_2$ and NaCl at 25°C and 0.101325 MPa.

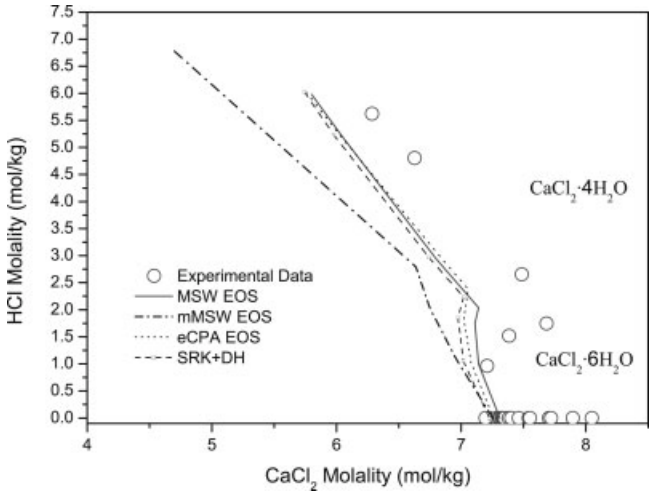

Figure 14. Phase diagram for the ternary aqueous system $CaCl_2$ and HCl at 25°C and 0.101325 MPa.

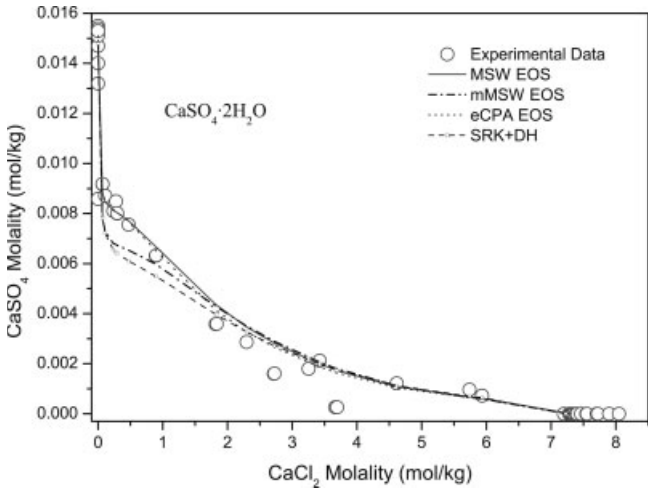

Figure 15. Phase diagram for the ternary aqueous system $CaSO_4$ and $CaCl_2$ at 25°C and 0.101325 MPa.

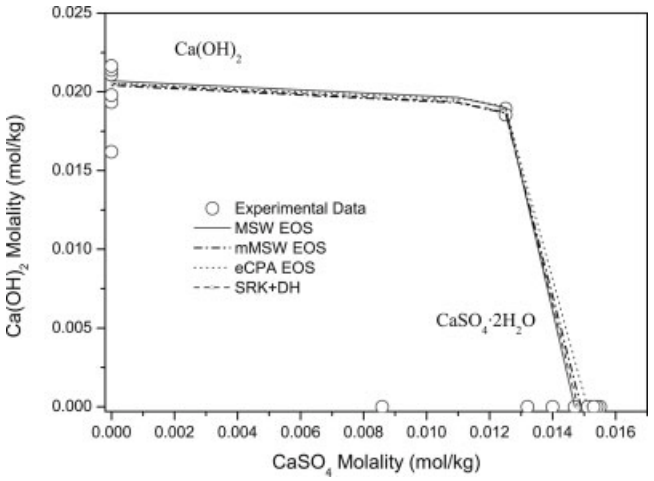

Figure 17. Phase diagram for the ternary aqueous system $CaSO_4$ and $Ca(OH)_2$ at 25°C and 0.101325 MPa.

speed can be increased significantly when the truncated DH term is employed.

4. The difference in performances of the nonelectrolyte terms, i.e. the short range terms of SRK, Peng-Robinson, CPA EOS, is small in general when only applied to the single solvent aqueous electrolyte systems at 25°C and 0.101325 MPa. The CPA EOS consumes two or three times more computation time due to its Wertheim association term compared with other EOS. The performance of these short-range terms can only be evaluated later when extended to multisolvent electrolyte systems.

5. It is expected that models based on physical foundations are more likely to present predictive features. To evaluate an engineering model for its physical foundations, it is important to compare the resulting optimized parameters with the related physical property. This comparison requires a very critical view, since it is clear that the parameters of such engineering models are not directly related to a measurable, physical property. Yet, some trends may be expected. When looking closely at the results of this work, we must conclude that we cannot find any such relationship. Hence, even though the properties could be correctly modeled, we would be very cautious in extrapolating outside the fitting region. More work should be performed on electrolyte EOS in order to improve their physical backgrounds.

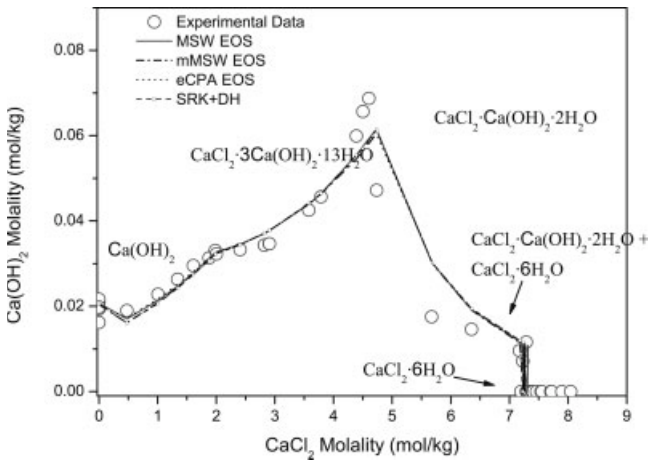

Figure 16. Phase diagram for the ternary aqueous system $CaCl_2$ and $Ca(OH)_2$ at 25°C and 0.101325 MPa.

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Notation

A = Helmholtz free energy
a = van der Waals attraction parameter
a = activity
b = van der Waals excluded-volume parameter
c = volume translation parameter
C = concentration
d_0 = the density of the solvent in kg/m$_3$
e = elementary charge
g = Gibbs free energy
$g(\rho)$ = the radial distribution function
G = Gibbs free energy
I = the molality based ionic strength
K = binary interaction parameter
K = Boltzmann constant
m = molality
M = molecular mass
n = number of moles
N = total number of moles in the system
NA = Avogadro's number
P = pressure
R = gas constant
SI = the saturation index of a salt, equal to the activity product of the salt divided by its solubility product
T = absolute temperature
V = molar volume
V = total volume

V_Φ = apparent molar volume
W = the weight for the data
x = mole fraction
X = mole fraction
Z = compressibility factor
z_i = the valence of ionic species i
Z_i = ion charge number

Greek letters

Δ = the association strength between two association sites belonging in two different molecules
β = the association volume of interaction between two association sites
ε = the association energy of interaction between two association sites
ε = the relative permittivity of the medium
ε_0 = the vacuum permittivity
Φ = the osmotic coefficient
γ = the mole-fraction based activity coefficient of a mixture
Γ = the MSA screening parameters
γ^* = the mole-fraction based activity coefficient of ion i in a mixture
γ^{m} = the molality-based activity coefficient of ionic component i in a mixture
φ = the fugacity coefficient
$\hat{\varphi}$ = the fugacity coefficient of a component in mixture
κ = the Debye screening length
μ = the chemical potential of component i
ν = the sum of stoichoimetric coefficients of all ions in the solution
ρ = the molar density
σ_{I} = the diameter of ionic species

Subscripts

a = anion
c = cation
chg = charge
dis = discharge
Ex = explicit
i, j = species i, j; component i, j; molecule i, j
Im = implicit
MSA = mean spherical approximation
RPM = restricted primitive model
sMSA = simplified mean spherical approximation

Superscripts

0 = pure compound
∞ = infinite dilution
A = association site A of the molecule
assoc = association
B = association site B of the molecule
cal = calculated
exp = experimental
m = molality
r = residual property

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