

Modeling of aqueous electrolyte solutions based on perturbed-chain statistical associating fluid theory incorporated with primitive mean spherical approximation

Bong-Seop Lee and Ki-Chang Kim[†]

Department of Chemical Engineering, College of Engineering, Kangwon National University,
192-1, Hyoja-2 dong, Chuncheon 200-701, Korea

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Abstract—In this work an equation of state applicable to the system containing electrolytes has been developed by coupling the perturbed chain statistical associating fluid theory (PC-SAFT) with the primitive mean spherical approximation. The resulting electrolyte equation of state is characterized by 4 ion parameters for each of the cation and anion contained in aqueous solutions, and 4 ion specific parameters for each of six cations (Li^+ , Na^+ , K^+ , Rb^+ , Mg^{2+} and Ca^{2+}) and six anions (Cl^- , Br^- , I^- , HCO_3^- , NO_3^- and SO_4^{2-}) were estimated, based upon the individual ion approach, from the fitting of experimental densities and mean ionic activity coefficients of 26 aqueous single-salt solutions at 298.15 K and 1 bar. The present equation of state with the estimated individual ion parameters has been found to satisfactorily describe not only the densities and mean ionic activity coefficients, but also osmotic coefficients and water activities of single-salt aqueous solutions. Furthermore, the present model was extended to two-salt aqueous solutions, and it has been found that thermodynamic properties such as mentioned above, of two-salt solutions, can be well predicted with the present model, without any additional adjustable parameters.

Key words: Electrolyte, Electrolyte Equation of State, Individual Ion Parameters, PC-SAFT, Primitive Mean Spherical Approximation

INTRODUCTION

Modeling for thermodynamic properties of aqueous electrolyte solutions is essentially needed for the design of a large variety of important chemical processes, such as waste water treatments, sea water desalinations, extractions and distillations with salting-out effects, and salts-induced biological separations, etc. An inorganic salt dissolved in solvent dissociate into its constituent base ions forming an electrolyte solution, and these ions significantly affect thermodynamic properties of the electrolyte solutions. Since characteristics of thermodynamic properties due to ions dissolved in electrolyte solutions are ascribed to short range solvent-ion interactions as well as long-range interactions among ions, much variety attempts to develop theoretical relations capable of accounting for these interactions of ions have been performed for a long time, and are summarized in several texts and reviews [1-5]. The short range ion-solvent interactions are mainly dominated by electrostatic forces between ions and permanent dipoles of solvent, while long range ion-ion interactions are subject to electrostatic forces between ions. When concentration of ions is dilute in the electrolyte solutions, non-ideal behaviors of electrolyte solutions are mainly influenced by the long range ion-ion interactions, whereas at high electrolyte concentrations short range attractive and repulsive interactions affect the non-ideality of electrolyte solutions. Thus, in modeling electrolyte solutions, non-ideal effects evoked from all of these interactions of ions have to be taken into account.

Up to date, a number of different models have been proposed

for representing the thermodynamic properties of electrolyte solutions. These models are divided into two kinds of approaches, i.e. the excess Gibbs free energy (activity coefficients) approach and the residual Helmholtz free energy or equation of state (EoS) approach. In the excess Gibbs free energy approach (g^E model), activity coefficients are derived from excess Gibbs free energy formalism. For examples of g^E model, Chen et al. [6] extended the NRTL model to correlate activity coefficients of electrolyte solutions, by using the local composition concept. Following the Chen's work, the extensions of their model [7,8] or other models such as the extended UNIQUAC model [9] and Wilson model [10] have been applied to correlate activity coefficients of electrolyte in aqueous solutions. However, excess Gibbs free energy models have the great disadvantage that they are not able to predict densities of electrolyte solutions, and also can not consider the pressure dependency of the activity coefficients. In spite of these disadvantages, these models have been successfully applied to electrolyte solutions until now. Whereas the residual Helmholtz free-energy (or EoS) approach has a merit to overcome these crucial disadvantages of g^E model. In this approach, the residual Helmholtz free-energy or EoS of the electrolyte systems is formulated with the combination of contributions from short range physical interactions of ion-solvent and solvent-solvent, associations or solvations, and long range ion-ion interactions. For the consideration of the short range physical interactions (and associations or solvations), non-electrolyte equations of state such as cubic EoS and equation of state based on the statistical associating fluid theory (SAFT), are commonly used. While for long range ion-ion interactions, after Debye-Hückel theory which was probably the first significant approach, various theories of electrolyte solution have been developed to overcome the limitation of Debye-Hückel theory

[†]To whom correspondence should be addressed.
E-mail: kichang@kangwon.ac.kr

that no longer provides an accurate description of the electrolyte solution at higher concentrations [1]. In the recent most works, the mean spherical approximation (MSA) models such as the restricted primitive model (RPM) or primitive model (PM) [1,11-13] are often used for the modeling of long range ion-ion interactions. The equation of state obtained from the residual Helmholtz free-energy formulated in the electrolyte solution can be applied to predict not only activity coefficients of ions, but also other thermodynamic properties of electrolyte solutions including densities and osmotic coefficients, etc. Several models based upon various types of EoS have been extended to electrolyte solutions since the 1980s [14-17], and details of these models are reviewed in the recent literature [18]. Especially, ever since 2000s, a number of attempts to extend the SAFT [19,20] to electrolyte solutions have been performed. For example, Liu et al. [21] combined the SAFT EoS and the low-density expansion of non-primitive MSA to account for solvent-solvent and ion-solvent associations. Galindo et al. [22] proposed the SAFT-VRE EoS coupled with the RPM to account for long range ion-ion interactions, and Tan et al. [23] and Ji et al. [24] developed the SAFT1-RPM EoS. In addition, Tan et al. [25] presented the SAFT2-RPM EoS in which their SAFT1-RPM EoS is modified to be applicable to the bivalent ions. In particular, Ji and Adidharma [26] developed the ion-based SAFT2 EoS, based on the SAFT2-RPM proposed by Tan et al. [25]. The ion-based EoS is characterized with the individual ion parameters which are applicable to different salts containing the same ion. Thus, when this equation is applied for the multi-salt aqueous solution, the number of parameters related to electrolytes are greatly reduced [27,28]. Carneretti et al. [29] proposed the electrolyte-PC-SAFT (ePC-SAFT) EoS which is developed by the combination of the PC-SAFT EoS [30] and the Debye-Hückel term to take account of the electrostatic ion-ion interactions, and Held et al. [31] also applied the ePC-SAFT EoS for describing thermodynamic properties of several aqueous electrolyte solutions. This equation (ePC-SAFT) can be noted to belong to an ion-based EoS. For other example of the ion-based EoS, Liu et al. [32] developed, apart from the SAFT, the electrolyte EoS which is constructed from the short-range Sutherland potential mapped with the two-Yukawa potential and also incorporated into the first-order MSA, to deal with short-range dispersion interactions of ion-ion, ion-solvent and solvent-solvent. In addition, more recently Kim and Lee [33] presented the electrolyte equation of state based on their own hydrogen-bonding nonrandom lattice fluid theory of which theoretical backgrounds are completely different from that of SAFT.

The purpose of this work is to extend the PC-SAFT EoS [30] to the electrolyte systems. The SAFT model has been developed very rapidly in the recent years, for describing the non-electrolyte systems containing chain-molecules such as polymers. Several models based on SAFT have been proposed [34], and the PC-SAFT EoS is a representative model among these models [35]. Recently, as stated earlier, Held and coworkers [31] described thermodynamic properties of 115 single-salt aqueous solutions using the ePC-SAFT EoS. Their results showed good predictions of densities with overall average relative deviation (ARD) of 0.75% and vapour pressures with overall ARD of 3.29%. However, the overall ARD of mean ionic activity coefficients is 9.17%, which is larger than that of densities or vapour pressures. Also, in view of our preliminary calculations, even though their model [29,31] is able to success-

fully predict densities and vapour pressures of single-salt aqueous solutions, it maybe seems to give rise to more or less larger deviations for reproducing mean ionic activity coefficients.

In this work, focussing on developing a equation of state capable to represent the mean ionic activity coefficients as well as other thermodynamic properties such as densities, water activities and osmotic coefficients in aqueous electrolyte solutions, we attempt to combine the PC-SAFT EoS and the primitive mean spherical approximation (primitive MSA) model for the long range electrostatic interactions between ions. In our model, the hydration effects of ions (cation and anion) specially are taken into account, and four specific parameters are used to characterize each ion. Four ion specific parameters involved in our model are estimated by simultaneously fittings of mean ionic activity coefficients and liquid densities of 26 single-salt aqueous solutions. In addition, our model coupled with estimated ionic parameters is applied for describing osmotic coefficients and water activities of aqueous solutions containing a single salt. Moreover, our model is tested for the performance of predicting thermodynamic properties of two-salt aqueous solutions.

THERMODYNAMIC MODEL

In the aqueous electrolyte solutions, several different types of interactions between chemical species such as ion hydrations, electrostatic interactions among ions and self-associations of water, in addition to the usual hard-core repulsion and attractive dispersion interactions, have an affect on the non-ideal behaviors of solutions. Thus, the successful modeling of electrolyte systems should take into account all of these interactions. However, since procedures or methods to account for all these interactions mentioned above are very complex or difficult, many researchers have taken for a long time an interest in this issue. Wu and Prausnitz [16], through the extension of the Peng-Robinson equation of state to the aqueous electrolyte systems, assumed two hypothetical paths for formation of an electrolyte system, and then constructed the Helmholtz free energy by summing up the separate contributions of each path. After the work of Wu and Prausnitz, Myers et al. [17] proposed the four steps of the path in which an electrolyte solution is formed starting from the reference state assumed to be an ideal gas mixture composed of ions and solvent molecules. According to their proposed path forming an electrolyte system, they developed the extended Peng-Robinson equation of state to be applicable to the electrolyte systems. In addition, their model was applied for describing the mean activity coefficients of 138 aqueous electrolyte solutions, and showed good results.

In this work, to formulate the Helmholtz free energy representation of the aqueous electrolyte solutions, based upon the work of Myers et al. [17], we accept the step I and III of their model, and then modify the step IV to take into account the effects of ions hydrated with water molecules, which were not considered in the Myers's model. Also the step II is partially changed to consider the effects of self-association between the solvent (water) molecules. Details of the step I and III of Myers's model, and those of the step II and IV modified in this work are explained as follows:

- step I. Initially, it is assumed that a reference fluid mixture is an ideal gas mixture composed of charged ions and solvent molecules. For the first step, the charges on all of the ions are removed. The

change in the Helmholtz free energy for discharging the ions is obtained from the Born equation [36] for ions in a vacuum. After all of the ions are discharged, the mixture is taken as an ideal gas mixture of hypothetical neutral ions and solvent molecules.

- step II. The short-range attractive dispersion interactions and repulsive interactions between the neutral chemical species in the mixture are turned on, and also self-association between water molecules are occurred. Then the PC-SAFT model is used to account for the change in the Helmholtz free energy due to this step.

- step III. The neutral ions are recharged. The change in the Helmholtz free energy caused by this step is calculated from the Born equation for ions at infinite dilution in a dielectric solvent.

In the final step, to take into account the hydration effects of charged ions, the step IV is changed as:

- step IV. The charged ions (cations and anions) are hydrated with water molecules, and then the long-range electrostatic interactions between hydrated ions (charged) in the solutions are turned on. In general, the hydration of charged ions can be regarded as the cross-association (or solvation) of charged ions with water molecules. Then the contribution to the Helmholtz free energy of the hydration of charged ions, which is coupled with the self-association of water molecules in the step II, can be obtained from the Wertheim's association formulations [37]. While the long-range electrostatic interactions between hydrated (charged) ions are accounted for by the primitive MSA [12,13].

The total change of the Helmholtz free energy for forming the aqueous electrolyte solution on 4 steps explained above is as follow:

$$A^{res} = A^{discharg} + A^{pc-saft} + A^{charg} + A^{solv} + A^{ele} \quad (1)$$

where the $A^{discharg}$ and A^{charg} are related to the discharging process of ions in the step I and the charging process of neutral ions in the step III, respectively, and the $A^{pc-saft}$ term is the change of the Helmholtz free energy caused by the step II. While the A^{solv} and A^{ele} are the contributions to Helmholtz free energy caused by the hydration of charged ions and the long-range electrostatic interactions of hydrated ions of the step IV, respectively.

Here, the $A^{pc-saft}$ term can be described by the PC-SAFT model [30] such as:

$$A^{pc-saft} = A^{hc} + A^{disp} + A^{self} \quad (2)$$

where the A^{self} term represents the self-association between the water molecules. This term can be combined with the A^{solv} term.

$$A^{assoc} = A^{self} + A^{solv} \quad (3)$$

Then, the A^{assoc} is calculated from the association term of the SAFT model [19,20]. The $A^{discharg}$ and A^{charg} are obtained from the Born equation, and the sum of two terms is expressed as the A^{Born}

$$A^{Born} = A^{discharg} + A^{charg} \quad (4)$$

Finally, the residual Helmholtz free energy of electrolyte solutions can be expressed as follow:

$$A^{res} = A^{hc} + A^{disp} + A^{assoc} + A^{Born} + A^{ele} \quad (5)$$

Here, the hard-sphere chain contribution term, A^{hc} , is expressed as [30]:

$$A^{hc} = A^{hs} + A^{chain} \quad (6)$$

The hard-sphere contribution A^{hs} , chain contribution A^{chain} and dispersive attractive interaction contribution A^{disp} terms can be described based upon the PC-SAFT model. In particular, it is noted that the A^{hs} and A^{disp} terms account for the repulsive hard sphere interactions and dispersive attractive interactions, respectively, which are turned on among neutral species such as solvent, uncharged cation and anion, as explained in the above step II. The equations relating to A^{hs} and A^{disp} terms are summarized in Appendix. The d_{ii} of Eqs. (A2) and (A3) in Appendix is a temperature-dependent segment diameter of component i , and is given by [20,30]

$$d_{ii} = \sigma_{ii} \{1 - 0.12 \exp(-3\varepsilon_{ii}/kT)\} \quad (7)$$

where σ_{ii} and ε_{ii} denote the temperature-independent segment diameter, and the dispersion energy of interaction between segments of chemical species i (solvent, uncharged cation and anion), respectively. In this work, we treat an ion as a single-segmented particle, and then the segment number of ion, m_i , is equal to unity. Also the segment diameter of uncharged ions are assumed to be independent of temperature, namely, $d_{ii} = \sigma_{ii}$. Thus the segment diameter of ion, σ_{ii} , is equivalent to the diameter of uncharged ion i . Therefore, the chain contribution term of Helmholtz free energy, A^{chain}/NkT , refers to only solvents, as the segment number of ion, m_i , is already assumed to be unity, and then is expressed as [19,30]

$$A^{chain}/NkT = x_i(1 - m_i) \ln g_{ii}^{hs} \quad (8)$$

where x_i is the mole fraction of solvent i (water). The g_{ii}^{hs} is the radial distribution function for like segments of solvent i in the hard sphere mixtures, and can be defined from Eq. (A2) in Appendix. Meanwhile, in the dispersion contribution term of Eqs. (A5) and (A6) in which the dispersion interactions of uncharged ion-uncharged ion, uncharged ion-solvent and solvent-solvent are taken into account, the segment diameter and dispersion energy between unlike species are defined as follows:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}), \quad \varepsilon_{ij}/k = \sqrt{\varepsilon_{ii}/k \cdot \varepsilon_{jj}/k}(1 - k_{ij}) \quad (9)$$

where k_{ij} is the binary interaction parameter between segments of the component i and j .

Association term: The A^{assoc} of Eq. (3), which is depicted by the sum of the Helmholtz free energy due to the self-association of water molecules in the step II and that due to the solvation (hydration) of charged ions with water molecules in the step IV, can be described based on the association relation of SAFT [19,20]. In this work, it is assumed that water molecule (component 1) has four association sites: two H sites representing the hydrogen atoms in the water molecule, and two e sites representing the lone pairs of electrons of the oxygen atom. Also the cation (component 2) and anion (component 3) have the number of hydration sites S_2 and S_3 on each ion, respectively. For the mixtures composed of water, charged cations and anions, there are one type of hydrogen bonding (H site-e site) and two types of hydration (cation-e site and anion-H site). In this case, the associating Helmholtz free energy contribution is expressed as [21]:

$$A^{assoc}/NkT = x_1[2\ln X_{1e} - (X_{1e} - 1) + 2\ln X_{1H} - (X_{1H} - 1)] \\ + x_2 S_2 [\ln X_2 - (X_2 - 1)/2] + x_3 S_3 [\ln X_3 - (X_3 - 1)/2] \quad (10)$$

where X_i represents the mole fraction of molecule (or ion) not bonded

at site A. The fractions can be obtained by solving the non-linear relation of equations as follows:

$$X_{1e} = [1 + 2\rho x_1 X_{1H} \Delta_{11} + S_2 \rho x_2 X_2 \Delta_{12}]^{-1} \quad (11)$$

$$X_{1H} = [1 + 2\rho x_1 X_{1e} \Delta_{11} + S_3 \rho x_3 X_3 \Delta_{13}]^{-1} \quad (12)$$

$$X_2 = [1 + 2\rho x_1 X_{1e} \Delta_{21}]^{-1} \quad (13)$$

$$X_3 = [1 + 2\rho x_1 X_{1H} \Delta_{31}]^{-1} \quad (14)$$

where the association strength between site i and j , Δ_{ij} is given by:

$$\Delta_{ij} = \sigma_{ij}^3 g_{ij}^{hs} [\exp(\epsilon_{ij}^{assoc}/kT) - 1] \kappa_{ij}^{assoc} \quad (15)$$

Here ϵ_{ij}^{assoc}/k and κ_{ij}^{assoc} are the association energy and volume parameters between component i and j , respectively. In this work, the ion pairing effects between cation and anion are disregarded, and then ϵ_{23}^{assoc}/k ($=\epsilon_{32}^{assoc}/k$) and κ_{23}^{assoc} ($=\kappa_{32}^{assoc}$) are equal to zero. Also, ϵ_{11}^{assoc}/k and κ_{11}^{assoc} are self-association parameters of pure water. ϵ_{1i}^{assoc}/k ($=\epsilon_{i1}^{assoc}/k$) and κ_{1i}^{assoc} ($=\kappa_{i1}^{assoc}$) are cross-association (hydration) parameters between water molecule (1) and cation or anion ($i=2$ or 3).

Born Contribution term: The A^{Born} term of Eq. (4) is represented from the Born equation, such as [17,36]:

$$A^{Born}/NkT = -\frac{1}{4\pi\epsilon_0 kT} \sum_{ion} \frac{x_i (ez_i)^2}{\sigma_{ii}} + \frac{1}{4\pi\epsilon_0 DkT} \sum_{ion} \frac{x_i (ez_i)^2}{\sigma_{ii}} \quad (16)$$

where the first term of the right hand side is the contribution to the change of Helmholtz free energy for discharging the ions in a vacuum (step I), and the second term is that caused by the recharging process of the neutral ions in the dielectric solvent (step III).

Primitive MSA Contribution term: The first significant work towards the modeling for the electrostatic interactions between the charged particles is probably the Debye-Hückel approach. In the Debye-Hückel theory, ions are assumed to be the point charges in a uniform dielectric medium. But this Debye-Hückel theory is exact only in the limit of infinite dilution, and at higher concentrations of ions, as the size of ions becomes important, no longer provides an accurate description of the electrolyte solution. To deal with the long-range electrostatic interactions between the charged ions in electrolyte solutions, considerable developments have been carried out in statistical mechanics approaches such as molecular simulation, perturbation theory and integral equation theory. Integral equation theory among these approaches has been for a long time interested by many researchers, and this theory has been investigated based on three different approaches [1]: hypernetted chain (HNC), Percus-Yevick (PY) integral equation [38,39], and mean spherical approximation (MSA) [11-13]. Among these approaches, the MSA approach resulted from the solution of Ornstein-Zernicke integral equation is highly representative in the engineering application. Blum and Blum et al. [12,13] have derived the primitive MSA incorporated with the primitive model in which the solvent is assumed to be a continuous medium with specified dielectric constant D . In this work, the A^{ele} denoting the change of Helmholtz free energy for the long-range electrostatic interactions between charged ions in the step IV, is represented from the primitive MSA such as [13]:

$$A^{ele}/NkT = -\frac{\alpha^2}{4\pi\epsilon_0} \left[\Gamma \sum_{ion} \frac{\rho_i z_i^2}{1 + \Gamma d_{hi}} + \frac{\pi}{2\Delta} \Omega P_n^2 \right] + \frac{\Gamma^3}{3\pi\epsilon_0} \quad (17)$$

$$\alpha^2 = \frac{e^2}{DkT} \quad (18)$$

$$\Delta = 1 - \frac{\pi}{6} \sum_{ion} \rho_i d_{hi}^3 \quad (19)$$

$$4\Gamma^2 = \alpha^2 \sum_{ion} \rho_i \left[\frac{z_i - \frac{\pi}{2\Delta} d_{hi}^2 P_n}{1 + \Gamma d_{hi}} \right]^2 \quad (20)$$

where d_{hi} is the hydrated diameter of ion i in the aqueous solution, and the shielding parameter Γ , which has a meaning similar to the inverse screening length of the Debye-Hückel theory, is calculated from the analytical solution of the nonlinear relations of P_n and Ω such as followings:

$$P_n = \frac{1}{\Omega} \sum_{ion} \frac{\rho_i d_{hi} z_i}{1 + \Gamma d_{hi}} \quad (21)$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_{ion} \frac{\rho_i d_{hi}^3}{1 + \Gamma d_{hi}} \quad (22)$$

From the thermodynamic model of Helmholtz free energy in the aqueous electrolyte solutions explained such as above, the equation of state is obtained from the following relation

$$P/\rho kT = \frac{1}{V} \left(\frac{\partial A^{res}}{\partial \rho} \right)_{N,T} \quad (23)$$

and thus represented by the sum of each term for the Helmholtz free energy of Eq. (5), such as:

$$P/\rho kT = P^{hs}/\rho kT + P^{chain}/\rho kT + P^{disp}/\rho kT + P^{assoc}/\rho kT + P^{Born}/\rho kT + P^{ele}/\rho kT \quad (24)$$

where the hard-sphere, chain, dispersion and association terms are explained in detail elsewhere [30], thus they are not shown in this paper, and the Born term $P^{Born}/\rho kT$ is zero, as the Born term of Helmholtz free energy (Eq. (16)) is independent of density. While the electrostatic term is as [13]:

$$P^{ele}/kT = -\frac{\Gamma^3}{3\pi} - \frac{\alpha^2}{8} \left(\frac{P_n}{\Delta} \right)^2 \quad (25)$$

In the application of the present model described above to the single salt aqueous solutions, the present model requires 5 parameters of pure water, and 7 parameters related to each ion (cation and anion), namely, segment number m_i , segment diameter σ_{ii} , dispersion energy ϵ_i/k , hydrated diameter d_{hi} , and hydration relating parameters such as hydration (cross-association) energy ϵ_{1i}^{assoc}/k , hydration volume parameter κ_{1i}^{assoc} , and hydration site number S_i . Parameters of pure water are usually obtained through fittings of saturated vapour pressures and liquid densities data, whereas the determinations of parameters related to ions are more complex than the case of water, since the methods of treating parameters related to ions, in the electrolyte solution, are categorized into two approaches: salt parameter approach and individual ion parameter approach. The salt parameter approach has been often used in the most studies for modeling the equation of state of electrolyte solutions, especially based upon the cubic equation of state. In this approach, the ionic parameters for each of the cation and anion consisting in salt species are set equal to a single value which is treated as a salt parameter. Consequently the electrolyte equation of state is characterized by salt parameters. However, in the works of Galindo et al. [22] and

Cameretti et al. [29] extending the applicability of the SAFT-family equation of state to the electrolyte solutions, the diameter and attractive dispersion energy for each of cations and anions were assumed to be characteristic ion parameters which can be universally adapted for the same ion, regardless of salts containing it. Their models have provided, although they have not been applied for describing the mean ionic activity coefficients, good results for representing the densities and pressures of the electrolyte solutions. Additionally, Tan et al. [23,25] and Liu et al. [21] have clarified that it is desirable to introduce salt parameters besides ion parameters, for representing the mean ionic activity coefficients as well as the densities and pressures of the electrolyte solutions. Recently, in spite of the significant works of Tan et al. and Liu et al., Ji and Adidharma [26] and Liu et al. [32] have revealed the their ion-based EoS incorporated with only all ion parameters without salt parameters yield good descriptions of the mean ionic activity coefficients, densities and osmotic coefficients of the electrolyte solutions. Therefore, in this work, following with the works of Ji and Adidharma [26], and Liu et al. [32] that have adopted the individual ion parameters, ion relating parameters involved in the present model are assumed to be the individual ion parameters which are universally applicable to different salts containing the same ion.

Based upon the our model proposed in this work, the chemical potentials of each components (water, cation and anion) in the aqueous electrolyte solutions is obtained from the general relation such as:

$$\mu_i^{res}(T, V)/kT = \frac{1}{V} \left(\frac{\partial A^{res}/kT}{\partial N_i} \right)_{T, N_{i \neq k}} = \mu_i^{hs}/kT + \mu_i^{chain}/kT + \mu_i^{disp}/kT + \mu_i^{assoc}/kT + \mu_i^{Born}/kT + \mu_i^{ele}/kT \quad (26)$$

where μ_i^{hs} , μ_i^{chain} , μ_i^{disp} and μ_i^{assoc} are explained in detail elsewhere [30]. The Born term and electrostatic term are obtained from Eq. (16) and (17), respectively, such as:

$$\mu_i^{Born}/kT = -\frac{1}{4\pi\epsilon_0 kT} \left(1 - \frac{1}{D} \right) \frac{(e z_i)^2}{\sigma_{ii}} \quad (27)$$

$$\mu_i^{ele}/kT = -\frac{\alpha^2}{4\pi} \left[\frac{\Gamma z_i^2}{1 + \Gamma d_{hi}} + \eta d_{hi} \left[\frac{2z_i - \eta d_{hi}^2}{1 + \Gamma d_{hi}} + \frac{\eta d_{hi}^2}{3} \right] \right] \quad (28)$$

Thus, activity coefficients of cations and anions to be suitable for the unsymmetric condition ($m_i \rightarrow 0$, $\gamma_i = 1$) are expressed as the following [40]:

$$\gamma_i = \frac{V_{m_i \rightarrow 0}^{I, \infty}}{V^I} \exp \left[\frac{\mu_i^{res}(T, V) - \mu_i^{res, \infty}(T, V)_{m_i \rightarrow 0}}{kT} \right] \quad (29)$$

In addition, the mean ionic activity coefficient is as:

$$\gamma_{\pm} = (\gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)} \quad (30)$$

where γ_{\pm} is the activity coefficient based on the mole fraction scale, and is converted into the activity coefficient in the molality scale,

such as [41]:

$$\gamma_{\pm}^{(m)} = \gamma_{\pm} / (1 + 0.001 \nu m M_w) \quad (31)$$

where ν is summation of ν_+ and ν_- . Also, the activity coefficient of solvent (water) is defined as:

$$\gamma_w = \frac{V^{I, o}}{V^I} \exp \left[\frac{\mu_w^{res}(T, V) - \mu_w^{res, o}(T, V)}{kT} \right] \quad (32)$$

and the osmotic coefficient of electrolyte solutions is expressed as:

$$\phi = -\frac{1000}{\nu m M_w} \ln(\gamma_w x_w) \quad (33)$$

RESULTS AND DISCUSSION

For applying the present model proposed in the earlier section to the description of thermodynamic properties of single-salt aqueous solutions, it is first necessary to determine the parameters of present model: 5 parameters for the solvent (water) and 7 parameters for each ion (cation and anion). Parameters of water are equivalent to characteristic parameters of PC-SAFT EoS for the pure water. Hence, parameters of water, as usually determining parameters of the non-electrolyte EOS, were estimated from simultaneously fittings of the saturated vapour pressure and saturated liquid density data [42] at temperatures ranging from 278 K to 383 K. The estimated five parameters and fitting results are listed in Table 1. As shown in Table 1, the fitting results are satisfactory. ARDs for saturated liquid densities and vapour pressures are 0.214% and 0.246%, respectively.

In the case of ions, to reduce a number of parameters related to ions, the association (hydration) volume parameter of ion, κ_{li}^{assoc} is assumed to be 0.001 for all ions [16,21], and the number of hydration (association) site on each ion, S_i also is set to a fixed value (details mentioned hereafter). Consequently, individual ion parameters for each ion get to be 4: σ_{ii} , ϵ_{ii}/k , d_{hi} , and ϵ_{li}^{assoc}/k , as the ion is already assumed as a single-segmented particle ($m_i=1$) in the earlier section. These parameters can be determined from the fitting of thermodynamic properties of electrolyte solutions such as densities, pressures or osmotic coefficients, and mean activity coefficients, etc., dissimilar to the case of water. Meanwhile, in the individual ion approach as previously mentioned, since the ionic parameters obtained for one salt solution should be applicable to other electrolytes containing the same ion [26,31,32], the estimation of individual ionic parameters should be performed with a simultaneous correlation over several electrolyte solutions, analogous to the fitting of parameters in group-contribution approaches. Hence, in this work, 4 individual ionic parameters, σ_{ii} , ϵ_{ii}/k , d_{hi} , and ϵ_{li}^{assoc}/k for one ion are determined from the simultaneous fittings of density data and mean ionic activity coefficient data in various types of electrolyte solution containing the same cation or anion ion.

In this work, we have been concerned about the properties of six

Table 1. Estimated PC-SAFT parameters for pure water

Chemicals	Temp. range [K]	Parameters					ARD (%)	
		m_i [-]	σ_{ii} [Å]	ϵ_{ii}/k [K]	ϵ_{11}^{assoc}/k [K]	κ_{11}^{assoc} [-]	V^I	P^{sat}
Water (4-sites model)	278-383	1.0175	3.0348	339.39	1538.43	0.031733	0.214	0.246

Table 2. Individual ion parameters estimated from fittings of the experimental data of densities and activity coefficients at 298.15 K

Ions	σ_i^c [Å] ^a	S_i [-] ^b	m_i [-] ^c	Parameters ^d			
				σ_{ii} [Å]	ε_{ii}/k [K]	$\varepsilon_{ii}^{assoc}/k$ [K]	d_{hi} [Å]
Li ⁺	1.20	8	1.0	1.2902	2444.34	3572.10	5.7870
Na ⁺	1.90	8	1.0	1.6966	1834.09	2916.95	4.1905
K ⁺	2.66	8	1.0	2.6687	804.79	2202.33	4.1767
Rb ⁺	2.96	8	1.0	2.7225	609.16	1939.69	3.1589
Mg ²⁺	1.30	16	1.0	1.2619	8770.55	3605.65	6.1129
Ca ²⁺	1.98	16	1.0	1.4493	7225.76	3238.02	6.1050
Cl ⁻	3.62	7	1.0	3.3895	760.41	2047.51	5.3896
Br ⁻	3.90	7	1.0	3.6927	783.10	1909.65	4.0965
I ⁻	4.32	7	1.0	3.9939	885.56	1752.96	4.6424
HCO ₃ ⁻	3.12	7	1.0	3.4802	1202.24	1887.39	3.8233
NO ₃ ⁻	3.78	3	1.0	3.8142	1666.89	1811.04	4.0613
SO ₄ ²⁻	4.60	12	1.0	4.1002	1805.82	2037.65	4.3222

^a σ_i^c : Crystal ionic diameter taken from the literature [46]^{b,c} Assumed in this work^dObjective function for estimating individual ion parameters: $F_{obj} = \sum_i \{[(\rho_{exp} - \rho_{cal})/\rho_{exp}]^2 + [(\gamma_{exp} - \gamma_{cal})/\gamma_{exp}]^2\}_i$ **Table 3. Average relative deviations (ARDs) of correlated densities and mean ionic activity coefficients, from this work and other models**

Salts	Molality range [mol/kgH ₂ O]	This work				Ji and Adidharma [26]		Liu et al. [32]		References	
		ρ	$\gamma_{\pm}^{(m)}$	ϕ^*	a_w^*	ρ	$\gamma_{\pm}^{(m)}$	ρ	$\gamma_{\pm}^{(m)}$	ρ	$\gamma_{\pm}^{(m)}$, ϕ and a_w
LiCl	0.001-6.0	0.52	0.87	0.70	0.075	0.79	0.71	0.20	1.68	[50]	[52]
LiBr	0.001-6.0	0.66	0.69	0.40	0.050	1.02	1.32	0.29	1.84	[50]	[52]
LiI	0.001-3.0	0.63	1.32	0.81	0.035	0.32	1.35	0.15	1.97	[50]	[52]
LiNO ₃	0.001-3.0	0.26	3.64	1.93	0.057	-	-	-	-	[50]	[52]
Li ₂ SO ₄	0.001-2.0	0.07	3.07	5.98	0.134	0.38	1.16	-	-	[50]	[53]
NaCl	0.001-6.0	0.09	0.32	0.34	0.018	0.16	0.53	0.55	0.82	[50]	[52]
NaBr	0.001-6.0	0.50	0.43	0.40	0.031	0.51	0.77	0.52	0.35	[50]	[52]
NaI	0.001-6.0	1.02	1.00	0.80	0.109	1.35	0.56	0.34	0.29	[50]	[52]
NaHCO ₃	0.001-1.0	0.17	0.71	-	-	0.41	0.79	-	-	[50]	[54]
NaNO ₃	0.001-3.0	0.35	0.31	0.55	0.019	0.99	0.71	0.13	1.34	[51]	[52]
Na ₂ SO ₄	0.001-2.0	0.22	1.66	3.43	0.034	0.40	0.31	0.42	1.21	[50]	[53]
KCl	0.001-4.5	0.16	0.65	0.50	0.020	0.64	0.13	0.18	0.48	[50]	[52]
KBr	0.001-5.5	0.40	0.51	0.51	0.033	0.23	0.28	0.08	0.45	[50]	[52]
KI	0.001-4.5	0.73	0.31	0.38	0.018	0.96	0.67	0.17	0.37	[50]	[52]
KHCO ₃	0.001-1.0	0.56	0.51	-	-	0.18	0.67	-	-	[50]	[55]
KNO ₃	0.001-3.5	0.23	2.59	3.77	0.092	1.33	1.41	0.39	0.76	[50]	[52]
K ₂ SO ₄	0.001-0.7	0.32	3.89	2.44	0.007	0.22	0.49	0.47	2.46	[50]	[53]
RbCl	0.001-5.0	0.29	0.98	0.94	0.065	-	-	-	-	[50]	[52]
RbBr	0.001-5.0	1.77	0.53	0.39	0.016	-	-	-	-	[50]	[52]
RbI	0.001-5.0	1.25	0.92	0.72	0.041	-	-	-	-	[50]	[52]
MgCl ₂	0.001-2.0	1.25	0.97	0.46	0.021	0.40	1.04	0.69	1.46	[50]	[56]
MgBr ₂	0.001-2.0	1.49	1.58	0.57	0.015	0.59	0.41	0.82	1.66	[50]	[56]
MgI ₂	0.001-2.0	2.02	0.72	0.53	0.022	0.96	0.63	0.99	1.76	[50]	[56]
CaCl ₂	0.001-2.0	1.04	1.54	0.69	0.026	0.20	0.36	-	0.96	[50]	[56]
CaBr ₂	0.001-2.0	-	1.65	0.33	0.016	-	0.35	0.33	1.81	-	[56]
CaI ₂	0.001-2.0	2.53	0.90	0.80	0.041	0.40	0.48	0.67	1.87	[50]	[56]
Overall average		0.76	1.28	1.19	0.042	0.59	0.69	0.41	1.24		

*Predicted properties (osmotic coefficient and water activity)

cations (Li^+ , Na^+ , K^+ , Rb^+ , Mg^{2+} and Ca^{2+}), and six anions (Cl^- , Br^- , I^- , HCO_3^- , NO_3^- and SO_4^{2-}) that are widely encountered in chemical processes. In the procedure of determining parameters of ions, firstly, 4 electrolytes of NaCl, NaBr, KCl and KBr among alkali metal halide salts were selected. Then using the density data and activity coefficient data of 4 aqueous solutions composed of each salt, individual ionic parameters of Na^+ , K^+ , Cl^- and Br^- were estimated. Next, from the fitting of data of aqueous NaI and KI solutions using the estimated Na^+ and K^+ parameters, parameters of I^- were estimated. Using the estimated parameters of halide anions, parameters of Li^+

were estimated from the fitting of data of LiCl, LiBr and LiI aqueous solutions, and Rb^+ parameters were also estimated from the fittings of data of RbCl, RbBr and RbI aqueous solutions. In the next procedure, using the estimated parameters of monovalent alkali metal cations and halide anions, the parameters of other cations (Mg^{2+} and Ca^{2+}) were determined from the fitting of data of the respective solution containing same cation, and also those of other anions (HCO_3^- , NO_3^- and SO_4^{2-}) were estimated through the similar way. In all procedures for estimating parameters, all binary interaction parameters, k_{ij} of Eq. (9) were set to zero. Additionally, the numbers of hydra-

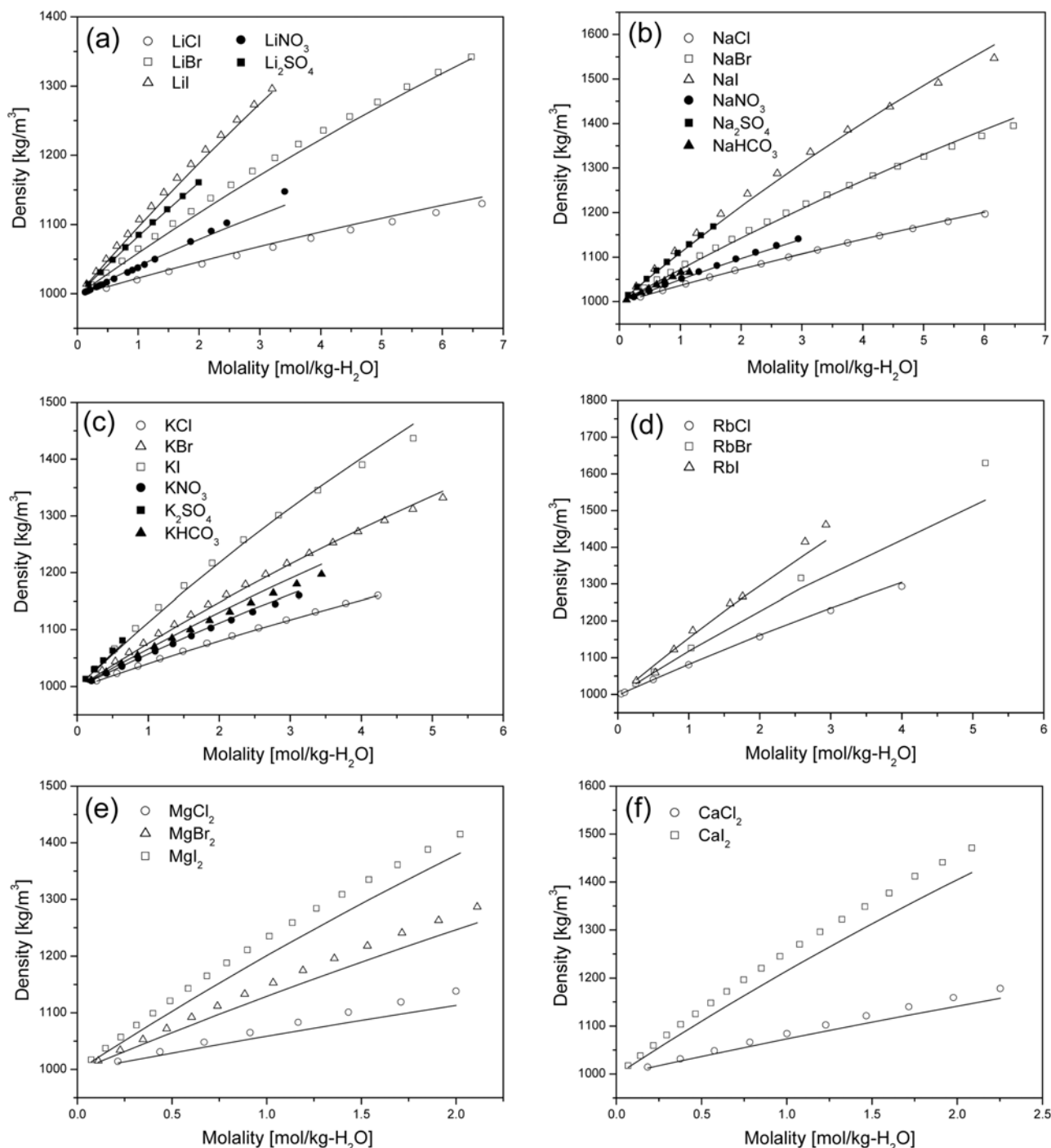


Fig. 1. Comparison of the correlated liquid densities with experimental data for aqueous electrolyte solutions at 298.15 K: —, correlated.

tion site S_i for all ions treated in this work, by considering the work of Liu et al. [32], and results of several literatures [43–45] in which hydration effect of ions was studied by the computer simulation and experimental method, were set to be fixed values such as: 8 for alkali metal cations, 16 for bivalent alkaline earth cations, 7 for halide anions, and also 7, 3, 12 for other anions, HCO_3^- , NO_3^- and SO_4^{2-} , respectively (refer to Table 2). Also the dielectric constant of

solvent (water) D involved in Eqs. (16) and (18) was obtained from the relation of which the dielectric constants of water were correlated with temperatures by Tan et al. [23], such as:

$$D = 281.67 - 1.0912T + 1.6644 \cdot 10^{-3}T^2 - 9.7592 \cdot 10^{-7}T^3 \quad (34)$$

Hence, the individual ionic parameters for 6 cations and 6 anions regressed by the above method are summarized in Table 2, and the

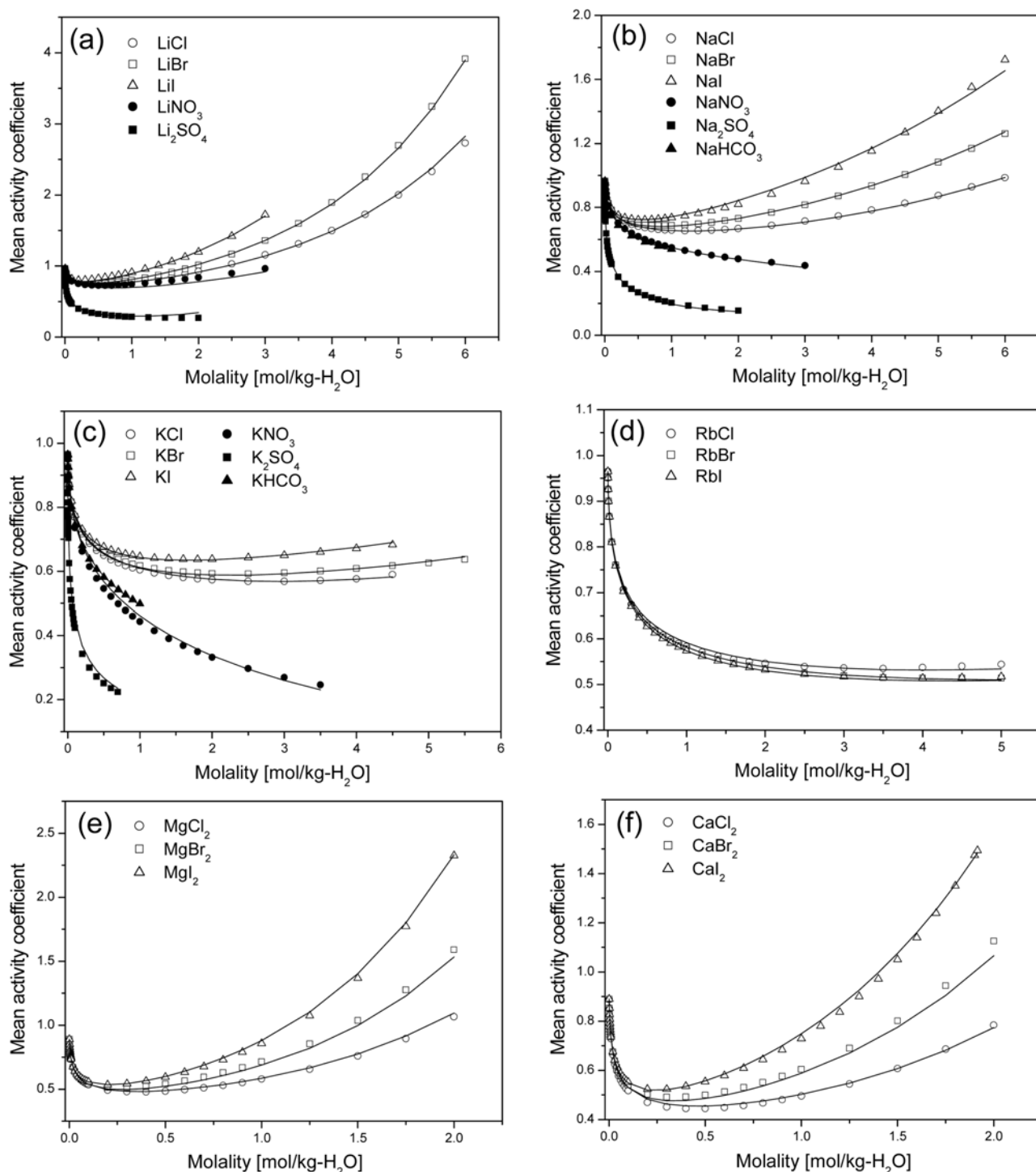


Fig. 2. Comparisons of the correlated mean ionic activity coefficient with experimental data for aqueous electrolyte solutions at 298.15 K: —, correlated.

comparisons of between correlated values with experimental data for the density and activity coefficients of 26 aqueous electrolyte solutions are shown in Table 3. As shown in Table 2, the diameters of all ions considered in this work are nearly close to but partly smaller than crystal ionic diameters [46], except for Li^+ and HCO_3^- . The dispersion energies of monovalent alkali metal cations (Li^+ , Na^+ , K^+ and Rb^+) decrease according to the ionic size, however, those of monovalent halide anions (Cl^- , Br^- and I^-) increase more or less with the ionic size, on the contrary to the case of alkali metal cations. The physical meaning of this trend is not obvious. In addition, the bivalent cations (Mg^{2+} and Ca^{2+}) yield a trend that they have much larger values of dispersion energies than the alkali metal cation, and also the dispersion energies of the oxygenated anions (HCO_3^- , NO_3^- and SO_4^{2-}) show a tendency to be larger than those of halide anions. Meanwhile, Table 3 shows that the correlated densities and mean ionic activity coefficients of electrolyte solutions are in good agreement with the experimental data with average ARDs of 0.76% and 1.28%, respectively. To give in detail the correlated results, the correlated densities and mean ionic activity coefficients are compared with experimental data in Figs. 1 and 2, respectively. Also, in Table

3, the results of present model are compared with results of other EoSs developed by Ji and Adidharma [26] and Liu et al. [32], based upon the concept of the individual ionic approach similar to the present model. Comparing the ARD of this model with ARDs of Ji and Adidharma, and Liu et al. shown in Table 3, the accuracies of present

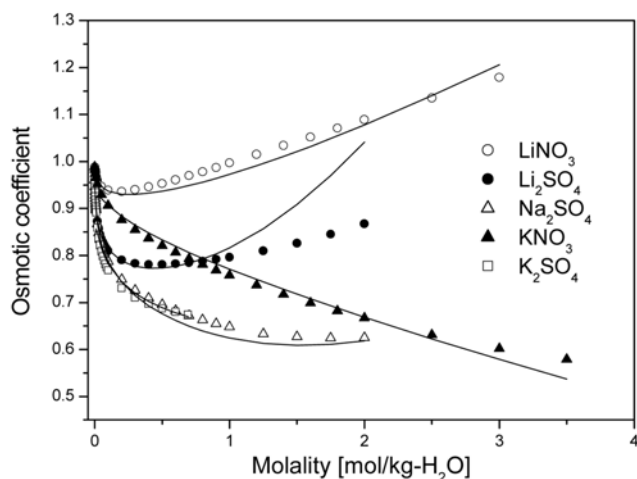


Fig. 3. Predicted and experimental osmotic coefficients of five aqueous electrolyte solutions with largest ARD: —, predicted.

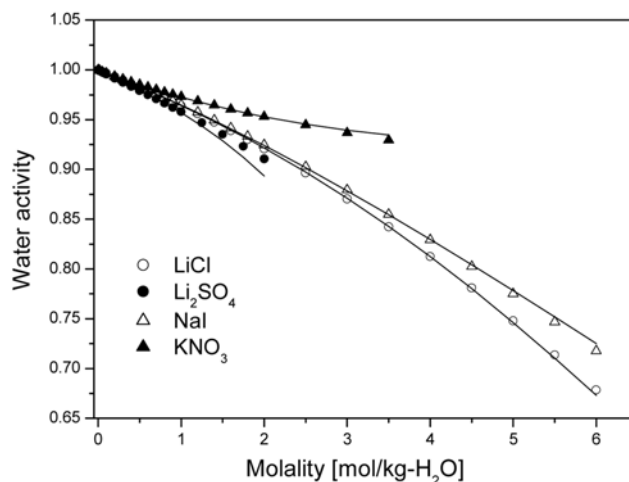


Fig. 4. Predicted and experimental water activities of four aqueous electrolyte solutions with largest ARD: —, predicted.

Table 4. ARDs for predicted densities of two-salt aqueous solutions at 298.15 K

Systems	No. of data points	ARD (%)	Ref.
NaCl+KCl	68	0.09	[57]
NaCl+CaCl ₂	71	0.56	[58]
NaCl+MgSO ₄	9	0.18	[59]
NaCl+Na ₂ SO ₄	9	0.06	[59]
Na ₂ SO ₄ +MgSO ₄	9	0.22	[59]
KCl+NaBr	41	0.19	[60]
KCl+MgCl ₂	46	0.40	[61]
KCl+CaCl ₂	71	0.56	[58]
Overall average		0.28	

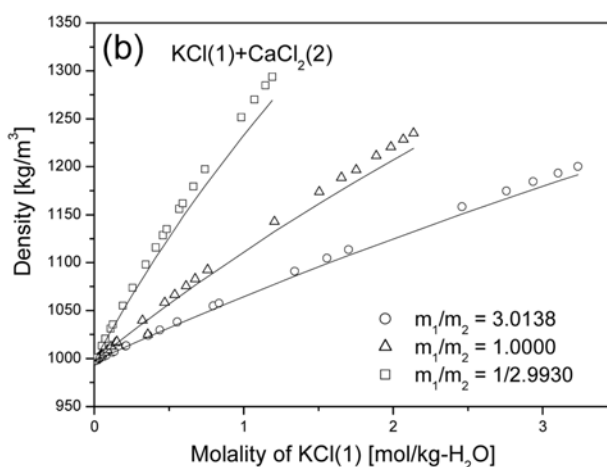
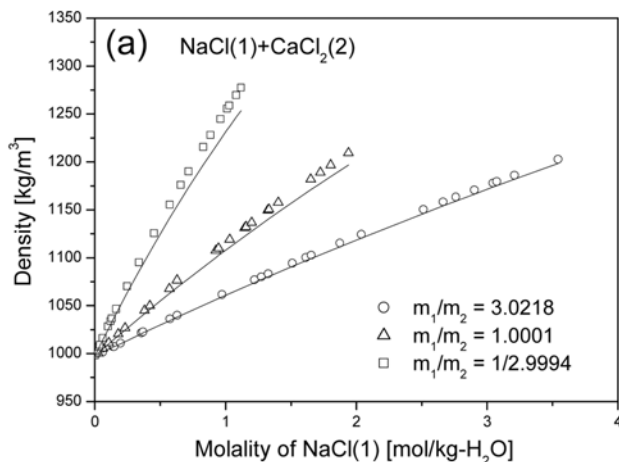


Fig. 5. Predicted and experimental densities of two-salt aqueous solutions at 298.15 K: —, predicted.

model may be comparable with these models.

Additionally, to validate the ability of the present model to represent other thermodynamic properties of electrolyte solutions, the osmotic coefficients and water activities of electrolyte solutions were predicted by using the present model coupled with the estimated individual ionic parameters, and the results are compared with the experimental data in Table 3. The average ARDs of osmotic coefficients and water activities are 1.19% and 0.042%, respectively, which are in line with experimental uncertainty. In addition, the predicted osmotic coefficients of 5 electrolyte solutions with the large ARD greater than about 2.0% are depicted in Fig. 3. As shown in Fig. 3, for the Li_2SO_4 aqueous solution, predicted osmotic coefficients significantly deviate from experimental values over the range of

molality larger than about 1.0 [mol/kg- H_2O]. Also, Fig. 4 reveals the predicted water activities of 4 salts which exhibit the large ARD greater than about 0.07%.

Furthermore, the present model with the parameters estimated from single-salt aqueous solutions can be readily applied to predict the thermodynamic properties of multi-salt solutions, without any additional adjustable parameters. The individual ionic parameters listed in Table 2 were then used to predict densities, osmotic coefficients, mean ionic activity coefficients and solubilities of two-salt aqueous solutions. The predicted densities for eight kinds of two-salt solutions were compared with the experimental data in Table 4. ARDs shown in Table 4 are less than 0.56%, and thus the predicted results are in good agreement with experimental data. Fig. 5

Table 5. ARDs for predicted osmotic coefficient of two-salt aqueous solutions at 298.15 K

Systems	This work			Ji and Adidharma [26]	Liu et al. [32]	Ref.
	No. of data points	Range of ionic strength, I	ARD (%)	ARD (%)	ARD (%)	
LiCl+NaCl	24	2.00-6.00	1.03	0.66	1.48	[62]
LiCl+KCl	21	2.00-5.00	3.97	10.80	-	[62]
LiCl+ MgCl_2	40	0.52-9.42	0.71	0.91	0.95	[63]
LiCl+ CaCl_2	24	0.49-8.76	1.09	0.93	1.24	[64]
NaCl+NaBr	12	2.83-4.39	0.31	0.34	0.75	[65]
NaCl+KCl	6	3.32-3.71	1.48	4.77	1.93	[65]
NaCl+KBr	12	2.97-4.61	0.98	-	1.40	[65]
NaCl+ NaNO_3	21	1.00-6.16	3.01	1.44	-	[66]
NaCl+ MgCl_2	20	0.91-5.93	0.62	0.44	1.52	[67]
NaCl+ CaCl_2	69	0.71-8.55	1.53	0.54	1.22	[68]
NaCl+ Na_2SO_4	25	0.91-13.33	1.42	1.10	1.30	[67]
NaCl+ K_2SO_4	19	0.41-2.13	1.25	-	1.14	[69]
NaBr+KBr	18	1.09-4.47	0.55	-	0.93	[65]
KCl+NaBr	18	1.87-4.25	1.13	-	0.98	[65]
KCl+KBr	18	2.03-4.35	0.42	4.97	0.11	[65]
KCl+ MgCl_2	35	0.22-6.00	2.82	6.30	1.81	[70]
KCl+ CaCl_2	66	0.99-6.26	2.84	7.57	-	[71]
KCl+ Na_2SO_4	22	1.30-4.39	2.01	-	1.54	[69]
KCl+ K_2SO_4	19	0.51-2.28	0.39	1.37	3.01	[69]
CaCl_2 + MgCl_2	67	0.60-13.50	0.70	0.74	1.68	[72]
Na_2SO_4 + MgCl_2	22	0.94-8.22	1.58	1.36	1.23	[73]
Na_2SO_4 + K_2SO_4	18	0.93-3.56	2.53	-	1.92	[69]
Overall average			1.47	2.77	1.38	

Table 6. ARDs for predicted mean ionic activity coefficient of two-salt aqueous solutions at 298.15 K

Systems	No. of data points	Range of ionic strength, I	ARD (%)		Ref.
			$\gamma_{\pm}^{(1)}$	$\gamma_{\pm}^{(2)}$	
NaCl(1)+LiCl(2)	36	0.01-4.0	0.73	-	[74]
NaCl(1)+KCl(2)	20	0.5-4.0	2.52	-	[75]
NaCl(1)+ NaNO_3 (2)	18	1.0-6.0	2.84	-	[76]
NaCl(1)+ MgCl_2 (2)	21	0.5-6.0	2.13	2.18	[77]
NaCl(1)+ CaCl_2 (2)	18	1.0-6.0	2.76	-	[76]
NaCl(1)+ Na_2SO_4 (2)	16	1.0-3.0	1.50	-	[78]
KCl(1)+ K_2SO_4 (2)	35	0.01-2.3	1.15	5.62	[79]
Overall average			1.95	3.90	

shows the predicted densities of 2 types of two-salt solutions with the largest ARD. Meanwhile, Table 5 reveals the comparisons of the predicted osmotic coefficients and experimental data for 22 aqueous solutions containing two salts. This table displays quite good

predictive results with an average ARD of 1.47%, compared with experimental data. Fig. 6 shows four typical examples with a large ARD, among the predicted results of osmotic coefficients. As can be shown in Fig. 6, for the KCl+LiCl system, the predicted osmotic

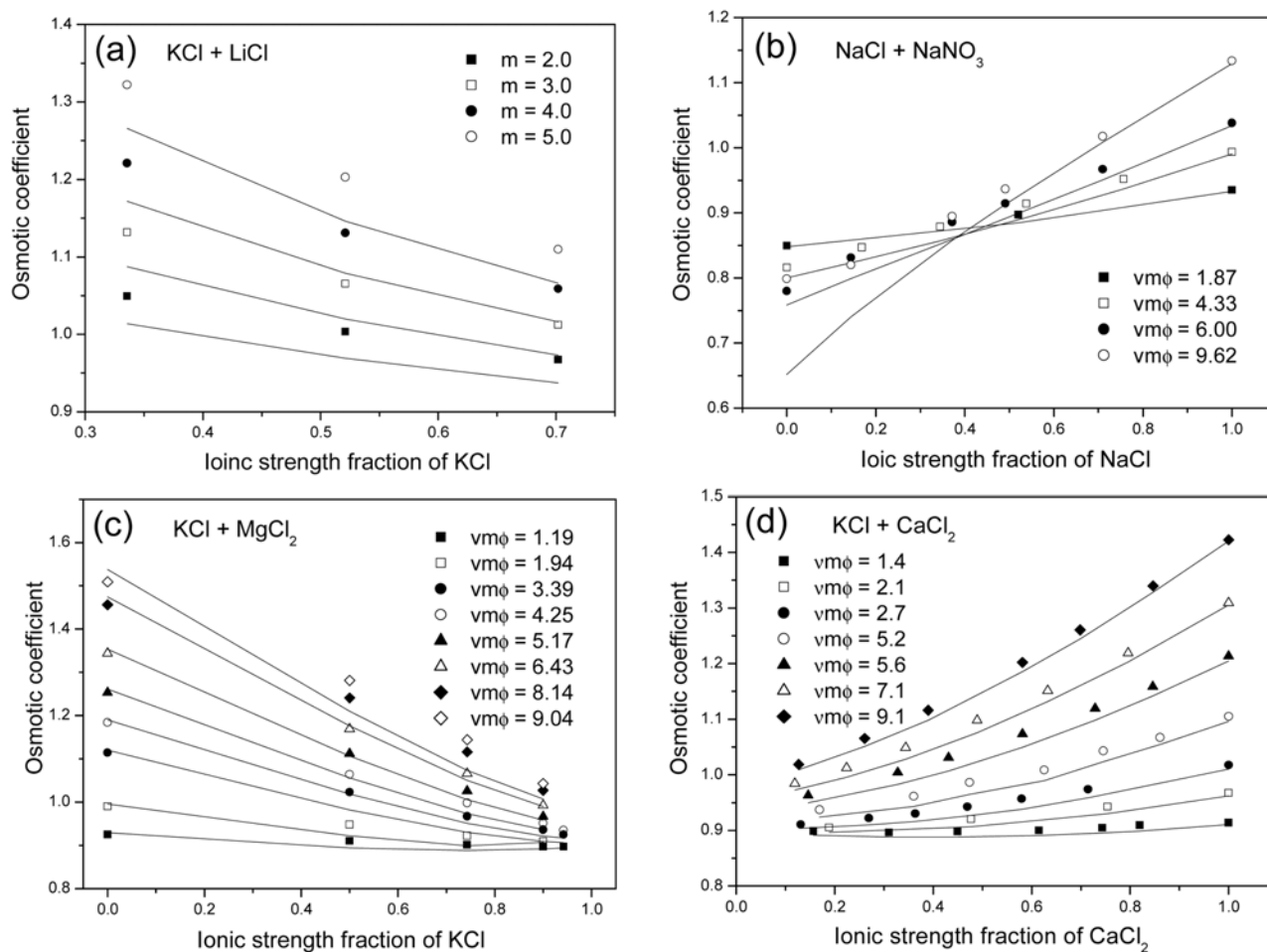


Fig. 6. Predicted and experimental osmotic coefficients of four two-salt aqueous solutions with largest ARD at 298.15 K: —, predicted; m is the total molality of salts and $vm\phi$ is an experimental condition used in the isopiestic technique for measuring osmotic coefficients.

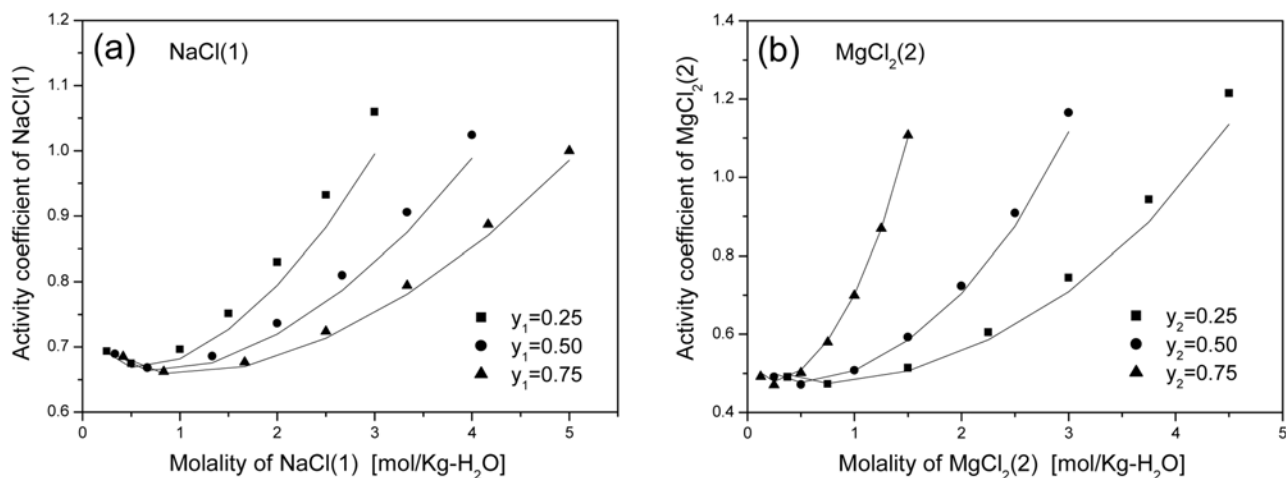


Fig. 7. Predicted and experimental mean ionic activity coefficients of the NaCl(1)+MgCl₂(2) aqueous solution at 298.15 K: —, predicted; y_i is the ionic strength fraction of salt i ($=I_i/I$).

coefficients are smaller than experimental data over the whole ranges of the ionic strength fraction of KCl, and also, for the NaCl+NaNO₃ system, the predicted osmotic coefficients are largely deviated from the experimental data only at high molality ranges of NaNO₃. In addition, the mean ionic activity coefficients for 7 types of two-salt

solutions were predicted. The predicted mean ionic activity coefficients were compared with experimental data, and their ARDs are listed in Table 6. As shown in Table 6, the present model gives the reasonable results for predicting the mean ionic activity coefficients in the two-salt solutions, with the ARDs less than about 2.8%, except

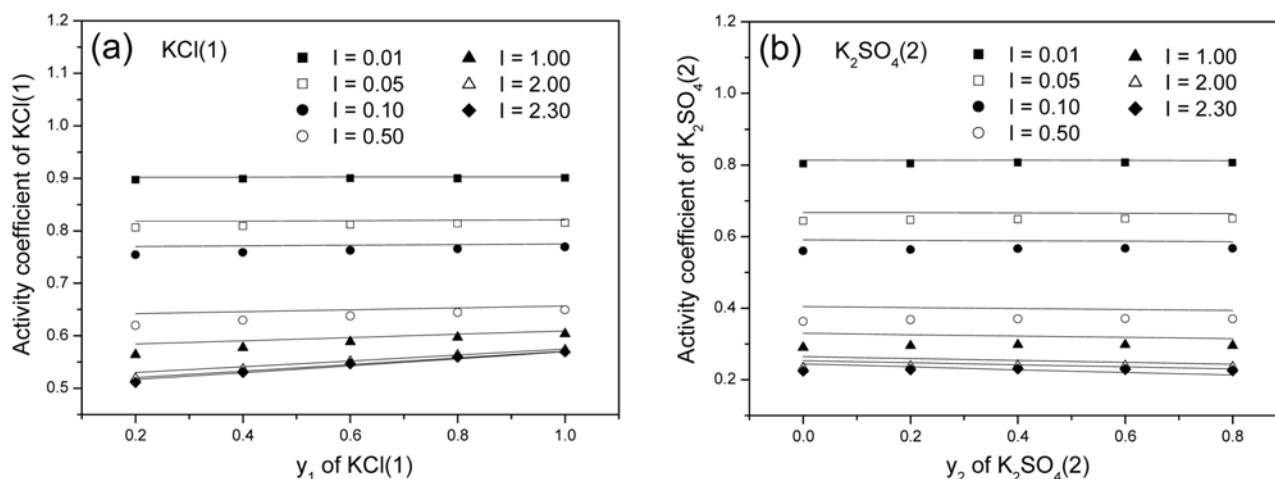


Fig. 8. Predicted and experimental mean ionic activity coefficients of the KCl(1)+K₂SO₄(2) aqueous solutions at 298.15 K: —, predicted; y_i is the ionic strength fraction of salt i ($=I_i/I$).

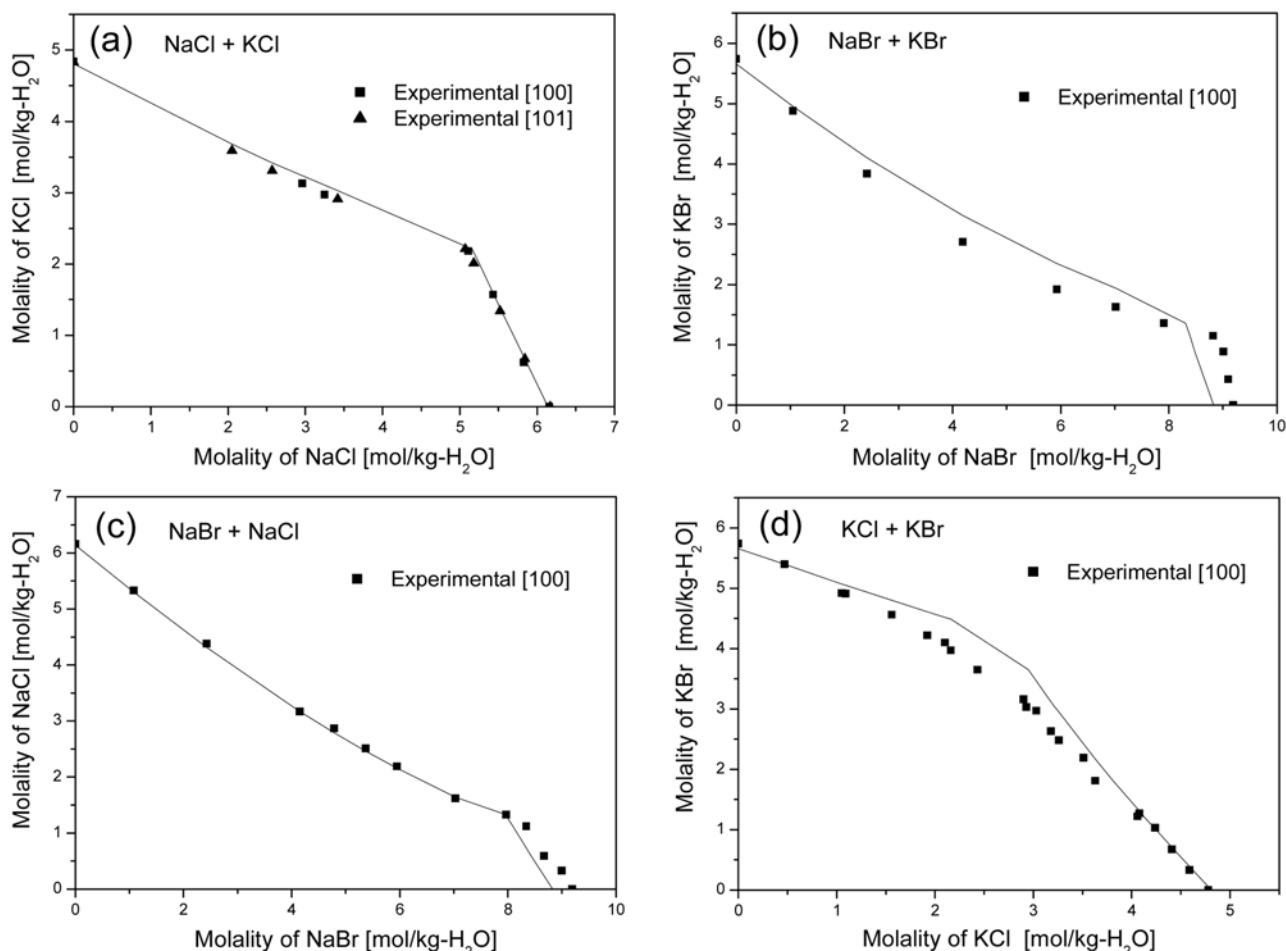
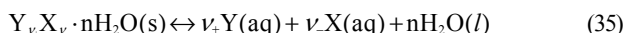


Fig. 9. Predicted and experimental solubilities of two-salt aqueous solutions at 298.15 K: —, predicted.

for the KCl+K₂SO₄ solution. Examples of the predicted results are shown in Figs. 7 and 8.

To further validate the performance of present model to describe thermodynamic properties of multi-salt solutions, the solubilities of salts in the two-salt solutions were predicted. For the strong electrolyte hydrated with *n* moles of water, the solubility equilibrium can be written as [47]:



where *Y* and *X* are the constituent cation and anion, respectively. The equilibrium constant of Eq. (35), i.e., the solubility product *K_{sp}* is as

$$K_{sp} = \frac{(x_w \gamma_w)^n (m_Y \gamma_Y)^{\nu_Y} (m_X \gamma_X)^{\nu_X}}{a_{Y_{\nu_Y} X_{\nu_X} \cdot nH_2O}}$$

where *a_{Y_{ν_Y} X_{ν_X} · nH₂O}*

 is the activity of the hydrated solid electrolyte. Assuming a pure solid electrolyte which has an activity of 1, the solubility product is defined as:

$$K_{sp} = (x_w \gamma_w)^n (m_Y \gamma_Y)^{\nu_Y} (m_X \gamma_X)^{\nu_X} \quad (36)$$

If the solubility products is known, the equilibrium concentration of salt can be calculated from Eq. (36) [47], since the activity coefficients of cation, anion and water can be estimated based upon the present model. In this work, we take four types of two-salt solutions such as the NaCl+KCl, NaBr+KBr, NaBr+NaCl and KCl+Br solutions, and the solubility products *K_{sp}* of each salts are used as the data available in the literature [24], such as: 38.05 for NaCl, 114.7 for NaBr·2H₂O, 8.003 for KCl and 13.53 for KBr. The predicted solubilities are compared with the experimental data, as shown in Fig. 9. The predicted solubilities are in good agreement with experimental data. However, the predicted results of the KCl+KBr solution somewhat deviate from the experimental data.

CONCLUSIONS

In this work, the electrolyte-EoS has been developed by incorporating the primitive mean spherical approximation model to take into account the electrostatic interactions of ions, into the PC-SAFT EoS. The obtained electrolyte-EoS was applied to represent the thermodynamic properties of aqueous electrolyte solutions. Four individual ionic parameters for six cations (Li⁺, Na⁺, K⁺, Rb⁺, Mg²⁺ and Ca²⁺), and six anions (Cl⁻, Br⁻, I⁻, HCO₃⁻, NO₃⁻ and SO₄²⁻) were regressed through the simultaneous fitting of the densities and mean ionic activity coefficients of electrolyte solutions. Using the estimated individual ionic parameters, the osmotic coefficients and water activities were predicted, and the predicted results are found to be well agreeable with the experimental data. Also, the present model is successfully applied for predicting the thermodynamic properties of the two-salt solutions, such as the densities, osmotic coefficients, mean ionic activity coefficients and solubilities of salts. Finally, it is found that the electrolyte-EoS proposed in this work may be useful for describing thermodynamic properties of single-salt aqueous solutions and two-salt aqueous solutions.

NOMENCLATURE

ARD (%) : average of relative deviation

$$= (1/N) \sum_i^N |(X_{exp} - X_{cal})/X_{exp}| \times 100; N: \text{No. of data point}$$

A	: Helmholtz free energy of the mixture
<i>a_w</i>	: water activity
D	: dielectric constant of solvent
<i>d_{ii}</i>	: temperature-dependent segment diameter of component <i>i</i>
<i>d_{hi}</i>	: hydrated diameter of ionic species <i>i</i>
<i>e</i>	: elementary charge
<i>g_{ij}^{hs}</i>	: radial distribution function for a mixture
<i>I</i>	: total ionic strength (=Σ _{ion} <i>I_i</i>)
<i>I_i</i>	: ionic strength fraction of salt <i>i</i> (=1/2Σ _{ion} <i>v_im_iz_i²</i>)
<i>k</i>	: Boltzmann constant
<i>K_{sp}</i>	: solubility product
<i>k_{ij}</i>	: binary interaction parameter between <i>i</i> and <i>j</i>
<i>M_w</i>	: molecular weight of water
<i>m</i>	: molality of salt
<i>m_i</i>	: number of segments per chain of chemical component <i>i</i>
<i>N</i>	: total number of molecules in the system
<i>N_{av}</i>	: Avogadro's number
<i>P</i>	: pressure
<i>R</i>	: gas constant
<i>S_i</i>	: association site number of charged ionic species <i>i</i>
<i>T</i>	: absolute temperature
<i>V</i>	: volume
<i>X_A</i>	: fraction of molecules of not bonded at association site <i>A</i>
<i>x_i</i>	: mole fraction of chemical component <i>i</i>
<i>y_i</i>	: ionic strength fraction of salt <i>i</i> (= <i>I_i</i> / <i>I</i>)
<i>z_i</i>	: charge number of ion <i>i</i>

Greek Letters

<i>Γ</i>	: primitive MSA parameter
<i>γ_±</i>	: mean activity coefficient based on mole fraction scale
<i>γ_±^(m)</i>	: mean activity coefficient based on molality scale
<i>ε₀</i>	: permittivity of free space
<i>ε_{ii}/k</i>	: dispersion energy parameter of chemical species <i>i</i>
<i>ε_{ij}^{assoc}/k</i>	: energy parameter of association between chemical species <i>i</i> and <i>j</i>
<i>η</i>	: packing fraction, i.e., ξ ₃ of Eq. (A3)
<i>κ_{ij}^{assoc}</i>	: volume parameter of association between chemical species <i>i</i> and <i>j</i>
<i>μ_i</i>	: chemical potential of chemical species <i>i</i>
<i>ν₊, ν₋</i>	: stoichiometric constant of cation and anion in salt molecule, respectively
<i>ρ</i>	: total number density of molecules
<i>σ_{ii}</i>	: segment diameter of chemical species <i>i</i>
<i>φ</i>	: osmotic coefficient

Superscripts

assoc	: association term
Born	: Born term
chain	: chain term
charg	: charging term
discharg	: discharging term
disp	: dispersion term
ele	: long-range electrostatic term
hs	: hard sphere term
<i>l</i>	: liquid state

m : molality of salt
 res : residual property
 self : self-association
 solv : hydration of charged ion
 pc-saft : PC-SAFT equation of state
 ° : pure state
 ∞ : infinite dilute state

Subscripts

e : electron pairs of the oxygen atom
 H : hydrogen atoms of water molecule
 i, j : chemical component i, j
 w : water
 +, - : ions (cation, anion)

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APPENDIX

In the mixture composed of neutral hard sphere particles, the Helmholtz free energy for the hard sphere repulsion, and the radial pair distribution function can be obtained from the relations of Boublik [48] and Mansoori et al. [49] expressed such as:

$$A^{hs}/NkT = \frac{6}{\pi\rho} \left[\frac{\xi_2^3 + 3\xi_1\xi_2\xi_3 - 3\xi_1\xi_2^2\xi_3}{\xi_3(1-\xi_3)^2} - \left(\xi_0 - \frac{\xi_2^3}{\xi_3} \right) \ln(1-\xi_3) \right] \quad (A1)$$

$$g_{ij}^{hs} = \frac{1}{(1-\xi_3)} + \left(\frac{d_{ij}d_{jj}}{d_{ii}+d_{jj}} \right) \frac{3\xi_2}{(1-\xi_3)^2} + \left(\frac{d_{ij}d_{jj}}{d_{ii}+d_{jj}} \right)^2 \frac{2\xi_2^2}{(1-\xi_3)^3} \quad (A2)$$

Here, ξ_0 , ξ_1 , ξ_2 and ξ_3 is defined as

$$\xi_n = \frac{\pi}{6} \rho \sum_i x_i m_i d_{ii}^n, \quad n \in \{0, 1, 2, 3\} \quad (A3)$$

In addition, the Helmholtz free energy due to dispersive attractive interactions between segments of chain molecules is described by the PC-SAFT model [30] such as:

$$A^{disp}/NkT = A_1^{disp}/NkT + A_2^{disp}/NkT \quad (A4)$$

$$A_1^{disp}/NkT = -2\pi\rho I_1(\eta, \bar{m}) \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT} \right) \sigma_{ij}^3 \quad (A5)$$

$$A_2^{disp}/NkT = -\pi\rho\bar{m} C_1(\eta, \bar{m}) I_2(\eta, \bar{m}) \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT} \right)^2 \sigma_{ij}^3 \quad (A6)$$

where $I_1(\eta, \bar{m})$, $I_2(\eta, \bar{m})$ and $C_1(\eta, \bar{m})$ terms have been explained in detail in the original paper of PC-SAFT EoS [30], therefore do not appear here.