

Modeling of Aqueous Electrolyte Solutions Based on Primitive and First-Order Mean Spherical Approximation

Yan Liu,[†] Zhibao Li,[‡] Jianguo Mi,^{*,†} and Chongli Zhong[†]

Department of Chemical Engineering, The Key Lab of Bioprocess of Beijing, Beijing University of Chemical Technology, Beijing, China, and Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China

A short-range Sutherland potential is mapped with the two-Yukawa potential and incorporated into the first-order mean spherical approximation (FMSA) theory to deal with the short-range dispersion interactions of ion–ion, ion–solvent, and solvent–solvent. An equation of state (EOS) based on primitive MSA and FMSA is constructed to describe the single- and multiple-salt solutions. With the universal and transferable ionic parameters derived from mean ionic activity coefficients and solution densities of single-salt solutions for five cations (Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and five anions (Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-}), the proposed EOS predicts the correct osmotic coefficients as well as water activities for 19 monovalent and bivalent two-salt solutions. Without any additional mixing parameter, the predicted osmotic coefficients for aqueous two-salt solutions are in good agreement with experimental data.

1. Introduction

An accurate description of thermodynamic properties of aqueous electrolyte solutions is of particular interest in many industrial chemical processes. In the past decade or so, much effort went into extension of the statistical mechanical theory of electrolyte solutions to higher concentrations, and significant progress was achieved. Among various statistical mechanical theories, the integral equation theory and the perturbation theory were investigated systematically. The integral equation theory, incorporated with hypernetted chain (HNC) or the mean spherical approximation (MSA), was widely used for obtaining the structure and thermodynamic properties of ionic fluid. Because the integral equation can be solved analytically for Coulomb interaction, a series of models were proposed, including the primitive MSA,¹ the restrictive primitive MSA,² and the nonprimitive MSA.^{3,4} The perturbation theory, starting from an appropriate reference system, had been proven to successfully account for spherical and nonspherical molecules, for nonspecific dispersion interactions, and for specific interactions such as association as well as polar and quadrupolar interactions.

Up to now, the most successful electrolyte theory of combining the integral equation and perturbation method has been the statistical associating fluid theory (SAFT).^{5,6} Since the interactions of hard sphere repulsion, Coulomb attraction, dispersion, and association are fully taken into account, SAFT can predict a plethora of interesting phenomena in electrolyte systems. For example, perturbed-chain SAFT (PC-SAFT) coupled with a Debye–Hückel term was tested to express the vapor pressure and liquid density of single-salt and two-salt solutions.⁷ SAFT with a variable range of attractive potentials for electrolyte solution (SAFT-VRE) was shown to describe the vapor pressure and the separate effects of ion–ion, ion–solvent, and solvent–solvent.^{8,9} In these models, the salts are dissociated fully to cations and anions, and individual ion parameters, not the salt molecule parameters, are included. These proposals made their models to be more rigorous theoretically. However, neither of these models was extended to multivalent ions and

multiple-salt solutions. Especially, SAFT coupled with the restricted primitive model (SAFT-RPM) was demonstrated to represent both single-salt and multiple-salt solutions, including their activity coefficients, osmotic coefficients, vapor pressures, and densities.^{10–13} In this model, each ion is characterized by a segment volume parameter, while each salt is characterized by another parameter, namely the salt hydrated diameter. The two parameters might make the model theoretically inconsistent. On the other hand, the parameters thus obtained did not display good correlation with expected aqueous electrolyte properties. Although the improved SAFT-RPM has changed the salt diameter to ion diameter,^{14,15} the segment volume parameter still exists. The two independent diameter parameters might arouse some confusion. In addition, a common dissatisfaction in this model is its accompanying mixing parameter for two-salt solutions. Generally, the mixing parameter degrades the performance of the model.

To remove this salt parameter and use all ion parameters, it is still necessary to analyze the interaction potential, especially the short-range dispersion potential. The van der Waals interaction derived from dispersion force is well-known in nonelectrolyte systems, whereas this type of interaction is not explicitly expressed in aqueous electrolyte solutions. To gain insight into the dispersion interaction, we can revisit the primitive MSA.¹ With this model, the ion–ion dispersion force is negligible at very small concentrations, and the combination of hard sphere repulsion and the Coulomb interaction are sufficient to describe the activity coefficients of the ions or the osmotic coefficients of the whole system. However, at high concentrations, the long-range Coulomb interactions are screened, and the dispersion forces play an increasingly important role.¹⁶ The model loses its effect. According to Manciu's argument,¹⁷ the ion–ion dispersions take effect only at short range and can be described with the Sutherland potential.¹⁸ The same situation exists in the nonprimitive model, where the effect of solvent is included. For PC-SAFT, SAFT-VRE, and SAFT-RPM, the ion–ion dispersions are ignored. Furthermore, since the important radial distribution function (RDF) has to be extracted numerically, the expression of dispersion interactions of ion–solvent and solvent–solvent must depend on special regressed functions, and these models require the use of appropriate mixing rules for the parameters when extended to multiple-salt solutions. In

* To whom correspondence should be addressed. E-mail: mijg@mail.buct.edu.cn.

[†] Beijing University of Chemical Technology.

[‡] Chinese Academy of Sciences.

order to obtain the accurate RDF, Tang^{19,20} developed a first-order mean spherical approximation method based on the perturbation expansion to solve the integral equation. The analytical RDF thus obtained was then applied to calculate chain bonding and the association term. The model was tested satisfactorily against computer simulation data for both pure and mixing Lennard-Jones fluids. The full predictability and consistency of FMSA provide great flexibility in practical application.

In this work, the FMSA method is further extended to aqueous electrolyte solutions. For simplicity, the dispersion forces of ion-ion, ion-solvent, and solvent-solvent are expressed with the same form. In accord with Tang's solution, the Sutherland potential for dispersion is mapped accurately to the two-Yukawa potential. The analytical RDF obtained from FMSA, in turn, is applied to the association term. An equation of state (EOS) is constructed based on primitive MSA and FMSA. In addition, the associating interactions are also considered. To make the EOS versatile for different salt solutions with common cation or anion, the required parameters for salt are derived from the dissociated ions and not from the salt molecule itself. Compared with RPM, the primitive MSA is more rigorous since cations and anions are not restricted to be of the same size, and can be easily implemented within FMSA. Compared with the non-primitive model, the primitive MSA can be easily extended to high concentrations of aqueous electrolyte solutions. As for associating interactions, the well-known association theory^{21,22} is still the best at present and is incorporated into our model. Because the ionic parameters are universal and transferable to different salts containing the same ion, such an approach can greatly reduce the number of regressed parameters needed to represent electrolytes and improve the predictive capability.

2. Theory

The systems of interest in this work are single- and two-salt solutions. Since the salts are fully dissociated, there are only three kinds of components in the solution, including cation, anion, and water solvent. In our model, the ions are treated as charged spheres with additional associating sites forming hydrogen bonds with water, and following Kunz's conclusion¹⁶ and Manciu's argument,¹⁷ the short-range dispersion interactions between ion-ion, ion-solvent, and solvent-solvent are included. The dispersion was expressed by the London potential originally,¹⁶ which can be generally given by the Sutherland potential:

$$\begin{cases} u_{ij}(r) = \infty, & r \leq \sigma \\ u_{ij}(r) = -4\epsilon_{ij}\left(\frac{\sigma_{ij}}{r}\right)^6, & r > \sigma \end{cases} \quad (1)$$

where r is the distance between the centers of two particles, σ_{ij} is the unlike diameter, and ϵ_{ij} is the unlike dispersion energy. The unlike potential parameters are usually represent by like potential parameters as follows:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (2)$$

For analytical FMSA, the potential can be accurately mapped with a two-Yukawa form

$$u_{ij}(r) = -k_1 \epsilon_{ij} \frac{\exp[-z_1(r - \sigma_{ij})]}{r/\sigma_{ij}} - k_2 \epsilon_{ij} \frac{\exp[-z_2(r - \sigma_{ij})]}{r/\sigma_{ij}} \quad (3)$$

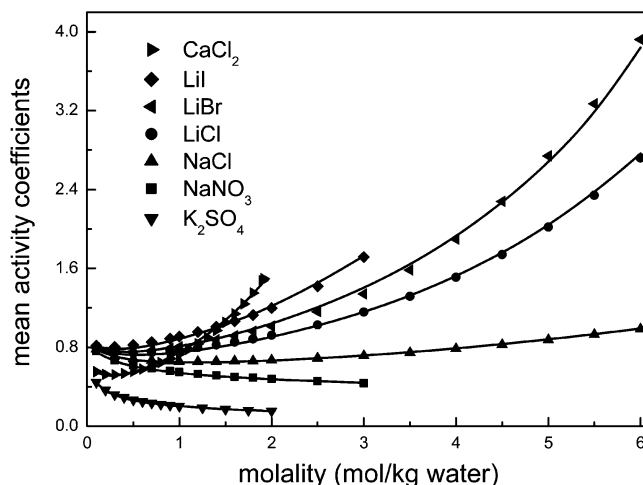


Figure 1. Correlated mean ionic activity coefficient of salts in water. The symbols are the experimental data,^{28–30} and the solid lines are calculated with the model.

Table 1. Parameters for Cations, Anions, and Water Regressed from Experimental Data^{28–32}

ion	σ	ϵ/k	$\epsilon^{\text{assoc}}/k$	S
Li ⁺	3.1876	135.15	2140.8	8
Na ⁺	3.1066	152.45	1262.8	8
K ⁺	3.7407	153.95	567.58	8
Mg ²⁺	3.6681	479.61	2049.1	16
Ca ²⁺	3.5841	468.24	1592.4	16
Cl ⁻	3.2737	431.86	953.28	6
Br ⁻	3.5080	363.71	756.16	6
I ⁻	4.0757	330.14	561.34	6
NO ₃ ⁻	3.9337	563.74	598.65	4
SO ₄ ²⁻	3.8751	1835.4	1774.6	10
water	3.3501	135.45	1401.0	4

in which the mapping parameters we obtained are $k_1 = 1.593$, $k_2 = 2.405$, $z_1 = 2.587$, and $z_2 = 6.505$.

The residual Helmholtz free energy can be expressed by

$$a^{\text{res}} = a^{\text{hs}} + a^{\text{ion}} + a^{\text{dis}} + a^{\text{assoc}} \quad (4)$$

where the superscripts mean residual, hard sphere, long-range ionic interaction, short-range dispersion, and association, respectively. Unlike ordinary statistical associating fluid theory, in which the chain term is included, the particles of ions and solvent are treated as hard spheres, and the corresponding chain term disappears. The Helmholtz free energy for the hard sphere repulsion had been well-developed:²³

$$a^{\text{hs}} = \frac{1}{\rho} \left[\frac{\left(\frac{\pi}{2} \xi_1 \xi_2 - \xi_2^3 / \xi_3^2 \right)}{\Delta} + \frac{\xi_2^3}{\xi_3^2 \Delta^2} + \frac{\xi_2^3}{\xi_3^2} \ln \Delta \right] - \ln \Delta \quad (5)$$

in which $\xi_n = \sum_m \rho_m \sigma_m^n$, $\Delta = 1 - (\pi/6)\xi_3$, and ρ denotes the total number density of solution.

The Helmholtz free energy due to dispersion contribution can be described with accurate FMSA, which is

$$a^{\text{dis}} = -2\pi\beta \sum_i \sum_j x_i x_j \epsilon_{ij} [k_1 G_{0,ij}(z_1) e^{z_1} + k_2 G_{0,ij}(z_2) e^{z_2}] - \pi\beta \sum_i \sum_j x_i x_j \epsilon_{ij} [k_1 (G_{1,ij}(z_1) e^{z_1}) + k_2 (G_{1,ij}(z_2) e^{z_2})] \quad (6)$$

where $G_{0,ij}(z)$ and $G_{1,ij}(z)$ are the Laplace transforms of the radial distribution functions of hard sphere and dispersion, respectively, and details are defined as in refs 25 and 26.

Table 2. Average Relative Deviation (ARD) Values of Fitted Mean Ionic Activity Coefficients (γ_{\pm}), Fitted Solution Densities (d), Predicted Osmotic Coefficients (φ), and Water Activities (a_w)

salt	ARD (%)				molality range
	γ_{\pm}	φ	d	a_w	
LiCl ^{28,31}	1.68	0.94	0.20	0.11	0.1–6.0
LiBr ^{28,31}	1.84	1.12	0.29	0.21	0.1–6.0
LiI ^{28,31}	1.97	1.41	0.15	0.08	0.1–3.0
NaCl ^{28,31}	0.82	0.57	0.55	0.06	0.1–6.0
NaBr ^{28,31}	0.35	0.30	0.52	0.03	0.1–4.0
NaI ^{28,31}	0.29	0.24	0.34	0.02	0.1–3.5
KCl ^{28,31}	0.48	0.21	0.18	0.02	0.1–4.5
KBr ^{28,31}	0.45	0.11	0.08	0.01	0.1–5.5
KI ^{28,31}	0.37	0.33	0.17	0.04	0.1–4.5
MgCl ₂ ^{29,31}	1.46	1.24	0.69	0.06	0.1–2.0
MgBr ₂ ^{29,31}	1.66	0.89	0.82	0.05	0.1–2.0
MgI ₂ ^{29,31}	1.76	0.92	0.99	0.10	0.1–2.0
CaCl ₂ ^{29,31}	0.96	1.05		0.04	0.1–2.0
CaBr ₂ ^{29,31}	1.81	1.25	0.33	0.06	0.1–2.0
CaI ₂ ^{29,31}	1.87	1.38	0.67	0.12	0.1–1.9
NaNO ₃ ^{28,31}	1.34	0.73	0.13	0.05	0.1–3.0
KNO ₃ ^{28,31}	0.76	0.39	0.39	0.01	0.1–3.0
Na ₂ SO ₄ ^{30,31}	1.21	0.95	0.42	0.04	0.1–2.0
K ₂ SO ₄ ^{30,31}	2.46	1.71	0.47	0.04	0.1–0.7

Table 3. ARD Values for Predicted Osmotic Coefficients of Aqueous Two-Salt Solutions

solution	ARD (%)	solution	ARD (%)
LiCl + NaCl ³³	1.48	NaBr + KBr ³⁶	0.93
LiCl + MgCl ₂ ³⁴	0.95	Na ₂ SO ₄ + MgCl ₂ ⁴⁰	1.23
LiCl + CaCl ₂ ³⁵	1.24	Na ₂ SO ₄ + K ₂ SO ₄ ³⁹	1.92
NaCl + NaBr ³⁶	0.75	KCl + NaBr ³⁶	0.98
NaCl + KCl ³⁶	1.93	KCl + KBr ³⁶	0.11
NaCl + KBr ³⁶	1.40	KCl + MgCl ₂ ⁴¹	1.81
NaCl + MgCl ₂ ³⁷	1.52	KCl + Na ₂ SO ₄ ³⁹	1.54
NaCl + CaCl ₂ ³⁸	1.22	KCl + K ₂ SO ₄ ³⁹	3.01
NaCl + Na ₂ SO ₄ ³⁷	1.30	CaCl ₂ + MgCl ₂ ⁴²	1.68
NaCl + K ₂ SO ₄ ³⁹	1.14		

The Helmholtz free energy contribution of ion–ion electrostatic interactions can be given with the primitive MSA:¹

$$a^{\text{ion}} = -\frac{e^2}{D\rho k_B T} \left(\Gamma \sum_i \frac{\rho_i q_i^2}{1 + \Gamma \sigma_i} + \frac{\pi}{2\Delta} \Omega P_n^2 \right) + \frac{\Gamma}{3\pi\rho} \quad (7)$$

where q_i is the charge of the i th ion, D is the dielectric constant of water; the details of Γ , Ω , and P_n are given by²⁷

$$4\Gamma^2 = \alpha^2 \sum_i \rho_i \left(\frac{q_i - \frac{\pi}{2\Delta} \sigma_i^2 P_n}{1 + \Gamma \sigma_i} \right)^2 \quad (8)$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_i \frac{\rho_i \sigma_i^3}{1 + \Gamma \sigma_i} \quad (9)$$

$$P_n = \frac{1}{\Omega} \sum_i \frac{\rho_i \sigma_i q_i}{1 + \Gamma \sigma_i} \quad (10)$$

In eq 8, $\alpha^2 = 4\pi e^2 / Dk_B T$.

As for the association contribution, the association theory allows one to consider more detailed associating mechanisms in solution. The water–water association can be expressed by the well-known SAFT EOS. The ion–solvent association (also called ion hydration) can be incorporated by taking into account a water model and adding associating sites into the ions, where the cation is allowed to bond only with water sites of type e, and the anion is allowed to bond only with water sites of type H, and no ion–ion association occurs. To clarify the expression, the cation, anion, and water solvent are signified as 1, 2, and 3, respectively. A water molecule is regarded as the hard sphere with four associating sites, two of which represent lone pairs (named 3e) and the others represent protons (named 3H). It is

assumed that there are S_1 sites on the cation associating with water and similarly S_2 sites on the anion. The Helmholtz free energy due to association is given by⁶

$$a^{\text{assoc}} = x_1 S_1 [\ln X_1 - (X_1 - 1)/2] + x_2 S_2 [\ln X_2 - (X_2 - 1)/2] + x_3 (2 \ln X_{3H} - X_{3H} + 2 \ln X_{3e} - X_{3e} + 2) \quad (11)$$

where X_A represents the mole fraction of nonassociating particles at site A. According to the mass-action equation, the fraction can be obtained by solving a group of equations as follows:

$$X_1 = \frac{1}{1 + 2\rho x_3 X_{3e} \delta_{13} + S_2 \rho x_2 X_{21} \delta_{12}} \quad (12a)$$

$$X_2 = \frac{1}{1 + 2\rho x_3 X_{3H} \delta_{23} + S_1 \rho x_1 X_{12} \delta_{21}} \quad (12b)$$

$$X_{3e} = \frac{1}{1 + 2\rho x_3 X_{3H} \delta_{33} + S_1 \rho x_1 X_{13} \delta_{31}} \quad (12c)$$

$$X_{3H} = \frac{1}{1 + 2\rho x_3 X_{3e} \delta_{33} + S_2 \rho x_2 X_{23} \delta_{32}} \quad (12d)$$

where S is the number of association sites and δ_{ij} is a function to characterize the strength of the association between sites i and j ; $\delta_{ij} = \delta_{ji}$ is given by

$$\delta_{ij} = \sigma_{ij}^3 g_{ij}^{\text{Yukawa}}(\sigma_{ij}) \exp(\epsilon_{ij}^{\text{assoc}} / k_B T - 1) \kappa_{ij} \quad (13)$$

$\epsilon_{ij}^{\text{assoc}}$ and κ_{ij} are the characteristic parameters related to the association energy and volume, respectively. For a two-Yukawa mixture, the contact value at σ_{ij} of the radial distribution function g_{ij}^{Yukawa} is expressed as in ref 26.

3. Results and Discussion

To test the new EOS, a number of calculations were performed in this work. For a single-salt–water aqueous solution, three parameters (σ , ϵ , ϵ^{assoc}) need to be regressed for cation, anion, and water, respectively. The interaction volume κ_{ij} can be set to 0.03 for all ions and water. In addition, the number of association sites S on each ion can be estimated according to the ionic size and the hydration strength. The parameters of the ions were derived from experimental data at 25 °C. In the regression procedures, the experimental data of mean ionic activity coefficients and densities were included, while those parameters for pure water were determined by fitting

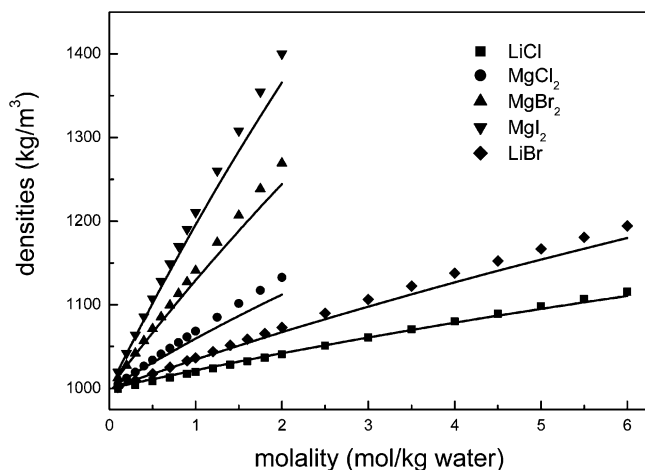


Figure 2. Correlated solution densities. The symbols are the experimental data,³¹ and the solid lines are calculated with the model.

to the experimental data²⁸ of the saturated liquid densities and the vapor pressure. It should be pointed out that, in our model, there are no additional binary interaction parameters applied between the ions and water molecules, especially for binary electrolyte solutions. Complete results for the adjusted parameters of five cations, five anions, and water are listed in Table 1. The experimental data are taken from refs 29–32. As we can see in Table 1, the diameter of each cation tends to have an obvious enlargement when compared with the corresponding Pauling diameter, while those anionic sizes have little variation. The enlarged diameter indicates that cations have strong hydration capacity.

The ability of our EOS to describe the average relative deviations (ARDs) of activity coefficients and solution densities of 19 aqueous solutions of monovalent and bivalent salts is exemplified in Table 2. The osmotic coefficients were thus predicted with the same set of parameters, and their ARDs are also listed in Table 2, along with the ARDs of the activities of water for reference. As is shown in Table 2, our model gives a good correlation of the mean ionic activity coefficients and densities, with average ARDs of about 1% and 0.4%, respectively. Meanwhile, the predicted osmotic coefficients and activities of water are also in good agreement with the experimental data with average ARDs of 0.8% and 0.06%, respectively. For clarity, Figure 1 shows the calculated activity coefficients of seven salts that exhibit the largest deviations from the experimental data, Figure 2 reveals the correlated densities of five salts that have the largest ARDs, and Figure 3 displays the predicted osmotic coefficients of seven single-salt solutions with the largest deviations. The corresponding results of the other salts are better than those shown in Figures 1–3.

The parameters listed in Table 1 are then used to predict the osmotic coefficients of two-salt solutions. The predictive results are summarized in Table 3, with an average ARD of about 1.5%. The results are in good agreement with experimental data.

To give insight into the predictive ability of our model for two-salt systems, we compare our predictive results with those from SAFT-RPM. NaBr + KBr and KCl + MgCl₂ are given as two typical examples to represent monovalent and bivalent two-salt solutions. It should be pointed out that most of the experimental data for osmotic coefficients presented in this paper are obtained by the using isopiestic technique, i.e., $\nu m' \varphi' = \text{constant}$, where the prime denotes the property of a reference salt. $\nu m = \sum_i \nu_i m_i$, in which ν_i is the number of moles of ions per mole of salt i , m is the total molality of salts ($= \sum_i m_i$), and φ is the osmotic coefficient of the solution. The results

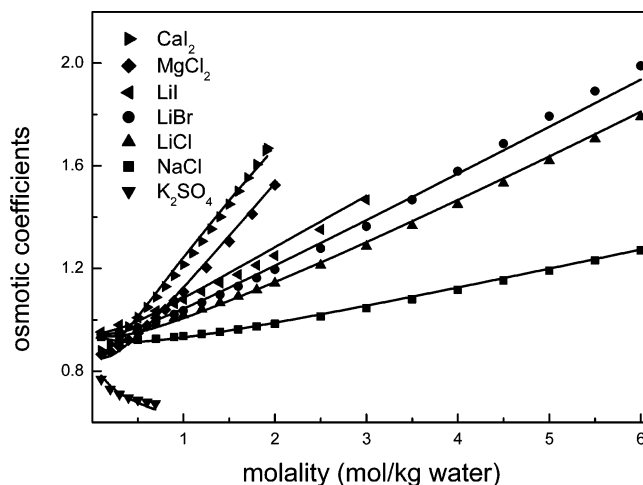


Figure 3. Predicted osmotic coefficient for single-salt solutions. The symbols are the experimental data,^{28–30} and the solid lines are predicted with the model.

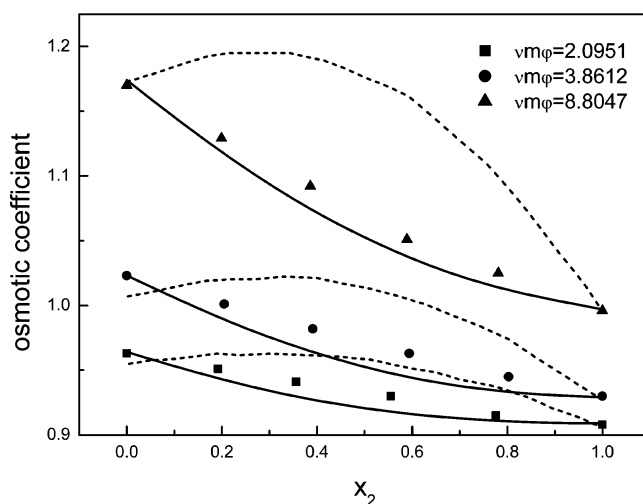


Figure 4. Comparison of the predicted osmotic coefficients for aqueous NaBr(1) + KBr(2) solution. The symbols are the experimental data,³⁶ dashed lines are predicted by SAFT-RPM, and solid lines are predicted by this work.

with different $\nu m \phi$ values are depicted in Figures 4 and 5, respectively. It is evident that results from SAFT-RPM deviate from experimental data obviously, while the new model yields much better results.

To further validate the new model, the predictive results for different kinds of two-salt solutions are illustrated in the following figures. Figures 6 and 7 show two examples of the model prediction for solutions containing two 1–1 type salts, i.e., for the aqueous LiCl + NaCl and NaCl + KBr solutions with different $\nu m \phi$ values. Figures 8 and 9 show two examples of the prediction for solutions containing 1–1 and 2–1 type salts, i.e., for the aqueous LiCl + CaCl and NaCl + MgCl₂ solutions with different $\nu m \phi$ values. Figure 10 shows an example for 1–1 and 1–2 type two-salt solutions, and Figure 11 shows an example for two 2–1 type salt solutions. All these figures display quite good predictive results compared with experimental data.

The advances of the new model for aqueous electrolyte at high temperatures and high pressures were also evaluated. The mean activity coefficients of NaCl solution, as an example, at elevated pressures and temperatures were predicted with the same parameters in Table 1. With the pressure increasing up to 600 bar, as shown in Figure 12, the predictive values are in

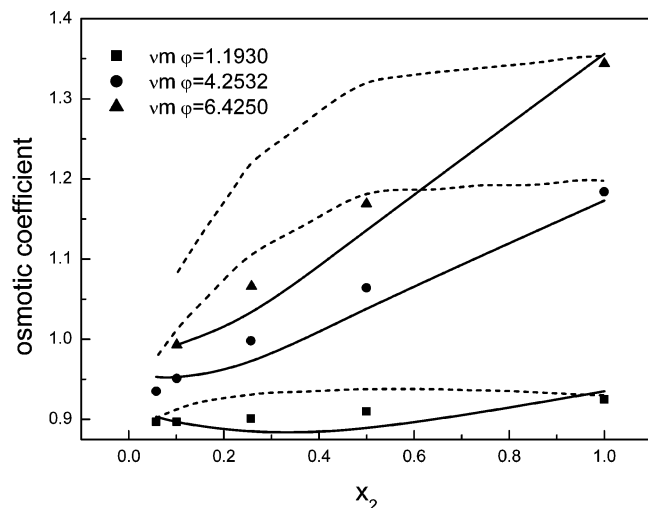


Figure 5. Comparison of the predicted osmotic coefficients for aqueous KCl(1) + MgCl₂(2) solution. The symbols are the experimental data,⁴¹ dashed lines are predicted by SAFT-RPM, and solid lines are predicted by this work.

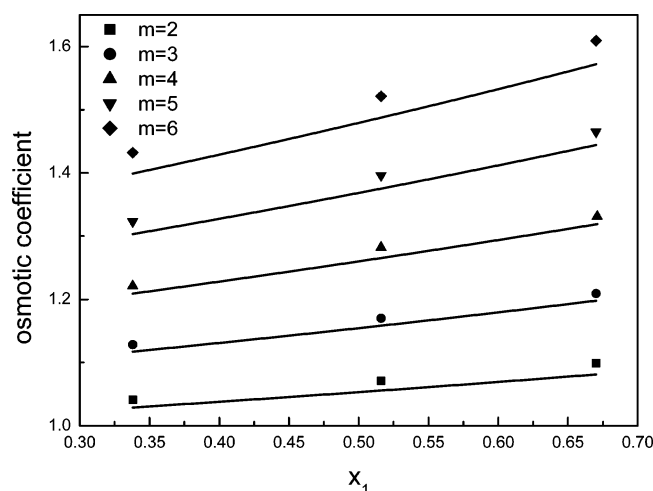


Figure 6. Predicted and experimental osmotic coefficients for aqueous LiCl(1) + NaCl(2) solution. The symbols are the experimental data,³³ and the solid lines are predicted results.

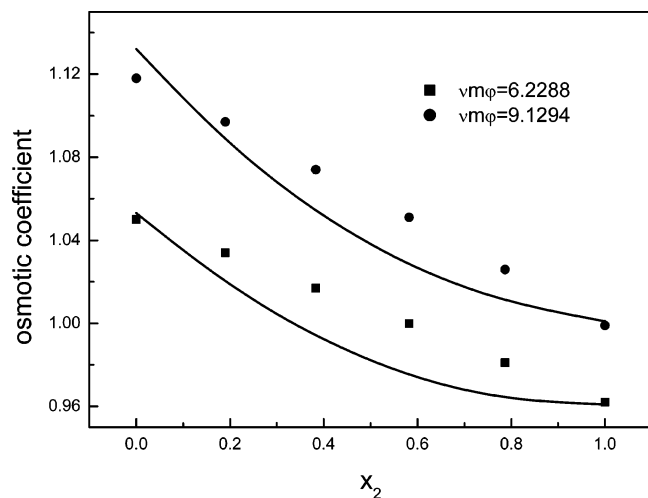


Figure 7. Predicted and experimental osmotic coefficients for aqueous NaCl(1) + KBr(2) solution. The symbols are the experimental data,³⁶ and the solid lines are predicted results.

good agreement with experimental data. However, at elevated temperatures, although the predictions described in Figure 13 are reasonable, the deviations between the predictions and

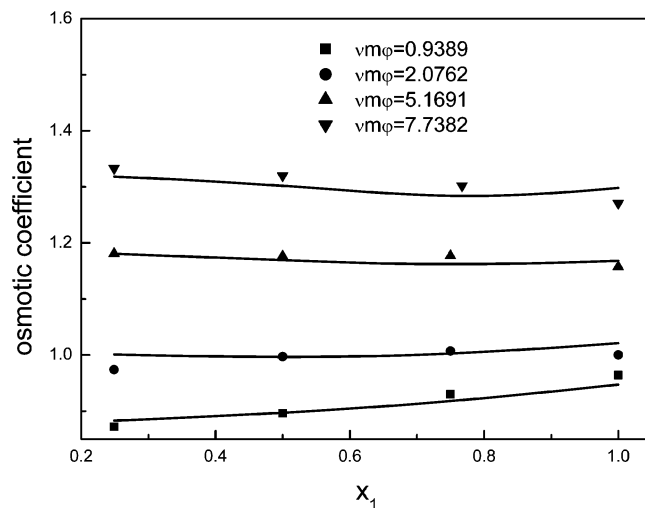


Figure 8. Predicted and experimental osmotic coefficients for aqueous LiCl(1) + CaCl₂(2) solution. The symbols are the experimental data,³⁵ and the solid lines are predicted results.

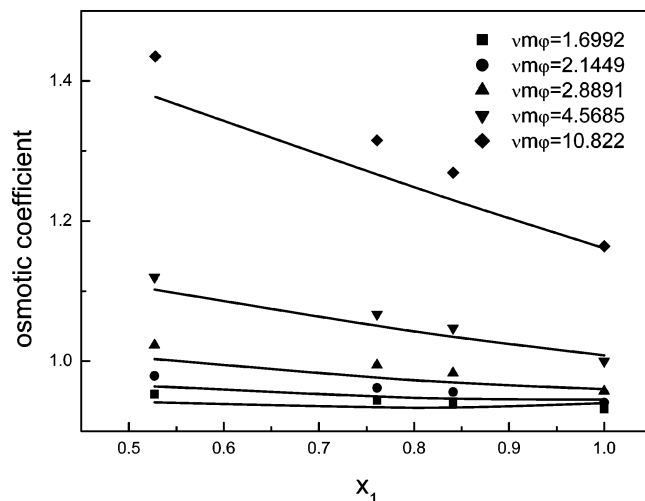


Figure 9. Predicted and experimental osmotic coefficients for aqueous NaCl(1) + MgCl₂(2) solution. The symbols are the experimental data,³⁷ and the solid lines are predicted results.

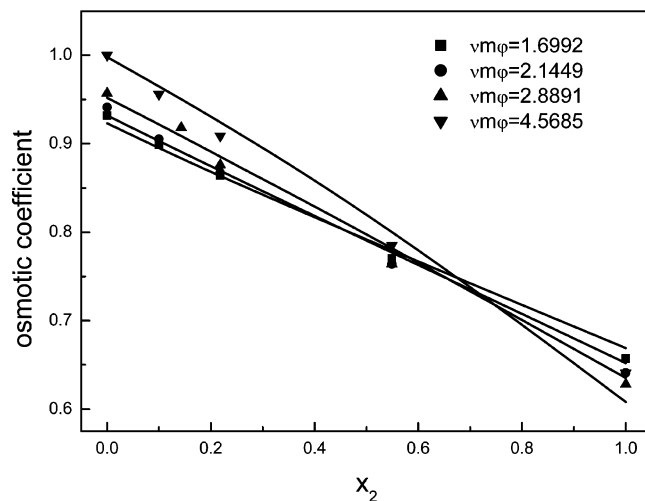


Figure 10. Predicted and experimental osmotic coefficients for aqueous NaCl(1) + Na₂SO₄(2) solution. The symbols are the experimental data,³⁷ and the solid lines are predicted results.

experiments increase. It can be generally explained that the increasing deviation is due to the fact that the model does not include properly the effects of ion pairing, and the intensity of

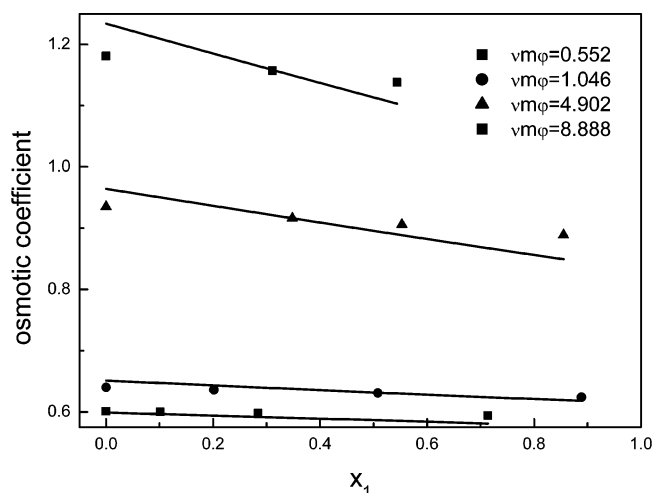


Figure 11. Predicted and experimental osmotic coefficients for aqueous $\text{CaCl}_2(1) + \text{MgCl}_2(2)$ solution. The symbols are the experimental data,⁴² and the solid lines are predicted results.

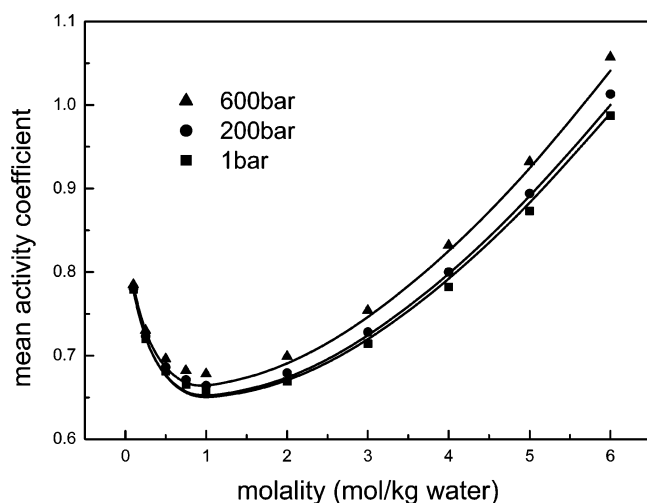


Figure 12. Predicted mean activity coefficients for aqueous NaCl solution at different pressures. The symbols are the experimental data,⁴³ and the solid lines are predicted results.

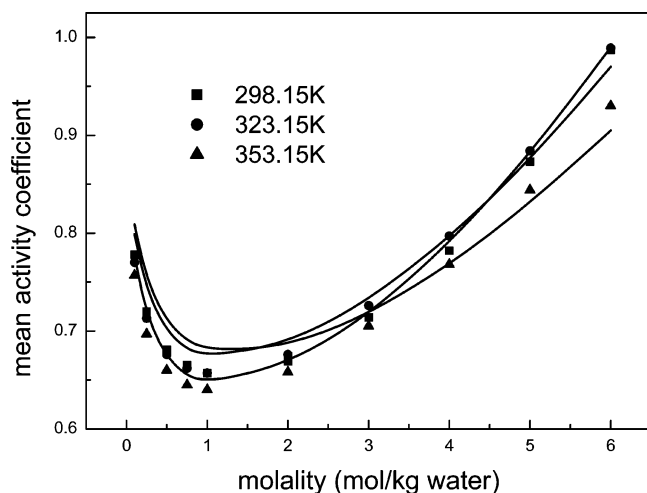


Figure 13. Predicted mean activity coefficients for aqueous NaCl solution at different temperatures. The symbols are the experimental data,⁴³ and the solid lines are predicted results.

ion–ion association can be further affected by temperature than by pressure. It has been recognized that ion association is an important effect in determining the thermodynamic properties in electrolytes due to strong electrostatic attraction between ions

of unlike charges. To improve the model, the associating energy of unlike ions should be included in the future investigation.

In general, the new EOS proposed in this work represents the excess energetic and volumetric properties of 19 monovalent and bivalent salt solutions as well as 19 two-salt solutions at ambient conditions with a good accuracy covering a wide range of concentrations. The parameters for salts are strictly based on independent ions and have clear physical definitions.

4. Conclusions

In this work, an equation of state based on primitive and first-order mean spherical approximation was proposed to represent the thermodynamic properties of aqueous single- and multiple-salt solutions. With the universal ionic parameters regressed from mean ionic activity coefficients and solution densities, the osmotic coefficients and water activities were accurately predicted. Especially, the model could be easily extended to two-salt systems without additional mixing parameters. The predicted results of osmotic coefficients of mixing monovalent and bivalent salt solutions are in good agreement with the experimental data. The predictive capability of the newly proposed EOS for complicated aqueous electrolyte solutions was validated. The effects of high pressures and high temperatures on the new model were also evaluated.

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Nomenclature

- a = Helmholtz free energy (kJ/mol)
- a_w = activity of water
- d = solution density (kg/m^3)
- D = dielectric constant of water
- e = elementary charge (C)
- g = radial distribution function
- G = Laplace transform of radial distribution function
- k = Yukawa parameter
- k_B = Boltzmann constant
- m = molality concentration (mol/kg of water)
- P_n = primitive MSA parameter
- q = ionic charge (C)
- r = distance between the centers of two particles (\AA)
- S = numbers of association sites on each particle
- T = absolute temperature (K)
- T^* = reduced temperature
- x = mole fraction
- X_A = mole fraction of nonassociating particles at site A
- z = Yukawa parameter

Greek Symbols

- $\beta = 1/k_B T$
- Γ = primitive MSA parameter
- γ_{\pm} = mean activity coefficient in molality scale
- δ_{ij} = associating strength between sites i and j
- ϵ/k = dispersion energy parameter (K)
- $\epsilon^{\text{assoc}}/k$ = association energy parameter (K)
- κ_{ij} = association volume between sites i and j
- ν = number of moles of ion per mole of salt
- ξ = packing factor
- ρ = number density
- σ = diameter (\AA)
- φ = osmotic coefficient
- Ω = primitive MSA parameter

Subscripts

H = hydrogen

e = lone pair

 i, j = component indices

Superscripts

assoc = association

dis = dispersion

hs = hard sphere

res = residual

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