



Chemical Engineering Thermodynamics

# Modeling for mean ion activity coefficient of strong electrolyte system with new boundary conditions and ion-size parameters<sup>☆</sup>

Miyi Li<sup>1,\*</sup>, Tao Fang<sup>2</sup><sup>1</sup> School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, China<sup>2</sup> Beijing Institute of Aerospace Testing Technology, Beijing 100074, China

## ARTICLE INFO

## Article history:

Received 18 November 2014

Received in revised form 26 February 2015

Accepted 6 March 2015

Available online 15 April 2015

## Keywords:

Activity coefficient

Electrolyte

Ion size

Poisson–Boltzmann equation

## ABSTRACT

A rigorous approach is proposed to model the mean ion activity coefficient for strong electrolyte systems using the Poisson–Boltzmann equation. An effective screening radius similar to the Debye decay length is introduced to define the local composition and new boundary conditions for the central ion. The crystallographic ion size is also considered in the activity coefficient expressions derived and non-electrostatic contributions are neglected. The model is presented for aqueous strong electrolytes and compared with the classical Debye–Hückel (DH) limiting law for dilute solutions. The radial distribution function is compared with the DH and Monte Carlo studies. The mean ion activity coefficients are calculated for 1:1 aqueous solutions containing strong electrolytes composed of alkali halides. The individual ion activity coefficients and mean ion activity coefficients in mixed solvents are predicted with the new equations.

© 2015 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

## 1. Introduction

The Debye–Hückel (DH) limiting law [1] is a monumental work for electrolyte systems, followed by many equations developed for these systems. Although it gives a good description for physical properties for dilute solutions, it fails at high concentrations for real systems. Another defect is ignoring the size of ions, leading to large deviations from real physical behavior. Fowler and Guggenheim [2] have improved the DH theory with the Güntelberg charging model, with the central ion and ion atmosphere being charged simultaneously. The equation can be applied for electrolyte systems up to  $0.1 \text{ mol} \cdot \text{kg}^{-1}$ , even in mixed solvent systems. Bromley [3] has introduced one more empirical term for ionic strength, which can be applied for solutions at concentrations up to  $6 \text{ mol} \cdot \text{kg}^{-1}$ . Mayer [4] has developed a DH equation with a statistical treatment of ion–ion interactions, based on his theory of clusters of real gases. Stokes and Robinson [5] have proposed the well known ionic hydrate model for aqueous electrolyte systems at high concentrations, assuming that the electrolyte dissociates and reaches ionic solvation equilibria (chemical reaction) in the solution, fitting the ionic hydrate numbers of water molecules and correlating the mean ion activity coefficients of electrolytes from 0.1 to  $4 \text{ mol} \cdot \text{kg}^{-1}$  with experimental data.

In the 1970s, the mean spherical approximation (MSA) [6,7] was derived from the Ornstein–Zernike integral method. It is based on the

linear Poisson–Boltzmann equation with an analytical solution for the central ion and surrounded ionic cloud with finite size. The MSA has been applied for the calculation of departures of real systems from ideal ionic solutions, with the solvent as a dielectric continuum, called primitive model. Ion radius and dielectric constant are fitted for osmotic coefficients and activity coefficients of strong electrolyte solutions [8–10]. In the correlation, the Pauling diameters are usually chosen for the anion, while cation diameters are set as adjustable parameters for the ionic strength. All these attempts exaggerate the size of smaller cations, which is interpreted as hydration. For larger ions, smaller diameters are obtained, sometimes even smaller than crystallographic diameters, which is difficult to be accepted. Simonin *et al.* [11,12] have taken into account the concentration-dependent solvent permittivity with the effect on the Helmholtz energy of the system, providing a better description for real electrolyte systems. Besides, the MSA and ion association have been applied together for 1:1 electrolytes in water with adjustable ionic diameters and associate constant [13]. The MSA approach is also combined with the modified non-random two-liquid approach [14]. It is suitable for the description of mixed-solvent electrolyte systems.

Outhwaite [15,16] has proposed a modified Poisson–Boltzmann (MPB) equation to fit the ion size and exclusive volume of cloud ions. The radial distribution function is represented as a symmetric function when ion species have different valences or ionic radii. Comparisons of the hypernetted chain closure (HNC) integral equation and Monte Carlo (MC) method for systems with different ion sizes [17] indicate that the symmetric Poisson–Boltzmann (PB) expression is viable for the primitive electrolyte model at low concentrations with high quality. Molero *et al.* [18] have made great efforts to examine the meaning of

<sup>☆</sup> Supported by the National Natural Science Foundation of China (21206010).

\* Corresponding author.

E-mail address: [limiyibit@163.com](mailto:limiyibit@163.com) (M. Li).

individual ion activity coefficients using the MPB equation and compared them with the MSA, HNC and MC simulations. It is found that the electric part of activity coefficient for single ion declines monotonically with the increases of ratio of cation to anion ionic size. Kjellander and Mitchell [19] define a long range contribution as a charge distribution like “dressed ion”, called dressed ion theory (DIT), which follows the DH expression. It assumes an effective point charge instead of bare charge of ions, a decay length instead of DH length, and so on. With these renormalized assumptions the entire theory can be cast in a linear PB form. Varela *et al.* [20] have exploited the dressed ion model to obtain static structure factors of bulk electrolytes or colloid systems and emphasized that the DIT is an exact theory, applicable for all primitive model systems with symmetric and non-symmetric electrolytes. It extends the classical DH theory considerably and the results are valid from low to finite concentrations. This theory is particularly useful in explaining concentrated electrolyte solutions, colloid media, double-layer, and interfacial phenomena in surfactant physics. On the basis of modern density functional analysis, Abbas and Nordholm [21] have considered long-range electrostatic interactions and short-range ion size effects by a generalized van der Waals analysis, named the corrected Debye–Hückel (CDH). In this theory, all ions are assumed to have the same diameter for symmetric salts, macro-ions or planner surfaces, with the excluded volume effect vanishing in the linear response. A mean diameter of cation and anion according to the original DH theory is used to fit experimental mean ion activity coefficients and osmotic coefficients up to  $1 \text{ mol} \cdot \text{kg}^{-1}$ . A new approach to consider the ion size of strong electrolyte has been made by Fraenkel [22], using the distance of closest approach between opposite ions in the DH treatment and defining another second distance of closest approach of similar ion, called the Smaller-ion Shell model. It is a DH level modification based on the LPB equation, providing some analytical expressions for real electrolyte systems regarding ion sizes, ion charges, and ion charge asymmetry. Although it is somewhat empirical and complex in two specially defined ionic cases, it can be used directly to correlate experimental activity coefficient data with adjustable parameters instead of numerical commutation such as integral equation methods.

The objective of this work is to develop a new mean ion activity coefficient expression for strong electrolyte systems to describe ion size contribution based on the Poisson–Boltzmann equation. Cations and anions are considered as charged hard spheres of unequal size dissolved in solvents. The ion size is more close to the real crystallographic diameters compared to other theories mentioned above by fitting those as adjustable parameters. The electrostatic potential distribution around the central ion is analyzed by introducing an ion atmosphere assumption similar to that in the DH theory, only the electrostatic forces between ions are considered, and the solvent is viewed as a continuum with dielectric constant. New outer boundary conditions for the PB equation are developed to obtain an analytical solution for electrostatic potential. The effective screening radius is represented as an empirical expression of ionic concentration. The derived mean ion activity coefficient equation is applied for single salt in pure water, fitted with experimental data at 298.15 K. The individual ion activity coefficients and mean ion activity coefficients in mixed solvent electrolyte systems are predicted with our model and parameters.

## 2. Modeling for the Mean Ion Activity Coefficient

We start from single 1:1 strong electrolytes in pure water, with the salt completely dissociating into ions, which are assumed as hard spheres interacting through Coulomb forces in a dielectric continuum solvent. For simplification, ion size and dielectric constant of solvent do not vary with ionic concentration. Some theoretical relations used here are based on the Debye–Hückel theory [1] and the solutions at low and moderate concentrations are considered. We first recall some

of the Debye–Hückel theory to give a specific derivation of our model and systems of alkali halides in water are investigated.

In the bulk thermodynamic relations of the Debye–Hückel theory, the non-ideality of solution is mainly attributed to the ion–ion interactions. The chemical potential for a given ion can be described as a sum of an ideal term and an excess term representing the electrostatic force. The relationship of chemical potential and activity coefficient of ion has been given elsewhere [1,5,24].

$$\mu_j = \mu_j^{\text{ideal}} + \mu_j^{\text{electro}} \quad (1)$$

$$\mu_j^{\text{electro}} = RT \ln \gamma_j \quad (2)$$

Superscripts “ideal” and “electro” refer to the ideal solution and electrostatic energy contribution, respectively,  $\gamma_j$  is the activity coefficient of ion  $j$  in the solution,  $R$  ( $8.314 \text{ kJ} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$ ) is the gas constant, and  $T$  (K) is the general absolute system temperature.

The problem starts from how to determine the contribution of electrostatic energy to the chemical potential. The DH theory calculates the local potential of an ion due to its ionic atmosphere and gives a radial distribution function using the Boltzmann law for ion  $j$  in the ionic atmosphere. The same expression for the charge density is used for ion  $j$ .

$$\rho_j = \rho_{j0} \exp \left[ -\frac{z_j e \psi(r)}{kT} \right] \quad (3)$$

$$\begin{aligned} \rho_e(r) &= \sum_j \rho_j z_j e = \sum_j z_j e \rho_{j0} \exp \left[ -\frac{z_j e \psi(r)}{kT} \right] \\ &= e \sum_j \rho_{j0} z_j - \frac{e^2 \psi(r)}{kT} \sum_j \rho_{j0} z_j^2 + \frac{e^2 \psi^2(r)}{2k^2 T^2} \sum_j \rho_{j0} z_j^2 + \dots \end{aligned} \quad (4)$$

where  $\rho_e$  is the average charge density at distance  $r$  from the central ion in molar scale,  $z_j$  is the valence of ion  $j$ ,  $e$  ( $1.60218 \times 10^{-19} \text{ C}$ ) is the fundamental electronic charge,  $\rho_{j0}$  is the overall average concentration of ion  $j$  ( $\text{mol} \cdot \text{cm}^{-3}$ ), and  $\psi$  indicates the local electrostatic potential outside the central ion. In Eq. (3), the Boltzmann distribution function is used to describe the concentration of ions around the central ion relative to the distance from the central ion. The thermal kinetic energy  $kT$  is assumed greater than the electrostatic energy  $z_j e \psi(r)$ , similar to that in the DH theory. The term  $e \sum \rho_{j0} z_j$  must be equal to zero, which indicates the electroneutrality of the solution. Using the second term of the Taylor series expansion in Eq. (4), the expression for the charge density becomes

$$\rho_e(r) = -\frac{e^2 \psi(r)}{kT} \sum_j \rho_{j0} z_j^2. \quad (5)$$

With the charge density  $\rho_e$  similar to the DH theory, the Poisson–Boltzmann equation can be obtained.

$$\nabla^2 \psi = \Delta \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi}{D} \rho_e \quad (6)$$

where  $D$  is the dielectric constant of solvent given by

$$D = 4\pi \epsilon_0 \epsilon_w \quad (7)$$

$\epsilon_w$  is the relative dielectric constant of water and  $\epsilon_w = 78.3$ ,  $4\pi \epsilon_0 = 1.11265 \times 10^{-10} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$ , and the Debye length  $\kappa_{\text{DH}}^{-1}$  is given by

$$\kappa_{\text{DH}}^{-2} = \frac{4\pi e^2}{DkT} \sum_j \rho_{j0} z_j^2. \quad (8)$$

Download English Version:

<https://daneshyari.com/en/article/167104>

Download Persian Version:

<https://daneshyari.com/article/167104>

[Daneshyari.com](https://daneshyari.com)