Missteps in the Analytical Formula of Smaller-Ion Shell Model

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ABSTRACT

Recently, a smaller-ion shell (SiS) model was developed to describe the electrostatic interaction between ions in solutions (D. Fraenkel, *Mol. Phys.*, **108**, 1435 (2010)). The analytical formula based on the SiS model reproduces experimental data very well with only one fitting parameter (namely, ion size parameter, a). However, a numerical simulation of the SiS model does not agree with the analytical formula. This indicates that the analytical formula does not represent the SiS model correctly. Therefore, the ion size parameter (a) obtained by fitting Fraenkel's analytical formula to the experimental data is physically meaningless.

Smaller-ion shell (SiS) model

Fraenkel's analytical formula

$$\log \gamma_+ = - \frac{z_s^2 q^2 \kappa}{2.303 \cdot 8\pi\epsilon_0\epsilon_r kT(1+\kappa a)} \left\{ 1 - \frac{2(e^{\kappa(a-b_s)} - 1) - \kappa(a-b_s)}{1+\kappa b_s} \right\}$$

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1. Introduction

With regard to the thermodynamic laws, there exists a gap between real and ideal solutions. To compensate for this discrepancy, the concept of activity was introduced. Activity is associated with the analytical concentration through the activity coefficient. The relation between the activity coefficient and ionic strength (I) has been actively investigated by many researchers for a long time.

A theory was first formulated by Debye and Hückel (the DH limiting law).¹ Since the DH limiting law is valid only at a very low I , the extended DH model that considers the ion size and is valid at higher I was proposed (Fig. 1A).¹ Subsequently, several other models were proposed to understand the behavior of ions in real solutions.^{2–6} Recently, Fraenkel proposed a smaller-ion shell (SiS) model that considers two ion size categories (Fig. 1B).⁷ According to the SiS model, the activity coefficients are given by

$$\log \gamma_+ = - \frac{z_s^2 q^2 \kappa}{2.303 \cdot 8\pi\epsilon_0\epsilon_r kT(1+\kappa a)} \left\{ 1 - \frac{2(e^{\kappa(a-b_s)} - 1) - \kappa(a-b_s)}{1+\kappa b_s} \right\} \quad (1)$$

$$\log \gamma_- = - \frac{z_l^2 q^2 \kappa}{2.303 \cdot 8\pi\epsilon_0\epsilon_r kT(1+\kappa a)} \left\{ 1 + \frac{2(e^{\kappa(b_l-a)} - 1) - 2\kappa(b_l-a)}{1+\kappa b_l} \right\} \quad (2)$$

$$\log \gamma_{\pm} = \frac{v_s \log \gamma_+ + v_l \log \gamma_-}{v} \quad (3)$$

Figure 1. Schematic illustration of the (A) extended Debye–Hückel (DH) model and (B) smaller-ion shell (SiS) model.

where γ_+ is the activity coefficient of a smaller ion, γ_- is the activity coefficient of a larger ion, $\gamma_{\pm}$ is the mean activity coefficient, subscripts “s” and “l” denote the smaller and larger ions, respectively, z is the charge number, q is the elementary charge, κ is the reciprocal Debye screening length, ν_s and ν_l are the ionic multiplicities (number of ions considered in the electrolyte molecular formula, and $\nu = \nu_s + \nu_l$), a is the distance of the closest approach between the smaller and larger ions, b_s is the distance of the closest approach between the smaller ions, and b_l is the distance of the closest approach between the larger ions. In Eqs. (1), (2), and (3), the crystal diameters are set to values of b_s and b_l , and the fitting parameter is only a . Equation (3) fits experimental data very well. However, there are many unclear points in the derivation of Fraenkel’s analytical formula, and there exist some doubts regarding the validity of the analytical formula.

In this study, the activity coefficients of the SiS model were calculated by a numerical simulation to confirm the validity of the analytical formula derived by Fraenkel. Since the DH limiting law and the extended DH model are very simple continuum models, their results can be reproduced by a numerical simulation.⁸ Similarly, the SiS model is also a continuum model and should be reproduced by a numerical simulation. In this paper, the author explains the difference in values between Fraenkel’s analytical formula and a numerical simulation and discusses the validity of Fraenkel’s analytical formula.

2. Numerical Simulation

The author used the finite element method to calculate the activity coefficient for the SiS model. The author considered only the case of a small central ion (since the same problems exist in the case of a large central ion), that is, the author calculates only γ_+ . The geometry of the model is shown in Fig. 2. The cyan semicircle domain contains both the smaller and larger ions. In this domain, the charge density (ρ_{DH}) is given by

$$\begin{aligned}\rho_{\text{DH}} &= \sum_i n_i z_i q \exp\left(-\frac{z_i q \phi}{kT}\right) \\ &= n_s z_s q \exp\left(-\frac{z_s q \phi}{kT}\right) + n_l z_l q \exp\left(-\frac{z_l q \phi}{kT}\right)\end{aligned}\quad (4)$$

Figure 2. Geometry of the SiS model made by COMSOL. The three-dimensional geometry was obtained by resolving the two-dimensional geometry around a dashed-dotted line.

where n is the number density, ϕ is the electric potential, k is the Boltzmann constant, and T is the absolute temperature. The blue domain is the SiS region and contains only the smaller ion. In this domain, the charge density (ρ_{SiS}) is given by

$$\rho_{\text{SiS}} = n_s z_s q \exp\left(-\frac{z_s q \phi}{kT}\right) \quad (5)$$

The white semicircle domain contains no atmospheric ions. A charge ($z_s q$) was positioned at the center as a point charge. In all domains, the Poisson equation was applied to obtain the profile of ϕ .

$$\nabla^2 \phi = -\frac{\rho}{\epsilon_0 \epsilon_r} \quad (6)$$

where ϵ_0 is the permittivity of the vacuum, and ϵ_r is the relative permittivity. For simplicity, the author considered a 1:1 electrolyte in this calculation, that is, $z_s = +1$ and $z_l = -1$. ϵ_r and T were set as 78.5 and 298 K, respectively, in all domains. The boundary condition was $\phi = 0$ at the rim of the large cyan semicircle. For various values of I , the nonlinear Poisson equation was numerically solved by COMSOL Multiphysics 5.0 to obtain ϕ . Further, γ_+ was calculated as follows by⁸

$$\log \gamma_+ = \frac{\sum \frac{1}{2} \phi(I=0) \rho_{r \geq b_s} dV}{2.303 kT} \quad (7)$$

where $\phi(I=0)$ is the potential at $I=0$, $\rho_{r \geq b_s}$ is the charge density in the domain ($r \geq b_s$), in which the atmospheric ions exist, and dV is the volume of an element in the finite element method.

3. Results and Discussion

Figure 3 shows the dependence of the activity coefficient on the ionic strength calculated from the numerical simulation and from Eq. (1). In the very low I region, Eq. (1) agrees with the numerical simulation, but they deviate from each other as I increases. The discrepancy increases as the thickness of SiS increases. This indicates that Fraenkel’s analytical formula does not represent the SiS model correctly. Incorrect derivation of the analytical formula is ascribed to the assumption that the inverse of the Debye length in the SiS region (κ_{SiS}) is almost identical to κ .⁷ In fact, κ and κ_{SiS} are given as follows:

$$\kappa = \left(\frac{q^2}{\epsilon_0 \epsilon_r kT} \sum_i n_i z_i^2 \right)^{1/2} \quad (8)$$

$$\kappa_{\text{SiS}} = \left(\frac{n_s z_s^2 q^2}{\epsilon_0 \epsilon_r kT} \right)^{1/2} \quad (9)$$

As can be seen from Eqs. (8) and (9), $\kappa_{\text{SiS}} < \kappa$. The assumption of $\kappa_{\text{SiS}} \approx \kappa$ means that the virtual number of the smaller ions in the SiS region is much larger than the real number of smaller ions. The analytical formula derived under this assumption results in the overestimation of the charge density in the SiS region. This overestimation increases with an increase in the thickness of the SiS, causing a large discrepancy between the analytical formula and the value obtained by numerical simulation.

The author successfully derived an analytical formula for the SiS model without assuming $\kappa_{\text{SiS}} \approx \kappa$ (see Supporting Information).

$$\log \gamma_+ = \frac{z_s q}{4.606 kT} [-\kappa_{\text{SiS}} \{A(-e^{-\kappa_{\text{SiS}} a} + e^{-\kappa_{\text{SiS}} b_s}) + B(e^{\kappa_{\text{SiS}} a} + e^{\kappa_{\text{SiS}} b_s})\} - \kappa C e^{-\kappa a}] \quad (10)$$

$$\log \gamma_- = \frac{z_l q}{4.606 kT} [-\kappa_{\text{SiS}} \{A'(-e^{-\kappa_{\text{SiS}} b_l} + e^{-\kappa_{\text{SiS}} a}) + B'(e^{\kappa_{\text{SiS}} b_l} + e^{\kappa_{\text{SiS}} a})\} - \kappa C' e^{-\kappa b_l}] \quad (11)$$

where A , A' , B , B' , C , and C' are constant. The analytical formula is in good agreement with the numerical simulation (Figs. S1 and S2).

Figure 3. Comparison between the numerically simulated values (symbols) and theoretical values obtained from Eq. (1) of γ_+ . M is in mol dm^{-3} . Theoretical values were calculated using $z_s = 1$, $z_l = -1$, $q = 1.6 \times 10^{-19} \text{ C}$, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$, $T = 298 \text{ K}$, $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$, and $\epsilon_r = 78.5$. At $z_s = 1$ and $z_l = -1$, $n_s = n_l = 6.02 \times 10^{23} \text{ l}^{-1}$.

The small discrepancy at high I is ascribed to the linearization of the Poisson–Boltzmann equation in the derivation of the analytical formula. The present analytical formula correctly expresses the illustration of the SiS model. Therefore, it can be concluded that Fraenkel’s analytical formula shows very good fit with experimental data, but the ion size parameter, a , is physically meaningless. It is not appropriate to discuss the ionic states in solutions based on the a parameter obtained by fitting of Fraenkel’s analytical formula. In addition, since the SiS model is very simple and may not correctly represent the real system, the newly derived correct analytical formula cannot reproduce some experimental values of $\gamma_{\pm}$ at high I (Fig. S3, NaCl and LiCl).

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-00161>.

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