Empirical Approach to Modeling Ion Size Effects in Diffuse Double Layer Theory

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Abstract

A novel empirical model for the diffuse double layer is found by generalizing the simple analytical equations of Gouy-Chapman theory. Two adjustable parameters are introduced into the Boltzmann equation for the exponential dependence of the ion-wall correlation functions on the diffuse layer potential. Optimal parameter values and model validation are provided by Monte Carlo simulations. Simple relationships are obtained between these empirical parameters and those commonly associated with the mean-spherical approximation. The new empiricism accurately models diffuse layer potential profiles and ion-wall correlation functions for a restricted 1:1 electrolyte in a primitive solvent.

Application to 1:1 Electrolytes

cation $z_1 = +1$, anion $z_2 = -1$.

Now solve empirical Poisson-Boltzmann equation

$$d^2 \phi(x) \over dx^2 = -{E^2 \sigma^2 \over RT \epsilon_x \rho} \sum_j z_j^2 \epsilon_j g_j(x)$$

to obtain the potential drop across diffuse layer

$$\phi_0 = {2 \over \alpha} \ln \left( {\alpha E \over \sqrt{\theta} + \sqrt{\alpha E^3 \over 4 \theta} + 1} \right)$$

and the potential profile in the diffuse layer

$$\tanh \left( \alpha \phi(x) \over 4 \right) = \tanh \left( \alpha \phi_0 \over 4 \right) \exp(-\kappa \sigma \alpha \theta x)$$

Figure 1. Dimensionless diffuse layer potential drop versus charge density for 1:1 electrolytes.

Figure 2. Dimensionless diffuse layer potential drop versus charge density for 2:1 electrolytes.

Figure 3. Dimensionless diffuse layer potential profiles versus dimensionless distance, with bulk concentration = 0.5 M and charge density = 0.20 C m$^{-2}$.

Figure 4. Ion-wall correlation functions versus dimensionless distance in diffuse layer for 1:1 electrolyte only and same parameters as in Fig. 3.

Figure 5. Plot of the parameter $\alpha$ determined by fitting the MC data to equation (35) against 60 pm $\langle \sigma \rangle$ and 300 pm $\langle \sigma \rangle$ for ion diameters of 200 pm $\langle \sigma \rangle$ and 400 pm $\langle \sigma \rangle$.

Figure 6. Plot of the parameter $\theta$ determined by fitting the MC data to equation (35) against 60 pm $\langle \sigma \rangle$ for ion diameters of 200 pm $\langle \sigma \rangle$ and 300 pm $\langle \sigma \rangle$.

Figure 7. Plots of diffuse layer capacity $C_d$ versus electrostatic charge density $n_{\text{eq}}$, for a 1:1 electrolyte at concentrations of 0.1 and 1 M. Solid curves show the GC estimates, and the broken curves, the results of the empirical model for ion size of 300 pm.

Figure 8. MC data $\bullet$ for potential in the diffuse layer plotted against the distance from oHlP in units of the ion diameter (400 pm) for electrolyte concentration of 2 M and $n_{\text{eq}} = 20 \mu\text{C m}^{-2}$. Solid curve gives the potential distribution according to the GC theory and the broken curve, according to the empirical model.

Analytical estimation of empirical parameters

$$\alpha = {2 \over \alpha_{0R}} - (12 \eta^2)^{1/2} + 4 \Gamma$$

$$\theta = {6 \eta^1/3 + 2 \eta^{2/3} - 3 \Gamma \over 5}$$

$$\alpha_{0R} = \left( {1 + \eta + \eta^2 + \eta^3 \over (1 - \eta)^3} \right) {\Gamma}^3 {18 \eta}$$

Nomenclature

$E$ field at oHlP; dimensionless charge density

$\sigma_{\text{w}}$ wall charge density / C m$^{-2}$

$g_i(x)$ ion-wall correlation function

$\phi(x)$ potential at position $x$ in diffuse layer; $\phi(x) = F(x)/RT$

$\phi_0$ potential drop across diffuse layer; potential at oHlP

$C_d$ diffuse layer differential capacity / F m$^{-2}$

$\alpha$, $\theta$ empirical parameters

$\epsilon_0$ vacuum permittivity

$\kappa$ Debye-Hückel reciprocal length

$\sigma$ ionic diameter

$z_i$ charge of ion $i$

$\eta$ MSA volume fraction

References


Fawcett, W. R.; Smagala, T. G. Langmuir, electrochemistry special issue, in press.


Smagala, T. G.; Fawcett, W. R. J. Electroanalytical Chemistry, in press.

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