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SHORT COMMUNICATION

An approximate analytic solution to the modified Poisson-Boltzmann equation: effects of ionic size

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Abstract A simple algorithm is presented for solving the modified Poisson-Boltzmann equation for the electric potential around a planar charged surface in contact with an electrolyte solution, which takes into account the effects of ionic size on the basis of ionic activity coefficient given by Carnahan and Starling (J Chem Phys (1969) 51: 635). An approximate analytic expression for the surface charge density/surface potential relationship is derived.

Keywords Modified Poisson-Boltzmann equation · Effects of ionic size · Surface charge density/surface potential relationship

Introduction

The electric potential distribution around a charged particle in an electrolyte solution, which plays an essential role in determining the electric behaviors of the colloidal particles, is usually obtained by solving the Poisson-Boltzmann equation [1–9]. The standard Poisson-Boltzmann equation for the electric potential distribution, however, assumes that ions behave like point charges and neglects the effects of ionic size. There are many theoretical studies on the modified Poisson-Boltzmann equation [10–15], which takes into account the effect of ionic size by introducing the activity coefficients of electrolyte ions [10, 16–18]. In the present paper on the basis of the equation for the ionic activity coefficients given by Carnahan and Starling [18], which is the most accurate among existing theories, we present a simple algorithm for solving the modified Poisson-Boltzmann equation and derive a simple approximate analytic expression for the surface charge density/surface potential relationship for a planar charged surface.

Theory

Consider a charged planar wall surface in contact with a symmetrical electrolyte solution of valence z and bulk concentration (number density) n (in units of m^{-3}) and take an x-axis perpendicular to the wall surface with its origin 0 at the wall surface. We denote the surface potential and the surface charge density of the wall by $\psi_o = \psi(0)$ and σ, respectively. The potential distribution $\psi(x)$ obeys the Poisson equation for the region $x > 0$, viz.,

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_{\mathrm{el}}(x)}{\varepsilon_r\varepsilon_o} \tag{1}$$

Here, ε_r is the relative permittivity of the electrolyte solution, ε_o is the permittivity of a vacuum, and $\rho_{\mathrm{el}}(x)$ is the space charge density resulting from the electrolyte ions and is given by

$$\rho_{\mathrm{el}}(x) = ze\{n_+(x) - n_-(x)\} \tag{2}$$

where $n_+(x)$ and $n_-(x)$ are, respectively, the concentrations of cations and anions at position x and e is the elementary electric charge. In the standard Poisson-Boltzmann approach, in

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which ions are assumed to be point charges, the ion distribution is given by the Boltzmann distribution, viz.,

$$n_{\pm}(x) = n\exp\left(\mp\frac{ze\psi(x)}{kT}\right) \tag{3}$$

where k is Boltzmann's constant and T is the absolute temperature. Equation (1) as combined with Eqs. (2) and (3) thus becomes the following standard Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\varepsilon_r\varepsilon_o}\sinh\left(\frac{ze\psi(x)}{kT}\right) \tag{4}$$

which can be rewritten in the non-dimensional form as

$$\frac{d^2y}{dx^2} = \kappa^2\sinh y \tag{5}$$

where $y = ze\psi/kT$ is the scaled electric potential and

$$\kappa = \left(\frac{2z^2e^2n}{\varepsilon_r\varepsilon_o kT}\right)^{1/2} \tag{6}$$

is the Debye-Hückel parameter. The boundary conditions are

$$\left.\frac{d\psi}{dx}\right|_{x=0^+} = -\frac{\sigma}{\varepsilon_r\varepsilon_o} \tag{7}$$

$$\psi(x)\rightarrow 0 \text{ and } \frac{d\psi}{dx}\rightarrow 0 \text{ as } x\rightarrow\infty \tag{8}$$

The standard Poisson-Boltzmann Eq. (4) assumes that electrolyte ions are point-like charges. This assumption, however, becomes invalid especially in the region very close to a highly charged surface, where the concentration of counterions is very high. We must thus take into account steric interactions among ions of the finite size, by introducing ionic activity coefficient γ. We assume that the activity coefficients of cations and anion have the same value γ. The electrochemical potential $\mu_+(x)$ of cations and that of anions $\mu_-(x)$ at position x are thus given by

$$\mu_{\pm}(x) = \mu_{\pm}^{\AA} \pm ze\psi(x) + kT\ln[\gamma(x)n_{\pm}(x)] \tag{9}$$

which must take the same value as those in the bulk solution phase, where $\psi(x) = 0$, viz.,

$$\mu_{\pm}(\infty) = \mu_{\pm}^{o} + kT\ln(\gamma^{\infty}n) \tag{10}$$

where $\mu_{\pm}{}^{o}$ are constant trems and $\gamma^{\infty} = \gamma(\infty)$. By equating $\mu_{\pm}(x) = \mu_{\pm}(\infty)$, we obtain

$$n_{\pm}(x) = \frac{\gamma^{\infty}n}{\gamma(x)}\exp\left(\mp\frac{ze\psi(x)}{kT}\right) \tag{11}$$

so that Eq. (2) gives

$$\begin{aligned}\rho_{el}(x) &= \frac{\gamma^{\infty}}{\gamma(x)}zen\left\{\exp\left(-\frac{ze\psi(x)}{kT}\right)-\exp\left(\frac{ze\psi(x)}{kT}\right)\right\}\\ &= -\frac{2\gamma^{\infty}}{\gamma(x)}zen\sinh\left(\frac{ze\psi(x)}{kT}\right)\end{aligned} \tag{12}$$

Thus, Eq. (1) becomes the following modified Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\varepsilon_r\varepsilon_o}\cdot\frac{\gamma^{\infty}}{\gamma(x)}\sinh\left(\frac{ze\psi(x)}{kT}\right) \tag{13}$$

We now assume that cations and anions have the same radius a. We introduce the volume fraction ϕ_+ of cations and that of anions ϕ_- at position x. Then we have

$$\phi_{\pm}(x) = \left(\frac{4}{3}\pi a^3\right)n_{\pm}(x) \tag{14}$$

The total ion volume fraction $\phi(x)$ at position x is thus given by

$$\phi(x) = \phi_+(x) + \phi_-(x) = \left(\frac{4}{3}\pi a^3\right)\left\{n_+(x) + n_-(x)\right\} \tag{15}$$

Let the total ion volume fraction in the bulk solution phase be $\phi_B \equiv \phi(\infty)$. Then from Eq. (15), we obtain

$$\phi_B = \left(\frac{4}{3}\pi a^3\right)\cdot 2n \tag{16}$$

so that Eq. (15) becomes

$$\phi(x) = \frac{\phi_B\left\{n_+(x) + n_-(x)\right\}}{2n} \tag{17}$$

By substituting Eq. (11) into Eq. (17), we obtain

$$\phi(x) = \phi_B\frac{\gamma^{\infty}}{\gamma(x)}\cosh\left(\frac{ze\psi(x)}{kT}\right) \tag{18}$$

The modified Poisson-Boltzmann Eq. (13) becomes, by using Eq. (18),

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\varepsilon_r\varepsilon_o}\cdot\frac{\phi(x)}{\phi_B}\tanh\left(\frac{ze\psi(x)}{kT}\right) \tag{19}$$

which is rewritten in the non-dimensional form as

$$\frac{d^2y}{dx^2} = \frac{\phi(x)}{\phi_B}\cdot\kappa^2\tanh y \tag{20}$$

Now, we employ the expressions for $\gamma(x)$ derived by Carnahan and Starling [18], viz.,

$$\gamma(x) = \exp\left[\frac{\phi(x)\{8-9\phi(x)+3\phi^2(x)\}}{\{1-\phi(x)\}^3}\right] \tag{21}$$

and

$$\gamma^{\infty} = \exp\left[\frac{\phi_B\left(8-9\phi_B+3\phi_B^2\right)}{\left(1-\phi_B\right)^3}\right] \tag{22}$$

Then Eq. (18) becomes

$$\phi(x) = \phi_B \exp\left[-\left(\frac{\phi(x)\{8-9\phi(x)+3\phi^2(x)\}}{\{1-\phi(x)\}^3} - \frac{\phi_B\left(8-9\phi_B+3\phi_B{}^2\right)}{\left(1-\phi_B\right)^3}\right)\right]\cosh\left(\frac{ze\psi(x)}{kT}\right) \tag{23}$$

which is an equation for $\phi(x)$ for given values of ϕ_B and $\psi(x)$. Once $\phi(x)$ is obtained, we substitute the result into Eq. (19) to obtain the final form of the modified Poisson-Boltzmann equation.

In the zeroth-order approximation in the limit of very small ϕ_B, we have form Eq. (23) by approximating the exponential factor to be unity,

$$\phi(x) = \phi_B \cosh\left(\frac{ze\psi(x)}{kT}\right) \tag{24}$$

If we substitute Eq. (24) into Eq. (19), then the modified Poisson-Boltzmann Eq. (19) reduces back to the standard Poisson-Boltzmann Eq. (4). In order to obtain the first-order approximation for $\phi(x)$, we expand the exponential factor on the right-hand side of Eq. (23) in a power series of $\phi(x)$ and ϕ_B to give

$$\phi(x) = \phi_B \frac{\left(1+8\phi_B\right)\cosh\left(ze\psi(x)/kT\right)}{1+8\phi_B\cosh\left(ze\psi(x)/kT\right)} \tag{25}$$

By substituting Eq. (25) into Eq. (19), we obtain the following first-order approximation to the modified Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\varepsilon_r\varepsilon_o}\cdot\frac{\sinh\left(\dfrac{ze\psi(x)}{kT}\right)}{1+\left(\dfrac{16\phi_B}{1+8\phi_B}\right)\sinh^2\left(\dfrac{ze\psi(x)}{2kT}\right)} \tag{26}$$

which is rewritten in the non-dimensional form as

$$\frac{d^2y}{dx^2} = \frac{\kappa^2\sinh y}{1+\left(\dfrac{16\phi_B}{1+8\phi_B}\right)\sinh^2(y/2)} \tag{27}$$

It is possible to obtain the higher-order approximation to the modified Poisson-Boltzmann equation. As will be shown later, however, the above first-order approximation (Eq. (26)) is a good approximation with negligible errors for low ϕ_B ($\phi_B < 0.1$) and low-to moderate potentials. It is also to be noted that one can estimate the accuracy of an approximation for $\phi(x)$ by considering that Eq. (23) gives exact values of $\phi(x)$ for given values of ϕ_B and $\psi(x)$, as will be shown later in Fig. 1.

The modified Poisson-Boltzmann Eq. (26) can be integrated once to give

$$\frac{d\psi}{dx} = -\mathrm{sgn}(\psi_o)\frac{2\kappa kT}{ze}\cdot\sqrt{\frac{1+8\phi_B}{16\phi_B}}\cdot\sqrt{\ln\left[1+\left(\frac{16\phi_B}{1+8\phi_B}\right)\sinh^2\left(\frac{ze\psi(x)}{2kT}\right)\right]} \tag{28}$$

where $\mathrm{sgn}(\psi_o) = 1$ if $\psi_o > 0$ and -1 if $\psi_o < 0$. By evaluating Eq. (28) at $x = 0^+$ and substituting the result into Eq. (4), we obtain the following relationship between the surface charge density σ and the surface potential ψ_o:

$$\sigma = \mathrm{sgn}(\psi_o)\frac{2\varepsilon_r\varepsilon_o\kappa kT}{ze}\cdot\sqrt{\frac{1+8\phi_B}{16\phi_B}}\cdot\sqrt{\ln\left[1+\left(\frac{16\phi_B}{1+8\phi_B}\right)\sinh^2\left(\frac{ze\psi_o}{2kT}\right)\right]} \tag{29}$$

or equivalently

$$\psi_o = \mathrm{sgn}(\sigma)\frac{2kT}{ze}\cdot\mathrm{arcsinh}\left(\sqrt{\frac{1+8\phi_B}{16\phi_B}\left\{\exp\left[\left(\frac{4\phi_B}{1+8\phi_B}\right)\left(\frac{ze\sigma}{\varepsilon_r\varepsilon_o\kappa kT}\right)^2\right]-1\right\}}\right) \tag{30}$$

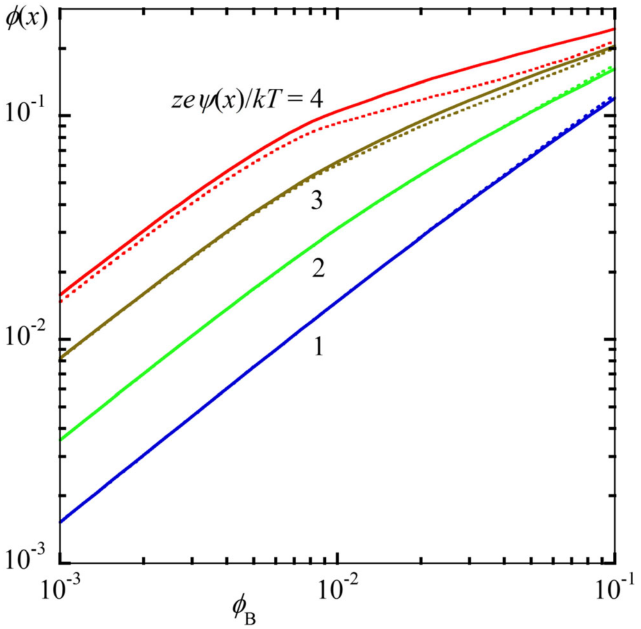

Fig. 1 Total ion volume fraction $\phi(x)$ of cations and anions at position x as a function of the scaled electric potential $ze\psi(x)/kT$ and the total bulk ion volume fraction $\phi_B \equiv \phi(\infty)$. *Solid lines* are the exact results obtained via Eq. (23) and the *dotted lines* are the approximate results obtained via Eq. (25)

By integrating Eq. (28) once again, we have

$$\kappa x=\mathrm{sgn}(\psi_o)\sqrt{\frac{4\phi_B}{1+8\phi_B}}\int_y^{y_o}\frac{dy}{\sqrt{\ln\left[1+\left(\frac{16\phi_B}{1+8\phi_B}\right)\sinh^2\left(\frac{y}{2}\right)\right]}}\qquad(31)$$

where $y_o = ze\psi_o/kT$ is the scaled surface potential. Equation (31) gives the scaled potential distribution $y(x) = ze\psi(x)/kT$ as a function of the scaled distance κx.

Results and discussion

The principal results of this paper are Eqs. (29)–(31). These equations depend on the approximate expression given by Eq. (25) for the total volume fractions $\phi(x)$. This expression is the first-order approximation to Carnahan-Starling's Eq. (23). In order to estimate the accuracy of Eq. (25), in Fig. 1, we plot $\phi(x)$ calculated via Eq. (25) as a function of ϕ_B for four values of $y(x)$ (dotted lines) in comparison with the exact results (solid lines) obtained via Eq. (23). It can be seen that Eq. (25) is a good approximation to Eq. (23) for small ϕ_B ($\phi_B \leq 0.1$) and low-to-moderate values of the electric potential $y(x)$ ($|y(x)| \leq 3$). The maximum relative error of Eq. (25) is ca. 3 % for $y(x) = 1$, ca. 4 % for $y(x) = 2$, and ca. 7 % for $y(x) = 3$. Even for $y(x) = 4$, the maximum relative error is ca. 12 % at $\phi_B = 0.01$.

We have derived approximate expressions given by Eqs. (29)–(31) for the surface charge density σ/surface potential ψ_o relationship for a charged planar surface and the electric potential distribution $\psi(x)$ on the basis of the modified Poisson-Boltzmann Eq. (26). In the limit of $\phi_B \to 0$, Eqs. (29)–(31) tend to

$$\sigma=\frac{2\varepsilon_r\varepsilon_o\kappa kT}{ze}\sinh\left(\frac{ze\psi_o}{2kT}\right)\qquad(32)$$

$$\psi_o=\frac{2kT}{ze}\cdot\mathrm{arcsinh}\left(\frac{ze\sigma}{2\varepsilon_r\varepsilon_o\kappa kT}\right)\qquad(33)$$

and

$$\kappa x=\frac{1}{2}\int_y^{y_o}\frac{dy}{\sinh\left(y/2\right)}\qquad(34)$$

which gives

$$y(x)=2\ln\left[\frac{1+\tanh(y_o/4)\cdot e^{-\kappa x}}{1-\tanh(y_o/4)\cdot e^{-\kappa x}}\right]\qquad(35)$$

The above results agree with the results obtained by the standard Poisson-Boltzmann equation (Eq. (4)).

Figure 2 shows an example of the calculation of the surface potential ψ_o via Eq. (30) plotted as a function of electrolyte concentration n (given in units of M) in an aqueous monovalent electrolyte solution containing cations and anions of radius a = 0.4 nm (z = 1, ε_r = 78.55) for three values of the surface charge density σ (σ = 0.01, 0.02, and 0.05 C/m^2) at T = 298.15 K. The solid lines are the results obtained by the modified Poisson-Boltzmann equation (Eq. (30)) and the dotted lines are those obtained by the standard Poisson-Boltzmann equation (Eq. (33)). In Fig. 2, the exact numerical results obtained by Lopez-Garcia et al. [15] are also plotted as closed circles. The agreement between the approximate results obtained via Eq. (30) and the corresponding exact numerical results [15] is excellent with negligible errors. Figure 2 shows how the effects of ionic size on the surface potential becomes appreciable for higher surface charge density and higher electrolyte concentrations. For σ = 0.05 C/m^2 and n = 0.05 M, for example, the modified Poisson-Boltzmann equation (Eq. (34)) gives ca. ψ_o = 82 mV, while the standard Poisson-Boltzmann equation (Eq. (33)) gives only ca. 72 mV, the difference being higher than 12 %. The ionic size effect always gives rise to an increase in the surface potential ψ_o. This is because the ionic concentration becomes lower due to the ionic size effect, leading to a decrease in the ionic shielding effects so that the magnitude of ψ_o increases. If the surface charge density σ is low, on the other hand, then the ionic size effect becomes small. In order to see this more clearly, we expand ψ_o given by Eq. (30) in a power series of σ with the result that

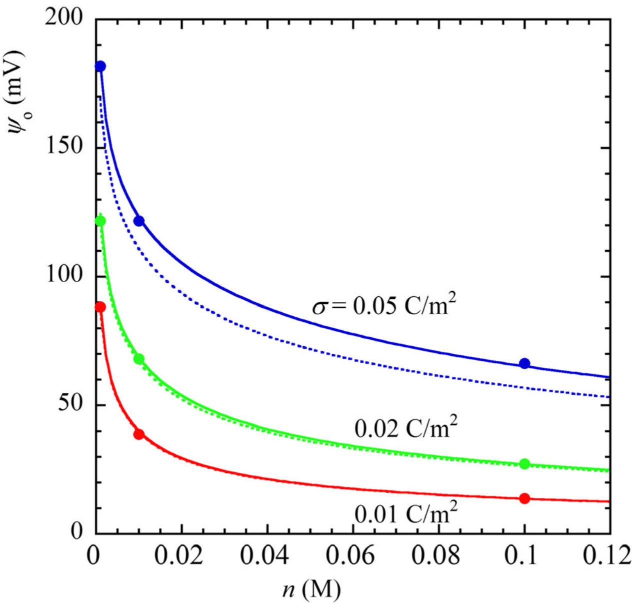

Fig. 2 Surface potential ψ_o of a charged planar surface in contact with an aqueous monovalent electrolyte solution as a function of electrolyte concentration n (given in units of M). The *solid lines* are the results obtained via the modified Poisson-Boltzmann equation (Eq. (30)) and *the dotted lines* are the results by the standards Poisson-Boltzmann equation (Eq. (33)). Calculated for the surface charge density σ = 0.01, 0.02, and 0.04 C/m^2, the ionic radius a = 0.4 nm, T = 298.15 K, and ε_r = 78.55. The exact numerical results obtained by Lopez-Garcia et al. [15] are also plotted as *closed circles*

$$\psi_o=\frac{\sigma}{\varepsilon_r\varepsilon_o\kappa}-\left(\frac{1}{24}-\frac{\phi_B}{1+8\phi_B}\right)\left(\frac{ze}{kT}\right)\left(\frac{\sigma}{\varepsilon_r\varepsilon_o\kappa}\right)^3+O\left(\sigma^5\right)\qquad(36)$$

We see that the first term on the right-hand side of Eq. (36) does not involve ϕ_B so that in the limit of $\sigma \rightarrow 0$, the ionic size effect vanishes. The ionic size effect appears only in terms of the third and higher orders of σ.

Finally, we give below an approximate expression for the differential electric double layer capacitance $C_d = d\sigma/d\psi_o$, viz.,

$$C_d = \varepsilon_r \varepsilon_o \kappa \sqrt{\frac{4\phi_B}{1+8\phi_B}} \cdot \frac{\sinh\left(\frac{ze\psi_o}{kT}\right)}{\sqrt{\ln\left[1+\left(\frac{16\phi_B}{1+8\phi_B}\right)\sinh^2\left(\frac{ze\psi_o}{2kT}\right)\right]}} \cdot \frac{1}{1+\left(\frac{16\phi_B}{1+8\phi_B}\right)\sinh^2\left(\frac{ze\psi_o}{2kT}\right)} \tag{37}$$

For $\phi_B \rightarrow 0$, Eq. (37) reduces to

$$C_d = \varepsilon_r \varepsilon_o \kappa \cosh\left(\frac{ze\psi_o}{2kT}\right) \tag{38}$$

which agrees with the differential electric double layer capacitance based on the standard Poisson-Boltzmann equation (33).

Conclusion

We have presented a simple algorithm for solving the modified Poisson-Boltzmann equation for the electric potential around a planar charged surface in contact with an electrolyte solution, which takes into account the effects of ionic size on the basis of ionic activity coefficient given by Carnahan and Starling [18]. We have derived approximate analytic expressions for the surface charge density/surface potential relationship (Eqs. (29) and (30)) and the potential distribution (Eq. (31)), and the differential capacitor of electrical double layer (Eq. (37)).

Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

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