

Ionic Size Effect on the Double Layer Properties: A Modified Poisson-Boltzmann Theory

Ping Lou^{†,‡,*} and Jin Yong Lee^{†,*}

[†]Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea. *E-mail: jinylee@skku.edu

[‡]Department of Physics, Anhui University, Hefei 230039, Anhui, P. R. China. *E-mail: loup@ahu.edu.cn

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On the basis of a simple modified Poisson-Boltzmann (SMPB) theory, taking into account the *finite ionic size*, the analytic expression for the effect of ionic size on the diffuse layer potential drop at negative charge densities has been given for the simple 1:1 electrolyte. It is shown that the potential drop across the diffuse layer depends on the size of the ions in the electrolyte. For a given electrolyte concentration and electrode charge density, the diffuse layer potential drop in a small ion system is smaller than that in a large ion system. It is also displayed that the diffuse layer potential drop is always less than the value of the Gouy-Chapman (GC) theory, and the deviation increases as the electrode charge density increases for a given electrolyte concentration. These theoretical results are consistent with the results of the Monte-Carlo simulation [Fawcett and Smagala, *Electrochimica Acta* 53, 5136 (2008)], which indicates the importance of including steric effects in modeling diffuse layer properties.

Key Words: Double layer, Size effect, Potential drop

Introduction

Recognizing the double layer is important not only in electrochemistry but also in a wide variety of areas including colloid science, membrane biology, and separation phenomena, a considerable theoretical work has improved the description of the inner and diffuse parts of the double layer,¹ since the 1970s. However, many of these theories have not been adopted by experimentalists. So far, most experimentalists who are involved with double layer problems still use the Gouy-Chapman (GC) theory^{2,3} of the diffuse layer to estimate important double layer properties. This is because most theoretical works involve complicated mathematical equations, which often due to the absence of analytical solutions. Therefore, these theories can not be easily used.

The finite ionic size may play an important role in a concentrated solution. Bikerman first showed that the deviation of the distribution function from Boltzmann's function takes into account the proper volume of the ions.⁵ Since then, a lot of works have followed.⁵⁻¹⁹ For a very comprehensive review of previous works, excellent recent articles^{7,18} should be referred. A simple modified Poisson-Boltzmann (SMPB) model of Kornyshev (2007)¹⁹ and Kilic, Bazant and Ajdari (2007)¹⁷ for steric effects in electrolytes has been reinvented many times: by Borukhov *et al.* (1997)^{11,12} and Iglic (1994),¹⁰ Eigen and Wicke (1954),⁸ also by Dutta (1950).⁶ Recently, using the SMPB theory, we have derived the exact analytic expression for the contact values of the difference profile of the counterion and coion, as well as of the sum (density) and product profiles, near a charged planar electrode which is immersed in a binary symmetric electrolyte.²⁰ In the *zero ionic size* or *dilute* limit, these contact values reduced to the contact values of the Poisson-Boltzmann (PB) theory. It was found that the analytic results of the SMPB theory for the difference, sum, and product profiles were in agreement with the results of the Monte-Carlo (MC) simulations.^{21,22} On the

other hand, Fawcett and Smagala⁴ examined the ionic size effects on the potential drop across the diffuse layer using MC simulations. They found that for a given electrolyte concentration and electrode charge density, the diffuse layer potential drop in the small ionic size system was smaller than that in the large ionic size system. At the higher concentration, the potential drop across the diffuse layer is smaller for a given value of the electrode charge density. In addition the deviation of this potential drop from the Gouy-Chapman theory increases as the electrode charge density increases for a given electrolyte concentration. Thus, a question arises: "Can the SMPB theory reproduce Fawcett and Smagala's MC data?"²⁴ This study will not only provide analytical solutions to the problem, but also give a further direct test of the basis of SMPB theory.

Model and Theory

Based on mean-field theory together with the lattice-gas approximation in statistical mechanics,^{11,12} the phenomenological free energy of a general electrolyte system can be written as^{11,12,23}

$$\begin{aligned} \Omega = & \frac{\varepsilon}{8\pi} \int d^3\mathbf{r} (\nabla\psi(\mathbf{r}))^2 - \int d^3\mathbf{r} \sum_i^m \mu_i c_i(\mathbf{r}) \\ & + \frac{k_B T}{a^3} \int d^3\mathbf{r} \left[\left(1 - \sum_i^m c_i(\mathbf{r}) a^3 \right) \right. \\ & \times \ln \left(1 - \sum_i^m c_i(\mathbf{r}) a^3 \right) + \sum_i^m c_i(\mathbf{r}) a^3 \ln (c_i(\mathbf{r}) a^3) \left. \right] \\ & + \int d^3\mathbf{r} \lambda(\mathbf{r}) \left(\nabla^2 \psi(\mathbf{r}) + \frac{4\pi}{\varepsilon} \sum_i^m z_i c_i(\mathbf{r}) \right), \end{aligned} \quad (1)$$

where e is the elementary charge, k_B is the Boltzmann constant and T is the absolute temperature, and ε is the dielectric constant. $c_i(\mathbf{r})$, μ_i and z_i are the local concentration, the chemical potential and the valence of the ionic species i , $i = 1, \dots, m$, respectively,

a is the effective size of the ions and solvent molecules. The term $\frac{k_B T}{a^3} \int d^3 \mathbf{r} (1 - \sum_i^m c_i(\mathbf{r}) a^3) \ln(1 - \sum_i^m c_i(\mathbf{r}) a^3)$ is the entropy of the solvent molecules that is responsible for the steric corrections to the PB equation.^{11,12}

The last two terms in Eq. (1) containing the Lagrange multiplier $\lambda(\mathbf{r})$ allow us to consider the local concentration $c_i(\mathbf{r})$ and the electrostatic potential $\psi(\mathbf{r})$ as independent fields. Following the method in Ref.²³ we can obtain

$$\nabla^2 \psi(\mathbf{r}) = \frac{4\pi e}{\epsilon} \sum_i^m z_i c_i(\mathbf{r}) \quad (2)$$

with

$$c_i(\mathbf{r}) = \frac{c_{ib} \exp(-\beta e z_i \psi(\mathbf{r}))}{1 - \sum_i^m c_{ib} a^3 + \sum_i^m c_{ib} a^3 \exp(-\beta e z_i \psi(\mathbf{r}))}, \quad (3)$$

where $\beta \equiv 1/k_B T$. $i = 1, \dots, m$ and c_{ib} is the bulk concentration of the ionic species i . Eqs. (2) and (3) are the SMPB equations. Notice that in the *zero ionic size* ($a \rightarrow 0$) or *dilute* limit ($c_{ib} \rightarrow 0$), Eqs. (2) and (3) reduce to the PB equation.²³ It should be pointed out that just like the PB equation, Eqs. (2) and (3) can be applied to any geometry and boundary conditions.

Here, for comparison with the results of the MC simulations of Fawcett and Smagala,⁴ we also consider a binary symmetric electrolyte and assume that the planar electrode has a negative charge. Thus, we have $m = 2$, $z_1 = -z_2 = 1$, $c_{1b} = c_{2b} = c_b$, and Eqs. (2) and (3) reduce to

$$\frac{dx^2 \psi(x)}{dx^2} = \frac{8\pi e c_b}{\epsilon} \frac{\sinh(e\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{e\beta\psi(x)}{2}\right)}, \quad (4)$$

where $\rho^* = 2c_b a^3$ is the reduced density, x is the perpendicular distance of an ion of species i from the electrode surface, and $c_i(x) = c_b g_i(x)$, $g_i(x)$ is the normalized density profile of an ion of species i (or called as the singlet distribution function for an ion of species i), for the counter-ions which is given by

$$g^+(x) = \frac{\exp(e\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{e\beta\psi(x)}{2}\right)} \quad (5)$$

and

$$g^-(x) = \frac{\exp(-e\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{e\beta\psi(x)}{2}\right)} \quad (6)$$

for the co-ions.

Following the trick in Refs.^{17,19} integrating Eq. (4), using the boundary conditions, $\psi(x)|_{x=0} = \phi$, $\psi(x)|_{x \rightarrow \infty} = 0$, and $\frac{d\psi(x)}{dx}|_{x \rightarrow \infty} = 0$, we can get

$$\sigma_m = - \sqrt{\frac{c_b \epsilon}{\pi \beta \rho^*}} \sqrt{\ln \left[1 + 2\rho^* \sinh^2\left(\frac{ze\beta\phi}{2}\right) \right]}, \quad (7)$$

where $\sigma_m = -\frac{\epsilon}{4\pi} \frac{d\psi(x)}{dx}|_{x \rightarrow 0}$ is the electrode charge density.

Then, the electrode potential, ϕ , is given by

$$\phi = -\frac{2k_B T}{e} \operatorname{arcsinh} \sqrt{\frac{\exp\left(\frac{2\pi}{\epsilon k_B T} \sigma_m^2 a^3\right) - 1}{4c_b a^3}}, \quad (8)$$

and the differential capacity of the double layer, C , which is calculated from the change in the electrode potential with the charge on the electrode, is given by

$$C = \frac{\partial \sigma_m}{\partial \phi} = \frac{\epsilon e}{4\pi a^3} \frac{\sqrt{\exp\left(\frac{2\pi}{\epsilon k_B T} \sigma_m^2 a^3\right) - 1} \sqrt{\exp\left(\frac{2\pi}{\epsilon k_B T} \sigma_m^2 a^3\right) - 1 + 4c_b a^3}}{|\sigma_m| \exp\left(\frac{2\pi}{\epsilon k_B T} \sigma_m^2 a^3\right)} \quad (9)$$

It is noted that as $a \rightarrow 0$, Eqs. (8) and (9) reduce to the following equations:

$$\lim_{a \rightarrow 0} \phi = \frac{2k_B T}{e} \operatorname{arcsinh} \sqrt{\frac{\pi}{2c_b \epsilon k_B T}} \sigma_m, \quad (10)$$

and

$$\lim_{a \rightarrow 0} C = \sqrt{\frac{\epsilon c_b e^2}{2\pi k_B T}} \sqrt{\frac{\pi}{2\epsilon k_B T c_b} \sigma_m^2 + 1}. \quad (11)$$

These are the full expressions of GC theory for ϕ and C , which is based on a model that ignores the ionic size effect. On the other hand, as $\sigma_m \rightarrow 0$, Eqs. (8) and (9) also reduce to the full expressions of GC theory, i.e., Eqs. (10) and (11), which means that at small σ_m , the effect of ionic size can be neglected.

On the other hand, the electrode potential, ϕ , is a sum of the potential drop across the inner layer (ϕ_{in}) (between the electrode surface and the contact distance) and the potential of the diffuse layer ($\phi^d(a/2)$) as shown in Figure 1:

$$\phi = \frac{4\pi \zeta(a/2)}{\epsilon} \sigma_m + \phi^d(a/2), \quad (12)$$

where $\phi_{in} = \frac{4\pi \zeta(a/2)}{\epsilon} \sigma_m$ has been used, which comprises the information about the thickness of the inner layer $\zeta(a/2)$ and the electric field $\left(\frac{4\pi \sigma_m}{\epsilon}\right)$ effective in this region. And, we have

$$\frac{1}{C} = \frac{1}{C_{in}} + \frac{1}{C_d} \quad (13)$$

for the differential capacity of the double layer, where $C_{in} = \frac{\epsilon}{4\pi \zeta(a/2)}$ is the inner layer capacity and C_d the diffuse layer capacity. Then, to compare with the results of MC simulations,

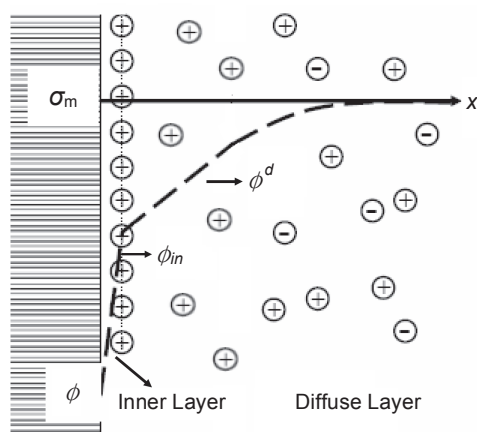


Figure 1. Schematic diagrams of the electrical double layers with respect to the double layer model. The long-dashed line represents potential profile when the surface charge is negative.

we use the following formula:

$$\phi^d = -\frac{2k_B T}{e} \operatorname{arcsinh} \sqrt{\frac{\exp\left(\frac{2\pi}{\epsilon k_B T} \sigma_m^2 a^3\right) - 1}{4c_b a^3}} - \frac{4\pi\zeta(a/2)}{\epsilon} \sigma_m \quad (14)$$

and

$$C_d = \frac{\frac{\epsilon}{4\pi\zeta(a/2)}}{\frac{\epsilon}{4\pi\zeta(a/2)} - C} C, \quad (15)$$

where C is given by Eq. (9).

Results and Discussion

Recently, Fawcett and Smagala⁴ have carried out Monte Carlo simulations of the diffuse double layer for two unrestricted electrolytes in which the component ions have ionic radii equal to the Shannon and Prewitt radii for Na^+ , Cs^+ , and Cl^- . The diffuse layer potential drops (ϕ^d) for the solutions of CsCl and NaCl as functions of electrode charge density for the electrode (σ_m) are shown in Figure 2. We adopted $\epsilon = 8.7341 \times 10^{-9}$ (F/m), $T = 298.2$ (K) and $\zeta(a/2) = 1.16 \times 10^{-10}$ (m) for NaCl and CsCl, while $a = 2.32 \times 10^{-10}$ (m) for Na and $a = 3.2 \times 10^{-10}$ (m) for Cs. The results of SMPB theory (Eq. (14)) for ϕ^d vs σ_m at different concentrations are compared with the corresponding MC data.⁴ It is clearly seen from Figure 2 that the GC theory overestimates the potential drop. Note that the ionic size effect becomes important when the negative charge density ($-\sigma_m$) is larger than 0.1 Cm^{-2} . When the charge density is more negative than -0.1 Cm^{-2} , the potential drop across the diffuse layer in the CsCl solution is larger than that in the NaCl solution. It is apparent that the potential drop in the small ion system is smaller than that in the large ion system for a given concentration. By comparing Figure 2 (a) with Figure 2 (b), it is noted that the potential drop across the diffuse layer at the higher concentration is smaller than that at the lower concentration for a given elect-

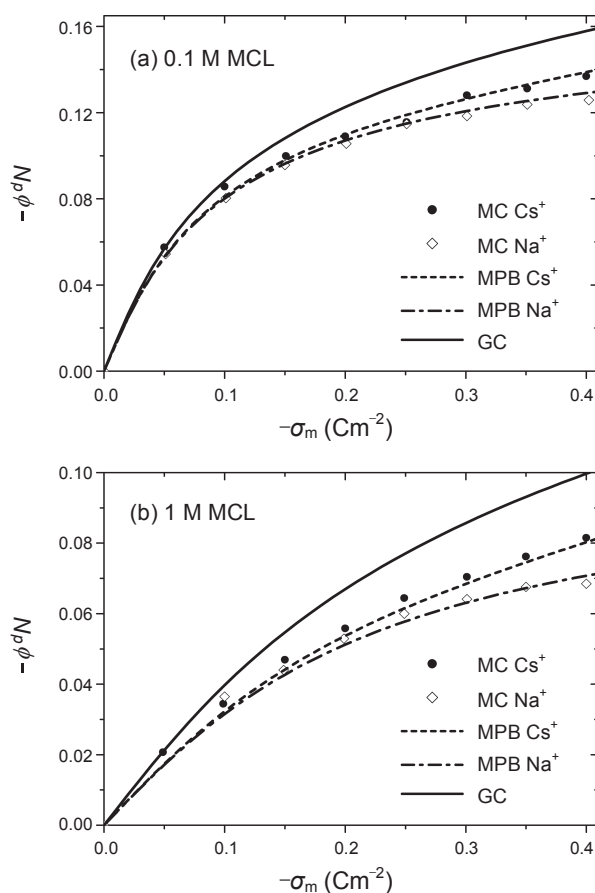


Figure 2. Plots of the potential drop across the diffuse layer ϕ^d for the solutions of CsCl and NaCl against electrode charge density for a negatively charged electrode ((a) for concentration 0.1 M and (b) for concentration 1.0 M). The filled symbol represents the MC data,⁴ the solid line is analytic expression of the GC theory (Eq. (10)). The dashed-dotted and dashed lines are the results of analytic expression of the SMPB theory (Eq. (14)).

rode charge density. It is also displayed that not only the diffuse layer potential drop is always less than the value of the GC theory, but also the deviation increases as the electrode charge density increases for a given electrolyte concentration.

It is clearly seen that the SMPB theory gives results that are in agreement with the MC data.⁴ Note that the only difference in the calculation performed here for NaCl and CsCl is the ionic size. Thus, the present study clearly shows that the deviation of this potential drop from the GC theory originates from the steric effects.

Moreover, Fawcett and Smagala⁴ also estimated the differential capacity of the diffuse layer, C_d , for the solutions of NaCl and CsCl using the extensive MC simulation. We calculated C_d values as functions of σ_m according to Eq. (15), and compared with MC results as well as GC theory in Figure 3. The values of this quantity are always larger than the GC theory for the negative charge density larger than 0.1 Cm^{-2} . In addition, the C_d values for the NaCl solution are higher than those for the CsCl solution.

It is clearly shown that the deviation of the differential capacity of the diffuse layer from the GC theory increases as the

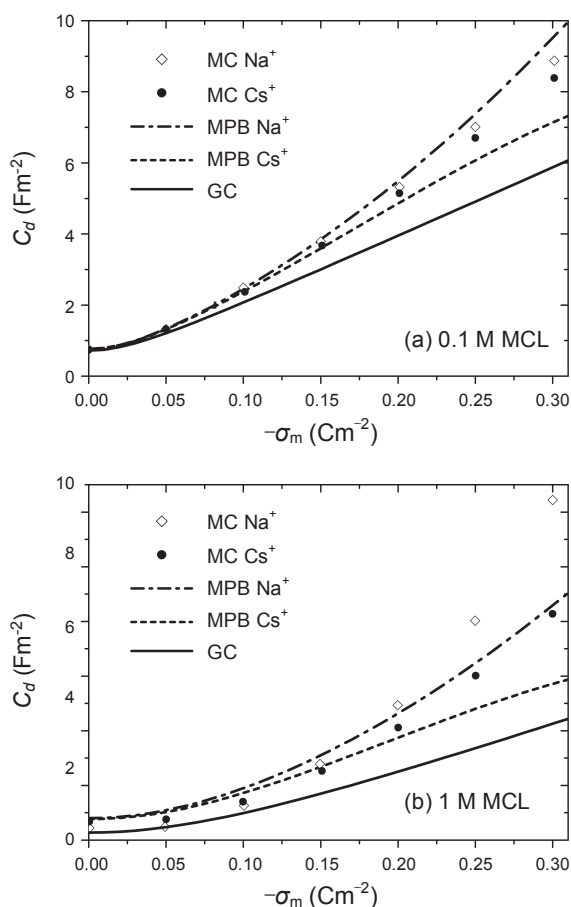


Figure 3. Plots of the differential capacity of the diffuse layer C_d for NaCl and CsCl against the electrode charge density at potentials negative of the pzc ((a) for concentration 0.1 M and (b) for concentration 1.0 M). The filled symbol represents the MC data,⁴ the solid line is analytic expression of the GC theory (Eq. (11)). The dashed-dotted and dashed lines are the results of analytic expression of the SMPB theory (Eq. (15)).

radius of the cation decreases. The differential capacity in the small ion system is larger than that in the large ion system for a given concentration, which is consistent with the MC results.⁴ These results reveal the importance of steric effects in modeling diffuse layer properties.

It should be mentioned that as the ion size gets smaller, the electrode potential, ϕ , is a sum of the potential drop across the inner layer (ϕ_m) (between the electrode surface and the contact distance) and the potential of the diffuse layer ($\phi^d(a/2)$) as shown in Figure 1, reduces to that of the original GC theory, instead of the potential of the diffuse layer ($\phi^d(a/2)$). The same case is for the differential capacity of the double layer (C), instead of the differential capacity (C_d) of the diffuse layer. These have been displayed by Eqs. (10) and (11). On the other hand, $\zeta(a/2)$ in the potential drop across the inner layer (ϕ_m), as well as in the inner layer capacity (C_m), is treated as the best-fit parameter.

Conclusions

In conclusion, we have obtained the analytic expressions of

the potential drop (ϕ^d) across the diffuse layer and the differential capacity (C_d) of the diffuse layer on the basis of SMPB theory. In particular, we have shown that the analytic expression allows us to account for the behaviors of ϕ^d and C_d that are displayed by the MC simulation.⁴ The most important features are: (i) the diffuse layer potential drop is always less than the value predicted by GC theory; (ii) the potential drop in the small ion system is smaller than that in the large ion system at fixed concentration for the negative charge density ($-\sigma_m$) larger than 0.1 Cm^{-2} , and as $-\sigma_m$ increases such a deviation increases; (iii) at higher concentration, the potential drop across the diffuse layer is smaller for a given value of the electrode charge density; (iv) the differential capacity of the diffuse layer C_d is always larger than the GC theory for the negative charge density larger than 0.1 Cm^{-2} and C_d for the small ion system is clearly higher than that for the large ion system. The SMPB theory to describe diffuse layer properties is analytical and easily used by experimentalists in the analysis of experimental data. For the case of 1:1 electrolytes, it requires only one adjustable parameter related to the ionic size that are easily estimated once the size is known.

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