Scientific paper

Relative Permittivity in Stern and Diffuse Layers

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Received: 16-09-2013

Paper based on a presentation at the 4th RSE-SEE 2013 Symposium on Electrochemistry in Ljubljana, Slovenia

Abstract

Stern layer and outer Helmholtz plane (i.e. the distance of closest approach) are considered within electric double layer models, where the orientational ordering of water dipoles is explicitly taken into account. It is shown that permittivity of the Stern layer is not independent of the surface charge density as it is frequently assumed in different theoretical models and simulations, but strongly depends on the magnitude of the surface charge density. Therefore, to predict the behaviour and realistic values of the surface potential and electric field, in the electrolyte solution near the charged surface, requires a surface charge density dependent permittivity of the Stern layer.

Keywords: Outer Helmholtz plane, Stern layer, relative permittivity, water ordering

1. Introduction

In the complex interface charged surface – surrounding biosystem, electric double layer (EDL) plays the leading role. It causes the ions and water molecules to rearrange near the charged surface and thus to screen the electric potential.[1–9] The electrostatic forces acting there make the counterions (i.e. ions with a charge of the opposite sign than the charged surface) to accumulate close to the surface, while the coions (i.e. the ions with a charge of the same sign as the surface) to deplete near the surface (Fig. 1).

Most of the theoretical models, of an electrolyte solution in contact with a charged surface, assume that the relative (dielectric) permittivity (ε_r) is constant everywhere in the solution.[5–8] The classical Poisson-Boltzmann (PB)[2–3,5] theory treats ions in the electrolyte solution as dimensionless and does not consider the reduced permittivity of electrolyte solution near the charged surface.[10] Thus the PB theory has been upgraded by hydration models, where interplay between solvent polarization and the diffuse double layer takes place.[11–18] Study of the orientational ordering of water dipoles at the charged surface has shown that dipoles on average are oriented perpendicularly to the charged surface.[8] The spatial decay of solvent polarization for increasing distance from the charged membrane surface was predicted.[11–17]

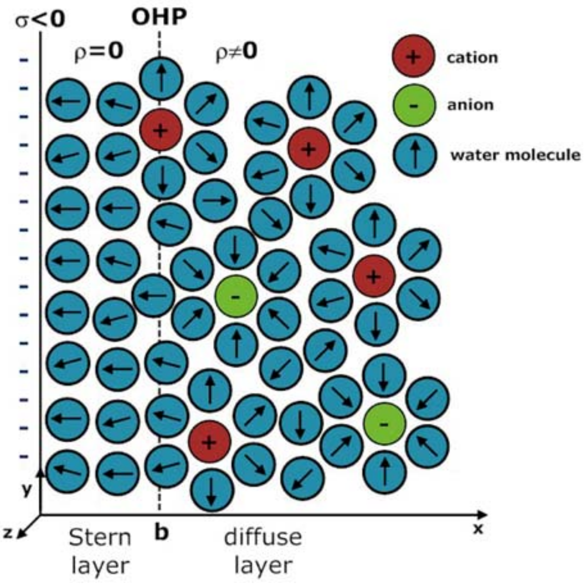

Figure 1. Schematic figure of an electrolyte solution, near a charged surface, consisting of Stern layer ($0 \le x \le b$) and diffuse electric double layer ($b \le x \le \infty$). The outer Helmholtz plane (OHP) is located at the distance of closest approach ($x = b$) which is approximately equal to the hydrated radius of the counterions involved. Note that the water dipoles are oriented in a close vicinty to the charged surface as well as around cations and anions in the bulk electrolyte solution. Here σ stands for the surface charged density and ρ for the volume charge density of the electrolyte solution.

Helmholtz[1] treated the double layer as a simple capacitor, assuming that the surface charge density (σ) is neutralized by the counterions located at a distance equal to their hydrated radius. Gouy[2] and Chapman[3] considered the thermal motion of ions within PB approach, while Stern[4] combined the Helmholtz[1] and Gouy-Chapman models[2–3] by introducing the outer Helmholtz plane (OHP), where the hydrated counterions are at the distance of closest approach ($x = b$) and the diffuse double layer starts (Fig. 1). In this work we combine Helmholtz model and EDL models which takes into account orientational ordering of water, resulting in a spatial variation of permittivity, and the cavity field. Two different EDL models are considered: the modified Langevin Poisson-Boltzmann model[8,19–20] for point-like ions and Gongadze-Iglič model[8,17] which takes into account the finite size of ions.

The permittvity within Stern layer (see Fig. 1) is calculated for different values of the surface charge density using finite element method (FEM) in Comsol Multiphysics 4.3a as described in details in the references therein.[8,17]

2. Results and Discussion

Taking into account that the ions in the Stern layer are depleted, the Helmholtz Langevin Poisson-Boltzmann (Helmoltz LPB) equation[19–20] for point-like ions can be written in the form:

$$\frac{d}{dx}\left(\varepsilon_r(x)\varepsilon_0\frac{d\phi}{dx}\right)=\begin{cases}0 & 0\le x<b\\ -2e_0n_0\sinh(\beta e_0\phi(x)) & b\le x<\infty\end{cases}\tag{1}$$

where the space dependent relative permittvity is[8,20]

$$\varepsilon_r(x)=n^2+n_{0w}\frac{p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\frac{\mathrm{L}(\gamma p_0E(x)\beta)}{E(x)},\tag{2}$$

and $\phi(x)$ is the electric potential, $E(x)$ is the magnitude of the electric field strength, e_0 is the unit charge, n is the optical refractive index of water, n_0 is the number density of ions in the bulk far away from the charged surface, n_{0w} is the constant number density of water molecules, p_0 is the magnitude of the water external dipole moment[17], ε_0 is the permittivity of the free space, $\beta = 1/kT$, kT is the thermal energy, $\mathrm{L}(u) = (\coth(u) - 1/u)$ is the Langevin function and $\gamma = (2 + n^2)/2$. In the Stern layer ($0 \le x <$ b) the electric field strength is constant, therefore also the relative permittivity in this region is constant, i.e. $\varepsilon_r(x) = \varepsilon_r\ (x = 0)$. The magnitude of the electric field strength $E(x)$ in the region $b \le x < \infty$ is spatial dependent and consequently also $\varepsilon_r(x)$ varies with the distance from the charged surface.[8,17] In the generalized HLPB model, the electronic polarization of water is taken into account by assuming that the point-like rigid (permanent) water dipole is embedded in the center of the sphere with a volume equal to the average volume of a water molecule in the electrolyte solution.[8,20] The permittivity of the single molecule's water sphere is n^2.

Within Helmholtz Gongadze-Iglič (Helmholtz GI) model,[8,17] the consideration of Stern layer and outer Helmholtz plane yields the following governing model equations:

$$\frac{d}{dx}\left(\varepsilon_r(x)\varepsilon_0\frac{d\phi}{dx}\right)=\begin{cases}0 & 0\le x<b\\ -2e_0n_sn_0\dfrac{\sinh(e_0\phi(x)\beta)}{\mathrm{D}\left(\phi(x),E(x)\right)} & b\le x<\infty\end{cases}\tag{3}$$

where the space dependent relative permittvity is[8,20]

$$\varepsilon_r(x)=\begin{cases}n^2+n_{0w}\dfrac{p_0}{\varepsilon_0}\left(\dfrac{2+n^2}{3}\right)\dfrac{\mathrm{L}(\gamma p_0E(x)\beta)}{E(x)} & 0\le x<b\\ n^2+n_sn_{0w}\dfrac{p_0}{\varepsilon_0}\left(\dfrac{2+n^2}{3}\right)\dfrac{\mathrm{F}\ (p_0E(x)\beta)}{\mathrm{D}\left(\phi(x),E(x)\right)\,E(x)} & b\le x<\infty\end{cases}\tag{4}$$

where $\mathrm{D}(\phi(x), E(x)) = 2n_0\cosh(e_0\beta\phi(x) + n_{0w}\sinh(\gamma p_0\beta E(x))/\gamma p_0\beta E(x))$, $\mathrm{F}(u) = (\coth(u) - 1/u)\sinh(u)/u$. The analytical expressions for the space dependences of the number density of ions and water molecules in the region $b \le x < \infty$ are given elsewhere.[8,17] For simplicity, we assume that in the region $0 \le x < b$ the numbery density of water $n_w(x)$ is constant and equal to $n_w(x = 0)$. This mean that we neglect the fact that the counterions partially occupy the region $(b - r) \le x < b$ (where r is the radius of a nonhydrated counterion) even their centres can be located only in the region $x \ge b$ (see Fig. 1). Therefore, also in the region $(b - r) \le x < b$ the water molecules are partially depleted and their number density $n_w(x)$ is smaller than the bulk water number density n_{0w} (i.e. partially depleted). The boundary conditions in both models are:

$$\left.\frac{d\phi}{dx}\right|_{x=0}=-\frac{\sigma}{\varepsilon_r(x=0)\varepsilon_0}.\tag{5}$$

The validity of Gauss's law at $x = b$ is fulfilled by the following equations:

$$\left.\frac{d\phi}{dx}\right|_{b_-}=\left.\frac{d\phi}{dx}\right|_{b_+},\tag{6}$$

where also $\phi|_{b^-} = \phi|_{b^+}$. In the case of Helmholtz GI model, the additional boundary conditions at $x = (b - r)$ should be taken into account.

Fig. 2 shows the space dependence of the electric potential $\phi(x)$ and electric field strength $E(x)$ within Helmholtz LPB model (Equation 1) for the distance of closest approach $b = 0.5$ nm. It can be seen that in the Stern layer

($0 \leq x < b$), the electric potential is a linear function of the distance from the charged surface x. Accordingly, the electric field strength in this region with zero volume charge distribution (see Equation 1) is constant. Consequently, also the relative permittivity in this region has a constant value ($\varepsilon_r(x) = \varepsilon_r\,(x = 0)$) as shown in Fig. 3. In the region $b \leq x < \infty$, the electric field strength $E(x)$ strongly decreases with increasing distance (x) (Fig. 2). The relative permittivity $\varepsilon_r\,(x)$ in the region $b \leq x < \infty$ increases due to saturation of water dipole orientation close to the surface $x = b$.[8,17]

Fig. 4 shows the relative permittivity $\varepsilon_r(x)$ and the number density of water $n_w(x)$ calculated within Helmholtz GI model. The number density of water molecules $n_w(x)$ close to the plane $x = b$ is decreased due to accumulation of counterions which is more pronounced for higher values of the surface charge density σ.[8,17] Lower values of $n_w(x)$ at $x = b$ within Helmholtz GI model lead to lower values of permittivity $\varepsilon_r\,(x = b)$ as predicted in Helmholtz LPB model (compare Figs. 3 and 4). The abrupt decrease of water number density at $x = b$ (see lower panel in Fig. 4) is the consequence of the fact that we totally neglect the volume of counterions in the region $(b - r) \leq x < b$, i.e. we neglect the volume of counterions with their centers located at $x = b$ (see also Fig. 1 and Equation 4). To this end,

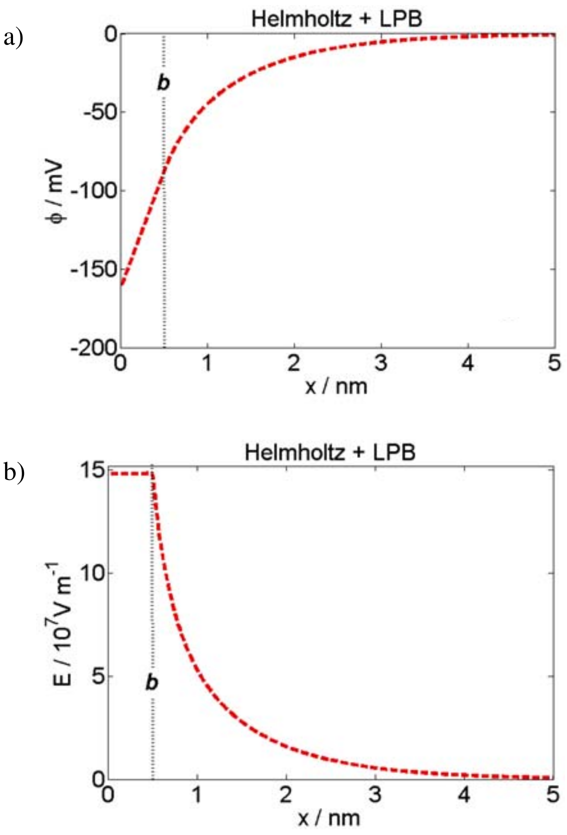

Figure 2. The electric potential $\varphi(x)$ (a) and electric field strength $E(x)$ (b) as a function of the distance from the charged surface located at $x = 0$ within the generalized Helmholtz LPB model (Equation 1). The model parameters are: surface charge density $\sigma = -0.1$ $C\,m^{-2}$, bulk concentration of ions $n_0/N_A = 0.1\ mol/l$, distance of closest approach $b = 0.5\ nm$, $p_0 = 3.1$ D and bulk concentration of water $n_{0w}/N_A = 55\ mol/l$.

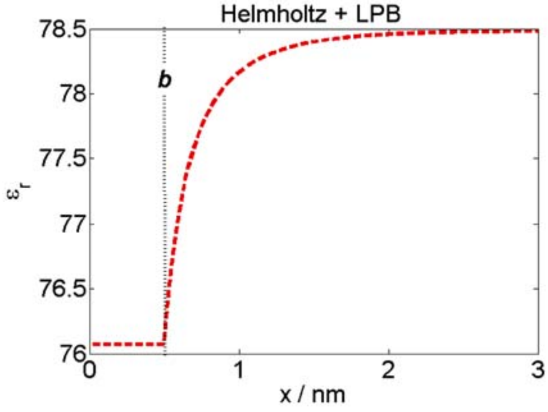

Figure 3. The relative premittivity $\varepsilon_r(x)$ as a function of the distance from the charged surface calculated within the generalized Helmholtz LPB model. The values of the model parameters are the same as in Figure 2.

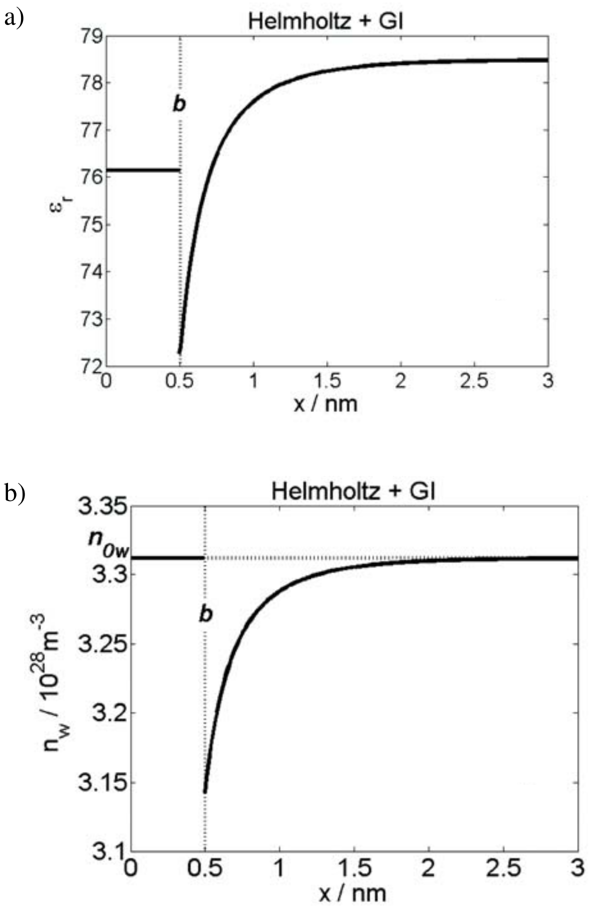

Figure 4. The relative premittivity $\varepsilon_r(x)$ (A) and water number density n_w (B) of Helmholtz GI model as a function of the distance (Equation 2). The values of the model parameters are the same as in Fig. 2.

also the relative permittvity decreases at $x = b$ in abrupt way (Fig. 4, upper panel).

Fig. 5 shows the calculated relative permittvity ε_r in the Stern layer at $x = 0$ and $x = b$ within Helmhotz GI model (see also Figs. 1 and 4) as a function of the magnitude of the surface charge density σ. The values of ε_r $(x = 0)$ and ε_r $(x = b)$ decrease with increasing magnitude of the surface charge density σ. As the orientation of water dipoles and the relative permittvity ε_r (x) (see Equation 4) depend on the electric field strength[6,7,8,17] (at larger electric field strengths the water dipoles are strongly oriented leading to decreased values of ε_r due to saturation effect[7,8,21]), the predicted decrease of ε_r (x) with increasing magnitude of σ is the consequence of the larger $E(x)$ at larger magnitudes of σ and depletion of water due to accumulation of counterions at outer Helmholtz plane[7,8]. The slope of ε_r $(x = b)$ as a function of σ diminishes at larger magnitudes of σ as a consequence of saturation of accumulation of counterions at larger magnitudes of σ.

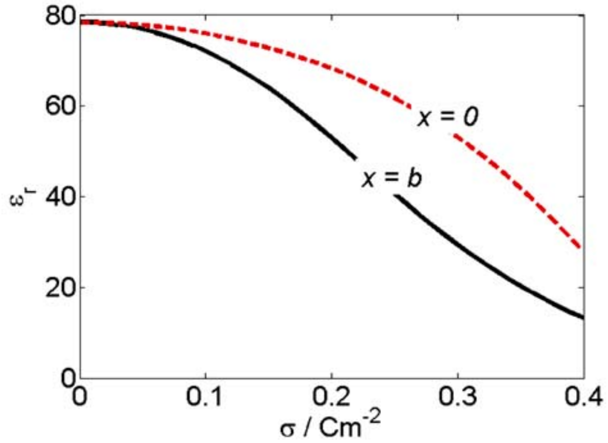

Figure 5. The relative premittivity ε_r *(x = 0)* and ε_r *(x =b)* in the Stern layer $0 \le x \le b$ (see also Figure 1) calculated within Helmholtz GI model as a function of the magnitude of the surface charge density σ. The values of the model parameters are the same as in Fig. 2.

The presented dependence of ε_r $(x = 0)$, calculated within Helmholtz GI model, is the same as the corresponding dependence of ε_r $(x = 0)$ within Helmholtz LPB model (compare also Figs. 2 and 4). Equations 2 and 4 give the same values of the permittivity for the same value of $E(x = 0)$ determined solely by the boundary condition at $x = 0$ (Equation 5), i.e. by the value of σ.

In conclusion, variety of EDL models has been published to date, most of which are based on the concept that the relative permittivity is constant in the whole system. The generalized Helmholtz LPB and GI models used in this work take into account that the dipole moment vectors of water molecules close to the charged surface are in average predominantly oriented in a direction perpendicular to the charged surface which leads to a substantial decrease of the relative permittivity in this region. On the other hand, further away from the charged surface all orientations of water dipoles are equally probable.[7,8,20]. In addition, the presented Helmhotz GI model takes into account also finite size of ions in the region out of Stern layer.[8,17] We have shown in this paper that relative permittvity within Stern layer depends on the magnitude of the surface charge density and is therefore one of the key input data that may contribute to more realistic results of simulations of EDL properties of an electrolyte solution near a charged surface.

3. Acknowledgements

This work was partly supported by the Slovenian Research Agency (ARRS). E.G. was also supported by a grant from the Slovenian Human Resources Development and Scholarship Fund.

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Povzetek

V okviru teorije električne dvojne plasti, ki obravnava orientacijsko urejanje vode v elektrolitski raztopini v stiku z naelektreno površino, upoštevamo razdaljo najmanjšega približanja hidriranih proti-ionov s pomočjo Helmholtzove ravnine in Sternove plasti. V članku je pokazano, da je relativna dielektričnost Sternove plasti močno odvisna od površinske gostote naboja naelektrene površine. Zaključimo, da realistično izračunavanje električnega potenciala in jakosti električnega polja v elektrolitu ob naelektreni površini zahteva upoštevanje spremenljive dielektričnosti v Sternovi plasti, ki je odvisna od površinske gostote naboja.