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Short communication

Charge Dependent Capacitance of Stern Layer and Capacitance of Electrode/Electrolyte Interface

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The influence of potential dependent relative permittivity of Stern layer on the capacitance of electrode-electrolyte interface is studied theoretically. A decrease of capacitance at larger magnitudes of electrode surface potential is predicted. At large electrode surface potentials the capacitance of metal-electrolyte interface is determined solely by the capacitance of Stern layer, whereas the contribution of the capacitance of diffuse layer is negligible.

Keywords: capacitance, electric double layer, Stern layer, relative permittivity, water ordering

1. INTRODUCTION

When metal electrode comes into contact with electrolyte solution an electric double layer (EDL), composed of charged surface of electrode and counter-ions is created (Figure 1). Counter-ions, i.e. ions with the sign of charge opposite to that of electrode surface, are accumulated at electrode surface, while co-ions, having the same sign of the charge as the electrode metal surface, are depleted from the metal-electrolyte interface. As a consequence the potential difference over the metal-electrolyte interface is generated [1,2]. The drop of electric potential at metal-electrolyte interface occurs mostly in electrolyte [2].

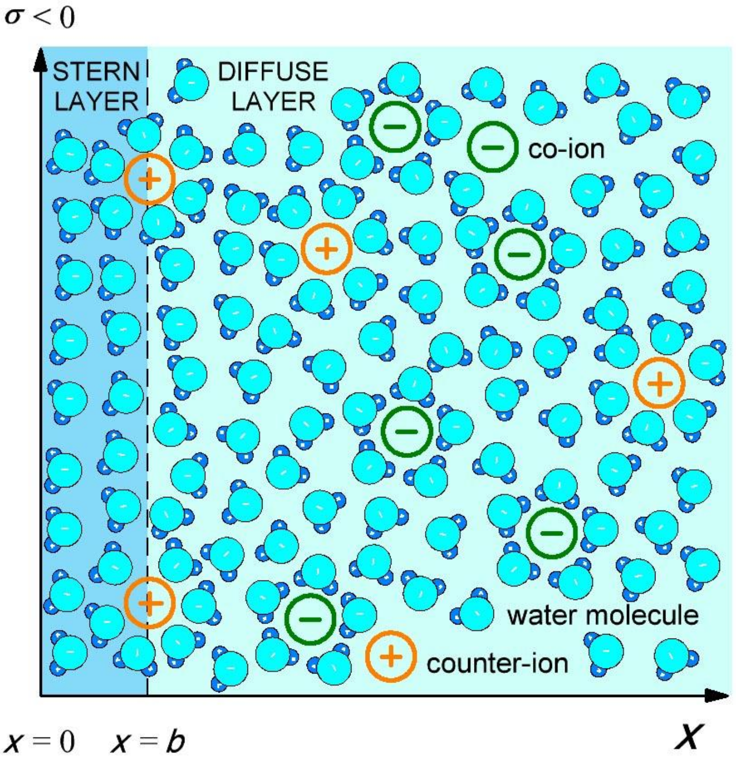

Figure 1. Schematic figure of the Stern layer $(0 \le x < b)$ and diffuse electric double layer $(b \le x < \infty)$. Outer Helmholtz plane (OHP) is located at the distance of closest approach (b) which is approximately equal to the hydrated radius of the counter-ions. The water dipoles are oriented within Stern layer as well as around counter-ions and co-ions in the bulk solution. The symbol σ denotes the surface charge density of the metal surface.

Most of the theoretical models of electrolyte solution in contact with charged surface assume that the relative (dielectric) permittivity is constant everywhere in the electrolyte solution [2-7] and do not consider the space dependence of relative permittivity of electrolyte solution near the charged surface [1] . Therefore the classical Gouy-Chapman theory of electric double layer [8,9] has been generalized by taking into account the water polarization in electrolyte solution near the charged surface resulting in spatial decay of relative permittivity in close vicinity of the charged surface [10-16] .

In this work we adopted Stern model [17] as a combination of Gouy-Chapman and Hemholtz models [18] where the outer Helmholtz plane (OHP) define a border between Stern layer and diffuse layer (Figure 1). The relative permittivity of Stern layer is calculated for different values of surface charge density of the metal surface within a simple theoretical model of orientational ordering of water. The total (differential) capacitance of the metal-electrolyte interface (C_{diff}) is calculated using the formula [19]:

$$\frac{1}{C_{diff}} = \frac{1}{C_S} + \frac{1}{C_{DL}} \quad , \tag{1.1}$$

assuming that C_{diff} is the capacitance of two capacitors in series, i.e. Stern layer capacitor (C_S) and diffuse layer capacitor (C_{DL}).

2. THEORETICAL MODEL

2.1. Capacitance of metal-electrolyte interface

In the above Equation 1.1 the influence of the final size of molecules is taken into account only by the distance of closest approach (b) (Figure 1) in the first term for the capacitance of Stern layer $C_S = \varepsilon_S \varepsilon_0 / b$. Here ε_0 is the permittivity of the free space and ε_S the electric field dependent relative permittivity of the Helmholtz/Stern layer. The capacitance of the diffuse layer ($x \geq b$) in the second term (C_{DL}) also depends on the size of molecules, which can be described within different theoretical approaches [20-21,10,11,5] . However, in this work we would like to keep all formulas analytical and simple. To this end C_{DL} is calculated within Gouy-Chapman model for point-like ions from Grahame equation [1,16,19]:

$$C_{DL} = \frac{d\sigma}{d\phi(x=b)} = \left(2\beta e_0^2 n_0 \varepsilon_r \varepsilon_0\right)^{\frac{1}{2}} \cosh(\beta e_0 \phi(x=b)/2) \quad . \tag{2.1}$$

Hence

$$\frac{1}{C_{diff}} = \frac{b}{\varepsilon_S \varepsilon_0} + \frac{1}{\left(2\beta e_0^2 n_0 \varepsilon_r \varepsilon_0\right)^{\frac{1}{2}} \cosh(\beta e_0 \phi(x=b)/2)} \quad . \tag{2.2}$$

Here n_0 is the bulk number density of salt ions, e_0 is the unit charge, ε_r is the constant permittivity of diffuse electric double layer in the region $b \leq x < \infty$ and $\beta = 1/kT$, where kT is the thermal energy.

Close to the charged metallic surface, i.e. for small values of x, the relative permittivity ε_r strongly depends on the distance from the charged metallic surface [10,11,13-16] . For simplicity reasons in this work the permittivity of diffuse layer (for $x \geq b$) in Equation 2.1 (ε_r) is considered independent on the electric field strength [1,19] , while due to strong orientation of water molecules in Stern layer the dependence of relative permittivity of Stern layer (ε_S) on the electric field strength [15] is taken into account. This means that also the capacitance of Stern layer (1st term on the right hand side of the Equation 2.2) depends on the electric field strength.

2.2. Capacitance of Helmholtz/Stern layer

In this subsection we shall first derive the electric field dependence of relative permittivity in Stern layer (ε_S). In the second step the dependence of capacitance of Stern layer $C_S = \varepsilon_S \varepsilon_0 / b$ on the electric field strength will be determined.

In the model a single water molecule is considered as the sphere with the point-like rigid (permanent) water dipole located at its centre [13,16]. The permittivity of the sphere is n^2, where $n = 1.33$ is the optical refractive index of water [13] . The polarization of water molecules P in Stern layer ($0 \le x < b$) can be expressed as [13,16] :

$$P = -n_{0w}\, p_0 \left(\frac{2+n^2}{3} \right) \mathrm{L}(\gamma p_0 E \beta) \quad , \tag{2.3}$$

where n_{0w} is the constant (bulk) number density of water molecules, E is the magnitude of the electric field strength, n^2 is the optical refractive index of water, p_0 is the magnitude of the water external dipole moment, $\mathrm{L}(u) = \coth(u) - 1/u$ is the Langevin function and $\gamma = (2+n^2)/2$. In Stern layer ($0 \le x < b$) the magnitude of electric field strength E is constant for given σ, therefore also relative permittivity (ε_S) is constant for given σ. The relative permittivity in Stern layer can then be written as (see also [13]) :

$$\varepsilon_S = n^2 + \frac{|P|}{\varepsilon_0 E} = n^2 + \frac{n_{0w}\, p_0}{\varepsilon_0} \left(\frac{2+n^2}{3} \right) \frac{\mathrm{L}(\gamma p_0 E \beta)}{E} \quad , \tag{2.4}$$

and finally the capacitance of Stern layer in the region $0 \le x < b$:

$$\frac{1}{C_S} = \frac{b}{\varepsilon_0 n^2 + n_{0w}\, p_0 \left(\frac{2+n^2}{3} \right) \frac{\mathrm{L}(\gamma p_0 E \beta)}{E}} \quad . \tag{2.5}$$

For $x \ge b$ we assume constant relative permittivity $\varepsilon_r = 78.5$ at room temperature.

2.3. Boundary conditions

The boundary conditions at $x = 0$ and $x = b$ are :

$$\left.\frac{d\phi}{dx}\right|_{x=0} = -\frac{\sigma}{\varepsilon_S \varepsilon_0} \quad , \quad \varepsilon_S \varepsilon_0 \left.\frac{d\phi}{dx}\right|_{x=b_-} = \varepsilon_r \varepsilon_0 \left.\frac{d\phi}{dx}\right|_{x=b_+} \quad , \quad \phi\big|_{x=b_-} = \phi\big|_{x=b_+} \quad , \tag{2.6}$$

where σ is the surface charge density of the metallic surface at $x = 0$. Due to constant electric field strength in Stern layer $\left.\frac{d\phi}{dx}\right|_{x=0} = \left.\frac{d\phi}{dx}\right|_{x=b_-}$ it follows from Equations 2.6 :

$$\left.\frac{d\phi}{dx}\right|_{x=b_+} = -\frac{\sigma}{\varepsilon_r \varepsilon_0} \quad . \tag{2.7}$$

The boundary condition 2.7 can be used in the region $b \le x < \infty$ to solve Gouy-Chapman equation and calculate the value of electric potential $\phi(x = b)$.

3. RESULTS AND DISCUSSION

Boundary condition at $x = 0$ (see Equation 2.6) and Equation 2.4 together yields the non-linear equation for the magnitude of electric field (E) in Stern layer :

$$\varepsilon_0 E\left(n^2+\frac{n_{0w}p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\frac{\mathrm{L}(\gamma p_0 E\beta)}{E}\right)=|\sigma| \quad . \tag{3.1}$$

Inserting the calculated value of E in Equation 2.4 yields the value of relative permittivity in Stern layer (ε_S) for given surface charge density σ. Figure 2 shows the relative permittivity ε_S as a function of surface charge density σ. It can be seen that ε_S strongly decreases with increasing magnitude of σ, which can be explained by saturation of orientational ordering of water dipoles in strong electric field at large values of σ [16,24,25]. For illustration Figure 3 shows the space dependence of relative permittivity for three different values of σ.

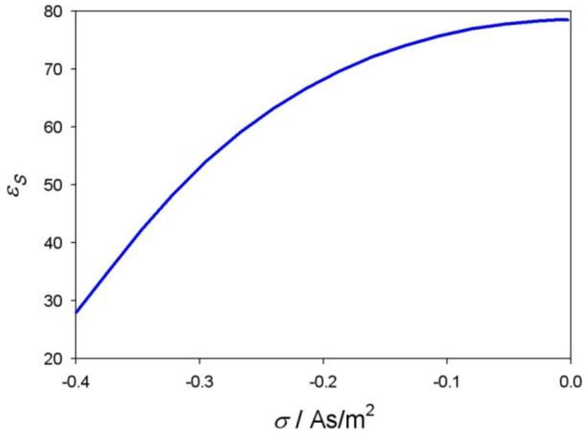

Figure 2. The relative permittivity ε_S in Stern layer $0 \le x < b$ as a function of the magnitude of the surface charge density of electrode surface (σ). The values of model parameters are : distance of closest approach $b = 0.4$ nm, $p_0 =$ 3.1 D and concentration of water n_{0w} / N_A = 55 mol/l.

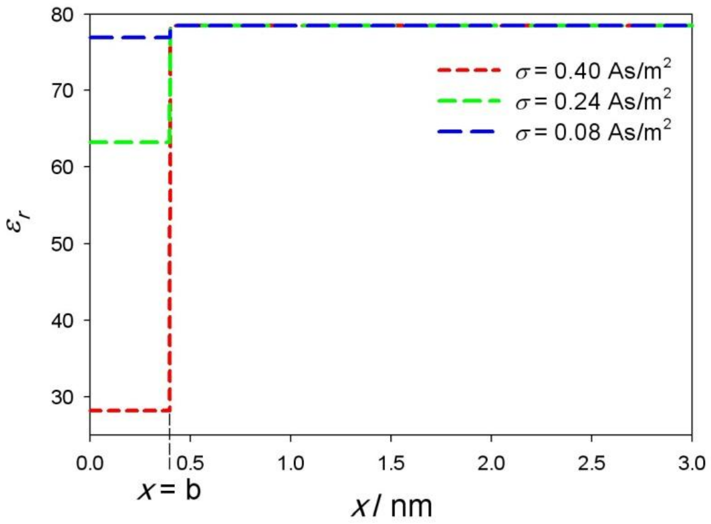

Figure 3. The space dependence of relative permittivity in Stern ($0 \le x < b$) and diffuse layer ($b \le x < \infty$) calculated for three values of electrode surface charge density (σ). The values of other parameters are the same as in Figure 2.

The electric potential dependence in the diffuse region $b \le x < \infty$ is calculated from Gouy-Chapman equation [1,3,4]:

$$\frac{d^2\phi}{dx^2} = \frac{2e_0 n_0}{\varepsilon_r \varepsilon_0} \sinh(\beta e_0 \phi(x)) \quad , \tag{3.2}$$

where the volume charge density of electrolyte solution $\rho = -2e_0 n_0 \sinh(\beta e_0 \phi(x))$ is taken into account. To calculate from Equation 3.2 the dependence $\phi(x)$ for $x \ge b$, the boundary condition defined by Equation 2.7 should also be considered.

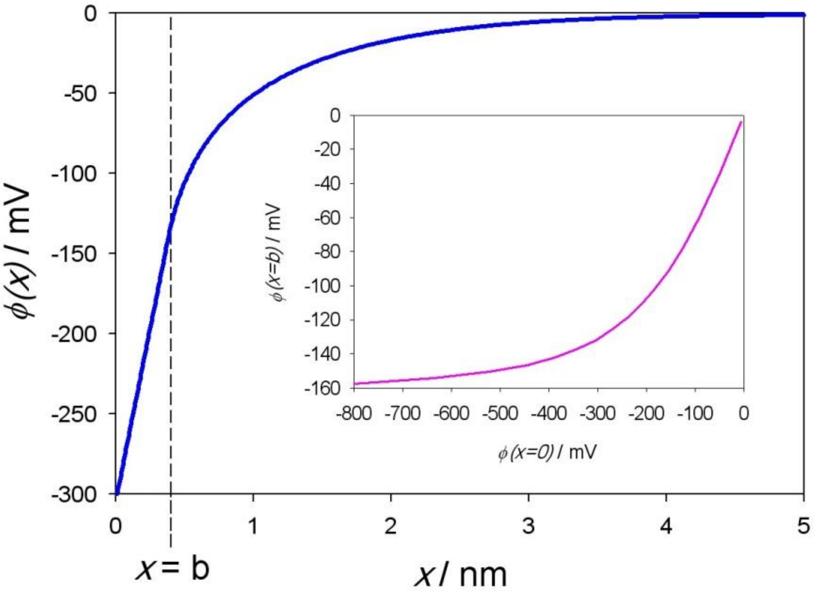

Figure 4. The calculated electric potential $\phi(x)$ as a function of the distance from the charged metallic surface. The model parameters are: surface charge density $\sigma = -0.21\ \mathrm{As/m^2}$, bulk concentration of ions $n_0 / N_A = 0.1$ mol/l, distance of closest approach $b = 0.4$ nm, $p_0 = 3.1$ D and concentration of water $n_{0w} / N_A = 55$ mol/l. The inset shows the interdependence between the potentials $\phi(x=b)$ and $\phi(x=0)$ calculated for different σ.

Figure 4 shows the space dependence of the electric potential $\phi(x)$. The linear space dependence of electric potential in Stern layer $0 \le x < b$ was determined by integration from the boundary conditions $x = 0$ (first Equation 2.6) and not from Eqution 3.2. The inset in Figure 4 shows the interdependence between electric potentials at $x = 0$ and $x = b$. Note that in Equation 2.1 for capacitance of diffuse layer C_{DL} appears the potential $\phi(x=b)$ [19] and not $\phi(x=0)$. For better understanding Figure 5 shows also the dependences of the surface potentials $\phi(x=0)$ and $\phi(x=b)$ on surface charge density σ.

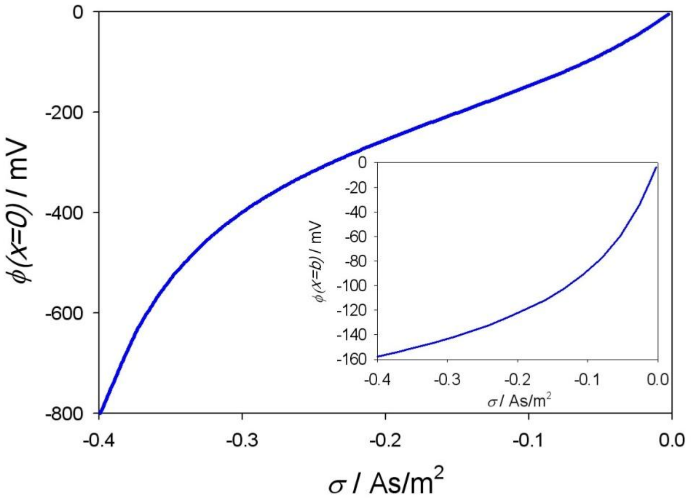

Figure 5. The calculated electric potential $\phi(x=0)$ as a function of the electrode surface charge density σ. Inset shows the dependence of $\phi(x=b)$ on σ. The values of model parameters n_0/N_A, b, p_0 and n_{0w}/N_A are the same as in Figure 4.

Figure 6 shows the capacitances of Stern (C_S) and diffuse layer (C_{DL}) and the total capacitance (C_{diff}) as functions of the surface potential $\phi(x=0)$. It can be seen in Figure 6 that diffuse layer capacitance C_{DL} increases, while Stern layer capacitance C_S decreases with increasing magnitude of $\phi(x=0)$. As the capacitance C_{diff} is calculated by Equation 1.1, this explains why at larger magnitudes of surface potential $\phi(x=0)$ the contribution of C_{DL} to C_{diff} is negligible and $C_{diff} \approx C_S$ as presented in Figure 6.

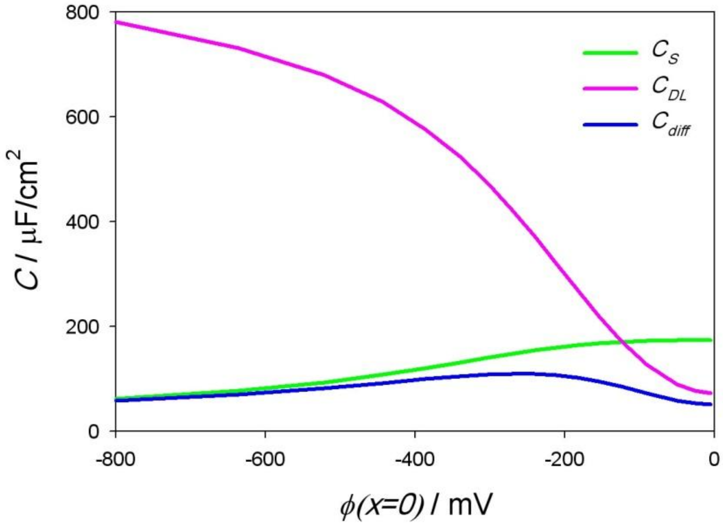

Figure 6. Differential capacitance of Stern (C_S) and diffuse layer (C_{DL}) and the total capacitance (C_{diff}) as a function of the surface potential $\phi(x=0)$. The values of model parameters n_0/N_A, b, p_0 and n_{0w}/N_A are the same as in Figure 4.

Figure 7 shows the calculated capacitance of electrode-electrolyte interface (C_{diff}) for relative permittivity in Stern layer which depends on surface charge density of electrode ($\varepsilon_S(\sigma)$), determined as described above, and for the case of constant value of relative permittivity in Stern layer ($\varepsilon_S = 30$). It can be seen that in the first case of $\varepsilon_S(\sigma)$ the capacitance C_{diff} exhibit a maximum and subsequent monotonous decreasing of C_{diff} with increasing magnitude of $\phi(x=0)$. On the contrary, for constant $\varepsilon_S = 30$ there is no maximum in C_{diff} and its decrease at large magnitudes of $\phi(x=0)$. The maximum in dependence of C_{diff} on surface potential $\phi(x=0)$ and decrease of C_{diff} at large magnitudes of $\phi(x=0)$ can be predicted also at constant relative permittivity by taking into account the finite size of ions (volume excluded effect) within Bikerman model [6,16,23]. In accordance, it was shown recently [16], that combination of volume excluded effect [20] and space dependence of relative permittivity in electrolyte solution [13] predict stronger decrease of C_{diff} at large magnitudes of $\phi(x=0)$ as predicted within pure Bikerman model .

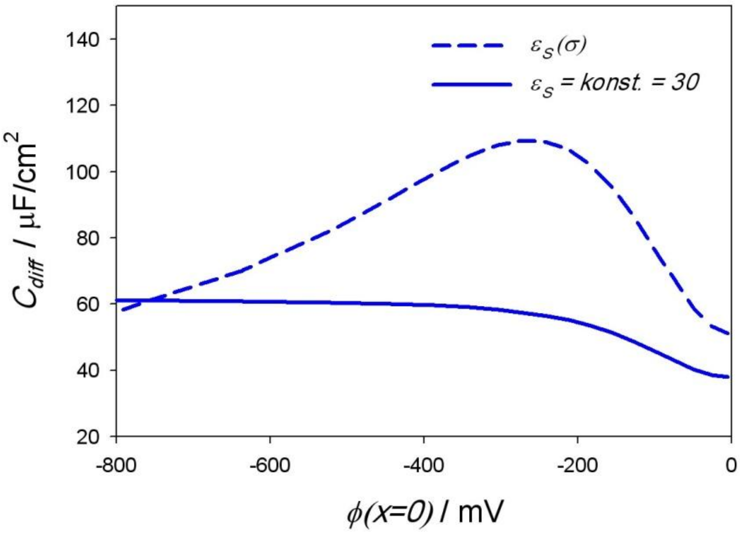

Figure 7. Differential capacitance of metal-electrolyte interface (C_{diff}) as a function of the surface potential $\phi(x=0)$ for the case voltage/surface charge dependent relative permittivity of Stern layer (Figures 2 and 3) and constant permittivity in Stern layer. The values of the model parameters are the same as in Figure 4.

4. CONCLUSIONS

Water is one of the most important molecules in biological systems [26]. In this work we attempt to uncover the relation between the electric potential dependent orientational ordering of water molecules in Stern layer and the capacitance of metal electrode-electrolyte interface. In order to keep our theory analytical and appropriate for analysis of experimental results as much as possible the finite volume of molecules was taken into account by the distance of closest approach only. In addition, also the transport phenomena in Stern and diffuse layers [27] are totally neglected . To this end the influence of conductivity of diffuse layer on the capacitance of Stern layer can not be described within the presented model.

Obtaining the charge/potential dependence of relative permittivity in Stern layer, the capacitance of electrode-electrolyte interface as a function of electrode charge/potential is calculated. A decrease of capacitance at larger magnitudes of electrode surface potential is predicted. It is also shown that at large electrode surface potentials the capacitance of metal-electrolyte interface is determined solely by the capacitance of Stern layer, whereas the contribution of the capacitance of diffuse layer becomes negligible.

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