Int. J. Electrochem. Sci., 10 **(2015)** 1 - 7

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short communication

On Asymmetric Shape of Electric Double Layer Capacitance Curve

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Received: 15 October 2014 / *Accepted:* 4 November 2014 / *Published:* 17 November 2014

The Stern model of electric double layer created at the contact of charged surface with electrolyte solution is modified by taking into account potential (voltage) dependence of relative permittivity in Stern layer due to orientational ordering of water dipoles in saturation regime. In addition, different sizes of hydrated anions and cations in electrolyte solution are taken into account by different values of distance of closest approach for both kind of ions. We showed that the proposed modifications enable us to predict the experimentally observed asymmetry of camel-like shape of the double layer capacitance dependence on the electrode potential.

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

1. INTRODUCTION

Within the classical Poisson-Boltzmann (PB) models of electrolyte solution in contact with charged surface [1, 2, 3, 4, 5, 6, 7], the ions in electrolyte solution were treated as dimensionless. Stern was the first [8] who attempted to incorporate the finite size of ions in PB models by assuming the distance of closest approach of counter-ions to the charged surface [9, 10, 11] (see Figure 1).

More sophisticated approach to take into account the finite size of ions in electrolyte solution being in contact with charged surface was introduced by Bikerman [12]. Different other generalized PB models to describe the finite size of ions were introduced also later [13, 14, 15, 16, 17, 18]. Also more recently, the finite size of ions and excluded volume effect were incorporated into generalized PB theory by using the lattice statistics approach [19, 20], by functional density approaches [21, 22, 23] and by a modified PB theory where the ions and solvent molecules were treated as hard spheres [24, 25, 26].

The majority of the theoretical models of electrolyte solution in contact with charged surface involve the assumption that the relative (dielectric) permittivity is constant everywhere in the electrolyte solution [5, 7, 19, 27, 28, 29] and do not consider spatial decay of relative permittivity in close vicinity of the charged surface [7, 30, 31, 32]. Therefore the classical PB theories [6, 29, 30] has been generalized by taking into account the water polarization in electrolyte solution resulting in decrease of relative permittivity near the charged surface in saturation regime of water dipole orientation [7, 24, 25, 26, 27, 32, 33, 34]. Taking into account the space dependence of permittivity close to the charged surface and the excluded volume effect within generalized PB approach [7, 35] result in theoretical prediction of so-called camel (saddle-like) shape of differential capacitance voltage dependence which was observed also experimentally [36, 37, 38], in Monte-Carlo simulations [39] and in molecular dynamic simulations [39].

Symmetric camel-like profile of differential capacitance may also be predicted by considering the finite size of ions only [5, 7, 31], i.e. without taking into account the space variation of permittivity near the charged surface. The predicted capacitance curves are symmetric (camel-like) with respect to zero potential [7, 31]. The symmetric camel-like double layer differential capacitance can be calculated also within simple Stern model by taking into account the decrease of permittivity in Stern layer and non-zero distance of closest approach for counter-ions [11].

On the other hand, the asymmetric double layer differential capacitance curve was predicted within modified lattice statistics PB approach of Kralj-Iglič and Iglič from 1996 [19] (the same lattice statistics model as presented by [19] was published later in 1997 also by [40]) as performed recently in [41] if different size of negatively and positively charged hydrated ions in electrolyte solution is taken into account within the lattice model. In [41] the double layer differential capacitance curve becomes asymmetric due to decrease of capacitance for positive values of voltage relative to the corresponding capacitance values for negative values of voltage. This is however not always the case in experiments (see for example [36]), where the measured differential capacitance for positive values of voltage may be higher than the capacitance for negative values of voltage.

Far from the charged plane the electrostatic field does not depend on the size of hydrated ions [42]. On the other hand, in the vicinity of the charged plane the counter-ions are accumulated while the co-ions are scarce. The influence of the counter-ions contained in the region close to the charged plane on the electrostatic field is the most important one [42]. To this end in this work, to account for different sizes of the hydrated ions in electrolyte solution [43, 44], we assume different values of the distance of closest approach for cationic and anionic counter-ions, respectively (see Figure 1). In the case of negatively charged surface the distance of closest approach b is adapted to positively charged counter-ions (Figure 1A), while in the case of positively charged surface the parameter b describes the distance of closest approach for negatively charged counter-ions (Figure 1B). It will be shown in the present paper that the double-layer differential capacitance curve becomes asymmetric when different values of closest approach are used for negatively and positively counter-ions and the potential (charge) dependent permittivity in Stern layer is taken into account [11].

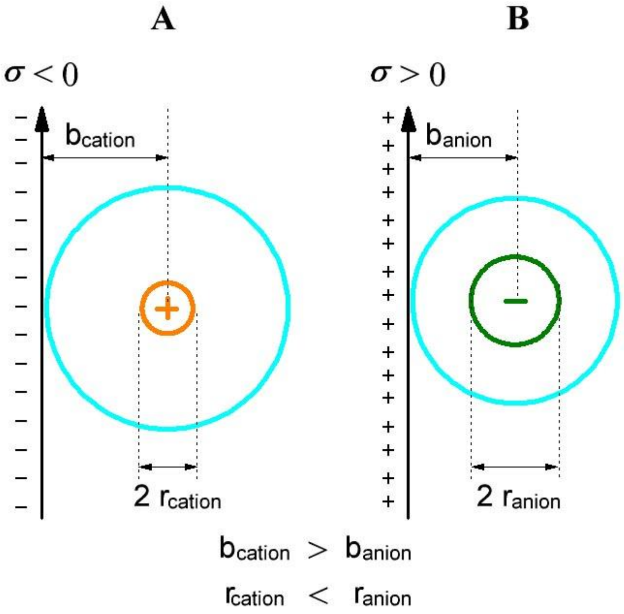

Figure 1. Distance of closest approach (*b*) in the case of negatively (A) and positively charged planar surface (B). In the first case (A) the distance of closest approach is defined by the radius of the hydrated cations (b_{cation}), while in the second case (B) the distance of closest approach is defined by the radius of hydrated anions (b_{anion}).

2. MODELS AND METHODS

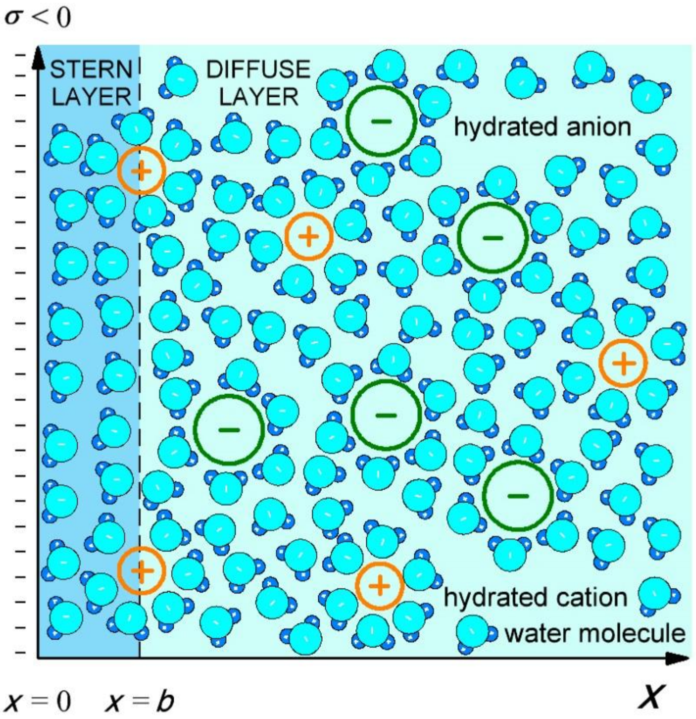

Figure 2. Graphical presentation of Stern and diffuse electric double layer in the case of negatively charged planar surface (σ < 0). Outer Helmholtz plane (OHP) is located at the distance of closest approach ($x = b$) which is equal to hydration radius of counter-ions (cations).

In this work we adopted Stern model as a combination of Gouy-Chapman (GC) and Helmholtz models where the outer Helmholtz plane (OHP) define a border between Stern layer and diffuse layer [11] (Figure 2). Within such a model the differential capacitance (C_{diff}) can be calculated as follows [38]:

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

where (C_S) is the capacitance of Stern layer and (C_{DL}) is the capacitance of diffuse layer (see Figure 2).

Capacitance of Stern layer (C_S) is equal to capacitance of parallel plate capacitor [45]:

$$C_S = \frac{\varepsilon_S \varepsilon_0}{b} \quad , \tag{2}$$

where ε_0 is dielectric constant, ε_S is relative permittivity of Stern layer and b is the distance of closest approach. Within GC model the capacitance of diffuse layer (C_{DL}) is [7, 30, 38]:

$$C_{DL} = \frac{d\sigma}{d\phi(x=b)} = \left(2\beta e_0^2 n_0 \varepsilon_r \varepsilon_0\right)^{1/2} \cosh(\beta e_0 \phi(x=b)/2) \quad , \tag{3}$$

where σ is surface charge density, ϕ is the electric potential at the distance of closest approach at $x = b$, e_0 is unit charge, n_0 is bulk number density of ions, $\beta = 1/kT$, kT is thermal energy, ε_0 is permittivity of vacuum and ε_r is relative permittivity of diffuse layer ($b \leq x < \infty$). Total differential capacitance (C_{diff}) is therefore:

$$\frac{1}{C_{diff}} = \frac{b}{\varepsilon_S \varepsilon_0} + \frac{1}{\left(2\beta e_0^2 n_0 \varepsilon_r \varepsilon_0\right)^{1/2} \cosh(\beta e_0 \phi(x=b)/2)} \quad . \tag{4}$$

Stern model assumes that ε_S and ε_r are constant. For simplicity reasons ε_r in diffuse layer is considered as constant value, but due to the dependence of relative permittivity (ε_S) on surface charge density (σ), the relative permittivity (ε_S) is calculated as follows. Water molecule as a sphere with permanent point-like dipole moment in the centre of the sphere (p_0) and with relative dielectric permittivity equal to the square of refractive index of water (n^2) [32], the vector of polarization of water molecules in Stern layer ($0 \leq x < b$) can be written as [7, 32, 46]:

$$P = -n_{0w} p_0 \left(\frac{2+n^2}{3}\right) \mathrm{L}(\gamma p_0 E \beta) \quad , \tag{5}$$

where n_{0w} is number density of water molecules, E is magnitude of the electric field strength, n is optical refractive index of water, p_0 is the magnitude of water external moment, L is Langevin function and $\gamma = (2 + n\ 2)/2$. Relative permittivity in Stern layer (ε_S) is therefore [11, 47]:

$$\varepsilon_S = n^2 + \frac{|P|}{\varepsilon_0 E} = n^2 + \frac{n_{0w} p_0}{\varepsilon_0} \left(\frac{2+n^2}{3}\right) \frac{\mathrm{L}(\gamma p_0 E \beta)}{E} \quad . \tag{6}$$

The capacitance of Stern layer ($0 \leq x < b$) can be therefore written as [11]:

$$C_S = \frac{\varepsilon_0 n^2 + n_{0w} p_0 \left(\frac{2+n^2}{3}\right) \frac{\mathrm{L}(\gamma p_0 E \beta)}{E}}{b} \quad . \tag{7}$$

For relative permittivity outside the Stern layer (ε_r) we assume constant value $\varepsilon_r = 78.5$ at room temperature. The relative permittivity within the Stern layer is calculated from Equation 6, where the magnitude of electric field in Stern layer is calculated from boundary condition at the charged surface (see also [11]):

$$\varepsilon_0 E\left(n^2+\frac{n_{0w}p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\frac{\mathrm{L}(\gamma p_0 E\beta)}{E}\right)=|\sigma| \quad . \tag{8}$$

The electric potential dependence in the diffuse region ($x \geq b$) is calculated from Gouy-Chapman equation [1, 2, 6] as described in [11].

3. RESULTS AND DISCUSSION

Differential capacitance (C_{diff}) as a function of the potential at planar charged surface ($x = 0$) (voltage), calculated for different values of the distance of closest approach b, can be seen in Figure 3. In the case of negative potentials ($\phi < 0$) at planar surface ($x = 0$), where high accumulation of cations and depletion of anions in the close vicinity of the charged planar surface take place, the distance of closest approach is defined by the radius of hydrated cations ($b \approx b_{cation}$) (Figure 1A). On the contrary, in the case of positive potentials ($\phi > 0$) at planar surface ($x = 0$), where high accumulation of anions near the charged planar surface and simultaneous strong depletion of cations [43, 44], the distance of closest approach is approximated by the radius of the hydrated anions ($b \approx b_{anion}$) (Figure 1B) (see also [42]). As hydrated radius of cations is assumed to be greater than hydrated radius of anions [43, 44], the surface potential at $x = 0$ is higher for negatively charged surface ($\sigma < 0$), therefore C_{diff} values are greater.

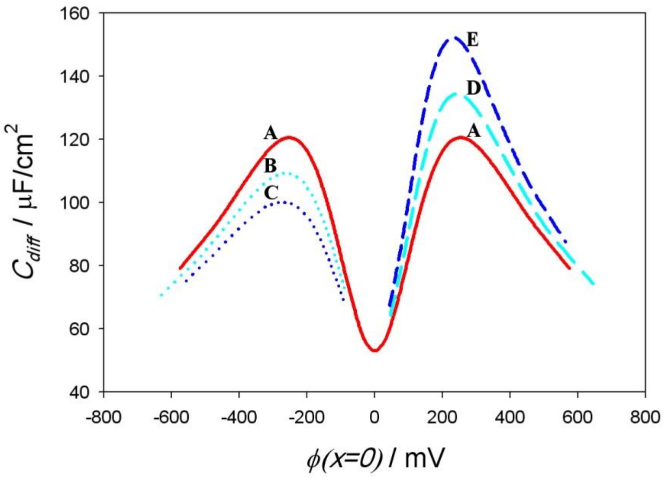

Figure 3. Differential capacitance (C_{diff}) as a function of the potential at planar charged surface calculated for different values of b: 0.35 nm (A), 0.30 nm (D), 0.25 nm (E), 0.40 nm (B) and 0.45 nm (C). Other model parameters are: bulk concentration of ions n_0/N_A = 0.1 mol/l, p_0 = 3.1 Debye, concentration of water n_{0w}/N_A = 55 mol/l and T = 298 K.

4. CONCLUSION

We have studied the differential capacitance within Stern model where the different sizes of hydrated cations and anions in electrolyte solution are taken into account by different values of the distance of closest approach for cations and anions. The strong dependence of the relative permittivity in Stern layer on the surface potential is also taken into account in the presented theoretical model. It is shown that these two assumptions of presented simple theoretical model may qualitatively describe some characteristics of the experimentally observed asymmetric camel-like dependence of differential capacitance [36, 37, 38]. In the future the described model should be upgraded by taking into account the excluded volume effect within GI model [7, 32], modified by taking into account different size of ions not only by different distance of closest approach for anions and cations, but also in lattice statistics where different kind of ions (anions and cations) occupy different number of lattice cells or alternatively by allowing several ions to be in single lattice cell [41, 48].

ACKNOWLEDGEMENTS
This work was in part supported by the Slovenian Research Agency (ARRS).

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