

Ben-Gurion University of the Negev
The Jacob Blaustein Institutes for Desert Research
The Albert Katz International School for Desert Studies



**Analysis of the Electrical Double Layer
With and Without Added Electrolyte**

Thesis submitted in partial fulfillment of the requirements for the degree of
"Master of Science" (or "Master of Arts")

By: VardanyanVardan

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Under the Supervision of Prof. Isaak Rubinstein and Prof. Boris Zaltzman

Department of Environmental Physics and Solar Energy

Author's Signature Date

Approved by the Supervisor..... Date

Approved by the Director of the School Date

Abstract

The Electric Double Layer (EDL) has been studied for over a century. The mean-field model of EDL in terms of the nonlinear Poisson-Boltzmann equation is well-established study instrument in a broad range of scientific research areas: electrochemistry, colloid chemistry, biophysics, etc. This equation describes the equilibrium distribution in space of the electrostatic potential and ionic concentrations in the system. In spite of the respectable age of analyzing EDL in terms of the Poisson-Boltzmann equation, there still remain numerous unresolved questions related to this approach. Thus, traditionally, the Poisson-Boltzmann equation has been analyzed for open systems. Typically, such a system consists of a charged surface with the ions dissociated from it and the ions of an electrolyte added to the system at a specified finite concentration. For a macroscopic system, this usually implies that the ions of the added electrolyte constitute an overwhelming majority compared to those dissociated from the interface. As opposed, to this approach, in this study we study, both analytically and numerically, a closed system, with the total mass of added salt as the control parameter. Our analysis particularly focuses on the case when the amount of ions of the added electrolyte is comparable to that of ions dissociated from the interface. We show that, in this case, a novel, previously undetected boundary layer forms near the interface as a fine sub-structure of the common EDL.

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List of frequently used symbols

$\tilde{\varphi}$	Electric potential
$\tilde{C}_{\pm}, \tilde{C}'_{\pm}$	Concentration of ions
$\tilde{\sigma}$	Surface charge
x	Dimensionless space variable
C_{\pm}, C'_{\pm}	Dimensionless concentration of ions
φ	Dimensionless electric potential
ε	Dimensionless Debye length, scaled by the concentration of cations dissociated from the metal wall
σ	The total number of gram-molecules of cations dissociated from a unit area of the metal wall
n_0	Dimensionless parameter which characterize various scalings of the total amount of added ions versus those that have dissociated from the wall.
$\tilde{\varepsilon}$	Dimensionless Debye length rescaled by n_0
V_0	Electric potential at the wall

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INTRODUCTION: ELECTRIC DOUBLE LAYER

The effect of any charged surface in an electrolyte solution will be to influence the distribution of ions in the solution. Ions of opposite charge (counterions), while in thermal motion, are attracted toward the surface while ions of like charge (coions) are repelled from it (Fig 1.). This leads to the formation of a charged ionic cloud near the interface. The total charge of the interface balances that of the cloud. Both together form the diffuse electric double layer (EDL). The EDL plays a key role in understanding the behavior of many physical, chemical and biological phenomena. The concept of the electric double layer was introduced by Helmholtz, who suggested a model of charges in two parallel planes as shown in Figure 1 (a),

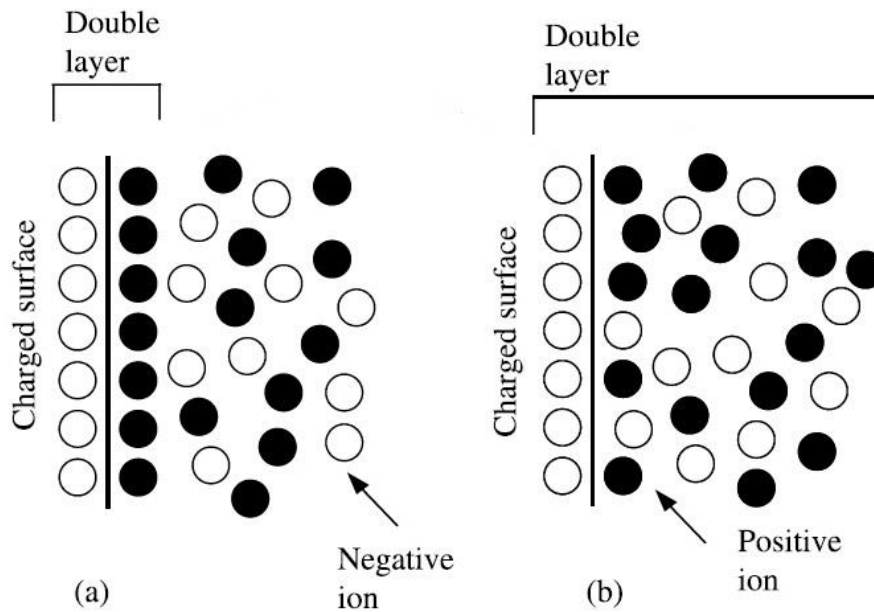


Figure 1: The electric double layer. (a) according to the Helmholtz model, (b) according to the Gouy and Chapman model.

forming a molecular condenser. However, thermal motion tend to drive the counterions away from the surface, forming a diffuse double layer, as shown in

Figure 1 (b). The theory for such a diffuse double layer was developed independently by Gouy and Chapman [1][2].

The two major applications of the EDL theories are the theory of stability of lyophobic colloids (DLVO theory [5], [6] and the theory of electrokinetic phenomena [12]- [14]. In the former, the electric field of EDL is used to evaluate the force of repulsion between two similarly charge colloidal particles. In the latter, the electrical space charge of EDL determines the slip-like flow effects in the surrounding fluid, [8], [9]. The two prototypical effects of this type are electroosmosis and electrophoresis, [10]-[18]. The former relates to the slip-like flow of the fluid induce by a tangential electric field applied to a charged solid liquid interface. The latter, a sort of adjoin-reciprocal phenomenon for the former, pertains to the motion of a charged macroscopic particle in an electrolyte solution under the action of an applied electric field.

The central issue in the EDL theories is the evaluation of the electrostatic potential. For many years the Poisson-Boltzmann (PB) theory has been used for this purpose. As a mean-field theory, the PB theory is based on the following assumptions

- 1) the only interaction to be considered is the Columbic interaction between charged particles, and mean electric field in the system that is each charged particles sense, only the mean electric field, rather than that produced by instantaneous positions of all other particles,
- 2) the dipole-dipole interactions are neglected,
- 3) the charges are taken as point-like objects neglecting any finite size effect,
- 4) the electrolyte solution is a continuous media with a dielectric constant,

5) the electrostatic potential $\varphi(x, y, z)$ is a continuous function . The charge density profile of all ions $\rho(x, y, z)$ is also a mean-field continuous function of the position.

The electrostatic potential, is described by Poisson's equation

$$-\varepsilon_r \varepsilon_0 \tilde{\Delta} \tilde{\varphi} = \rho = \sum_i z_i F \tilde{C}_i. \quad (1.1)$$

Here F is the Faraday's constant ($F = eN_A = 9.6 \times 10^4 C \times mol^{-1}$), $\tilde{C}_i (mol \times m^{-3})$ the concentration, ε_r is the relative permittivity, $\varepsilon_0 = 8.85 \times 10^{-12} C \times V^{-1} \times m^{-1}$ is the permittivity of a vacuum, z_i are the valences. It is assumed that the ions are in quasithermal equilibrium with a Boltzmann distribution

$$\tilde{C}_i = \tilde{C}_i^0 \exp\left(-\frac{z_i F \tilde{\varphi}}{RT}\right). \quad (1.2)$$

Here R is the universal gas constant ($R = 8.31 V \times C/mol \times K$), and \tilde{C}_i^0 is the reference concentration of $i - th$ species ($i = \pm$) taken at zero potential, $\tilde{\varphi} \rightarrow 0$. Substituting Eq. (1.1) into Eq. (1.2), we get the Poisson-Boltzmann (PB) equation for the electric potential $\tilde{\varphi}$:

$$-\varepsilon_r \varepsilon_0 \tilde{\Delta} \tilde{\varphi} = \sum_i z_i F \tilde{C}_i^0 \exp\left(-\frac{z_i F \tilde{\varphi}}{RT}\right). \quad (1.3)$$

In the mean field approximation, the mean electrostatic potential, is determined by the Poisson equation, valid for point like ions as long as they are in quasi-thermal equilibrium with their concentration obeying, the Boltzmann distribution with the mean electric potential in it . The equation is non-linear, thus it has closed-form analytical solutions only for some particular simple settings, such as the case of a symmetric binary $z:z$ electrolyte in a one-dimensional geometry.

In this case ($z: z, z = 1$) the solution describes the most common situation where diffuse charge is distributed in a thin “double layer” near a solid surface. The thickness of the diffuse layer is the Debye length,

$$r_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 RT}{F^2 \tilde{C}_0}} \quad (1.4)$$

The Neumann boundary condition, relates to the case of fixed surface charge density, and the Dirichlet boundary condition to the case of fixed potential at the surface.

The PB equation is a useful basis for analytical approximation, whereas its numerical solution for specific models and limits provides the ionic profiles necessary for applications.

The classical Poisson-Boltzmann equation for the equilibrium EDL has been solved for solution, that contains anions and cations of the salt added to the solution, and the profiles of the electric potential and ionic concentration have been found in Ref. [3], for some typical situations characterized either by a total absence of added electrolyte or by an exceeding excess of the number of added electrolyte ions compared to those dissociated from the charged interface. Fig. 1 illustrates the profiles of electric potential and concentrations of ions near charged surface.

The review article [4] includes detailed solution of the same problem in the case of single sided and double sided charged surface. In all the above studies the Debye length is characterized by reference concentration \tilde{C}_0 . Our goal in this study is to describe EDL width in terms of total mass of added salt. In particular, we wish to analyze the case when the number of both types of ions, added and dissociated, is

comparable. A clear understanding of this transitional situation will deepen our insight into the basic nature of diffuse electric double layer.

Our study is structured as follows. Section 2 outlines the formulation of the problem. Sections 3 and 4 provide the analytical solutions for two limiting cases: no added salt and sufficiently high total mass of added salt compared to that of dissociated particles. The intermediate case where these two masses balance is treated in Section 5. This includes a numerical solution of the main problem of our study and discussion of the results obtained. The conclusions are summarized in Section 6. Section 7 contains the Appendix with a numerical MATLAB code employed in Section 5.

PROBLEM FORMULATION

The physical phenomenon which we are about to study, is the interaction between the mobile charges dissociated from a solid surface immersed in an electrolyte solution, the ions of this solution and the fixed surface charge of the surface itself.

We consider the solution between two parallel negatively charged metal plates with surfaces area S_0 separated by distance L . Let this solution consist of the solvent (e.g., water), positive univalent ions (cations $z_+=1$) dissociated from the wall, and of negative univalent ions (anions, z_-), and univalent cations ($z_+ = 1$) of the salt added to the solution. Let the total number of gram-molecules of salt be $2N$ ($N = S_0Ln$, whereas n is the total number of gram-molecules of salt per unit volume), and let the surface charge density of the metal/solution interface be $\tilde{\sigma}(C/m^2)$. The Poisson equation for the electric potential $\tilde{\varphi}$ reads as follows

$$\varepsilon_r \varepsilon_0 \tilde{\Delta} \tilde{\varphi} = -\tilde{\rho} = -F(\tilde{C}'_+ + \tilde{C}_+ - \tilde{C}_-). \quad (2.1a)$$

Here ε_r is the relative permittivity, $\varepsilon_0 = 8.85 \times 10^{-12} C \times V^{-1} \times m^{-1}$ is the permittivity of the vacuum, $\tilde{\rho}$ is the density of the space charge, whereas \tilde{C}'_+ is the concentration of cations dissociated from the surface, \tilde{C}_+ (\tilde{C}_-) is the concentration of cations (anions) of the salt, and F is the Faraday's constant ($F = eN_A = 9.6 \times 10^4 C \times mol^{-1}$). We assume that the ions are in thermal equilibrium with the Boltzmann distribution

$$\tilde{C}_\pm = \tilde{C}_\pm^0 \exp\left(\frac{\mp F \tilde{\varphi}}{RT}\right), \quad (2.1b)$$

$$\tilde{C}'_+ = \tilde{C}'_+{}^0 \exp\left(\frac{-F \tilde{\varphi}}{RT}\right), \quad (2.1c)$$

where \tilde{C}_{\pm}^0 and $\tilde{C}_{+}^{0'}$ are the *a priori* unknown concentrations of the ions of the added salt and those dissociated from the metal surface at the location of zero electric potential, and R is the universal gas constant ($R = 8.31 \text{ V} \times \text{C/mol} \times \text{K}$). In this case equation (2.1a) is reduced to Poisson-Boltzmann equation

$$\varepsilon_r \varepsilon_0 \tilde{\Delta} \tilde{\varphi} = -F \left(\tilde{C}_{+}^0 \exp\left(\frac{-F \tilde{\varphi}}{RT}\right) + \tilde{C}_{+}^{0'} \exp\left(\frac{-F \tilde{\varphi}}{RT}\right) - \tilde{C}_{-}^0 \exp\left(\frac{F \tilde{\varphi}}{RT}\right) \right). \quad (2.1d)$$

The concentrations \tilde{C}_{\pm}^0 and $\tilde{C}_{+}^{0'}$ are related to the total mass of salt in per unit volume n and surface charge $\tilde{\sigma}$ through the following relations stemming from the ionic mass balance per unit area:

$$\tilde{C}_{\pm}^0 = \frac{nL}{\int_{-L}^0 \exp\left(\frac{\mp F \tilde{\varphi}}{RT}\right) d\tilde{x}}, \quad (2.2a)$$

$$\tilde{C}_{+}^{0'} = \frac{\sigma}{\int_{-L}^0 \exp\left(\frac{-F \tilde{\varphi}}{RT}\right) d\tilde{x}}. \quad (2.2b)$$

Here $\sigma = \tilde{\sigma}/F$ is the total number of gram-molecules of cations dissociated from a unit area of the metal wall

Since the two boundaries at $\tilde{x} = \pm L$ are symmetric about $\tilde{x} = 0$ (fig. 1), it is sufficient to solve the Poisson-Boltzmann equation only in the interval $-L < \tilde{x} < 0$. The boundary conditions for Eq.(2.1a) depend on the particular problem under consideration. It follows by symmetry that

$$\left(\frac{d\tilde{\varphi}}{d\tilde{x}}\right)\Big|_{\tilde{x}=0} = 0, \quad (2.3a)$$

And normalizing the potential at $\tilde{x} = -L$, we set:

$$\tilde{\varphi}(-L) = 0. \quad (2.3b)$$

Overall electroneutrality of the system (integration of Eq.(2.1 d) from $\tilde{x} = 0$ to $\tilde{x} = L$, taking into account Eqns. (2.2),(2.3a)) yields

$$\varepsilon_r \varepsilon_0 \left(\frac{d\tilde{\varphi}}{d\tilde{x}} \right) \Big|_{\tilde{x}=-L} = \tilde{\sigma} \quad (2.3c)$$

Let us define the following dimensionless variables:

$$x = \frac{\tilde{x}}{L} \quad (2.4a)$$

$$\varphi = \frac{F\tilde{\varphi}}{RT} \quad (2.4b)$$

$$C_{\pm} = \frac{\tilde{C}_{\pm}^0}{C_0} \quad (2.4c)$$

$$C'_+ = \frac{\tilde{C}'_+}{C_0} \quad (2.4d)$$

Here, $C_0 = \sigma/L$. In terms of dimensionless variables (2.4), equations (2.1d), (2.3) are rewritten as

$$\varepsilon^2 \varphi_{xx} = \frac{nL}{\sigma} \frac{1}{\int_{-1}^0 e^{\varphi} dx} e^{\varphi} - \frac{nL}{\sigma} \frac{1}{\int_{-1}^0 e^{-\varphi} dx} e^{-\varphi} - \frac{1}{\int_{-1}^0 e^{-\varphi} dx} e^{-\varphi}, \quad (2.5a)$$

$$\varphi_x(0) = 0, \quad (2.5b)$$

$$\varphi(0) = 0, \quad (2.5c)$$

The electric field is related to the surface charge density σ by the electrostatic boundary condition at $x = -1$

$$\varepsilon^2 \varphi_x(-1) = 1, \quad (2.6)$$

where

$$\varepsilon^2 = \frac{\varepsilon_r \varepsilon_0 RT}{F^2 L \sigma}. \quad (2.7)$$

For $T = 300^0K$, and L and σ in the realistic range of $10^{-6} < L < 10^{-4}$ (m) and $10^{-3} < \sigma < 10^{-5}$, respectively, ε lies in the range $10^{-7} < \varepsilon^2 < 10^{-3}$. That is for most aqueous systems ε is a very small number.

The right-hand side of Eq. (2.5a) contains the ‘phase’ integrals in terms of the unknown electric potential $\varphi(x)$. Presence of these integrals in the right hand side of the Poisson-Boltzmann equation is the main particularity of our model compared with the common mean field models of EDL based on the Poisson Boltzmann equation. As a result, we are unable to obtain a closed-form analytic solution for the electric potential. Instead, each integral must be evaluated either through approximation or numerically. Let us define the ratio between the total mass of ions dissociated from the unite area of the wall and those of the added salt as

$$\frac{nL}{\sigma} \equiv n_0. \quad (2.8)$$

Here n_0 is a dimensionless parameter which may conveniently characterize various scalings of the total amount of added ions versus those that have dissociated from the wall. We are particularly interested in the following three cases:

CASE I: No added salt, $n_0 = 0$. In this case, whose study was pioneered by Gouy [1], the Poisson-Boltzmann equation (2.5a) is reduced to:

$$\varphi_{xx} = -\frac{1}{\varepsilon^2 \int_{-1}^0 e^{-\varphi} dx} e^{-\varphi}$$

CASE II: The total amount of cations dissociated from the wall is negligible compared to the total mass of the added salt ($n_0 \gg 1$).

CASE III: The total amount of dissociated particles is comparable to the total mass of added salt ($n_0 = O(1)$).

In what follows we analyze these three cases beginning with the simplest one pertaining to the system with no added salt.

CASE I: NO ADDED SALT, INFINITE LAYER, $n_0 = 0$

This simplest version of Eq. (2.5) pertains to an infinite layer bounded on the left at $x = -1$, by a charged surface with the only ions in solution being those dissociated from the wall. For an infinite layer, there is no natural ‘macroscopic’ length in the system, which implies that L in Eq. (27) is fixed arbitrarily, that is the parameter ε is arbitrary too. Let us introduce a new parameter

$$\tilde{A} = \frac{1}{\varepsilon^2 \int_{-1}^{\infty} e^{-\varphi} dx}, \quad (3.1)$$

With this notation, equation (2.5a) is rewritten as follows

$$\varphi_{xx} = -\tilde{A}e^{-\varphi}$$

As we show below, for a semi-infinite layer, and a finite charge, $\sigma > 0$, the potential drop over the entire solution layer is infinite. The full boundary value problem for this case is:

$$\varphi_{xx} = -\tilde{A}e^{-\varphi} \quad (3.2a)$$

$$\varphi(-1) = 0 \quad (3.2b)$$

$$\varphi_x \rightarrow 0, \quad x \rightarrow \infty \quad (3.2c)$$

It follows from electroneutrality of the system (integration of Eq.(3.2a) from $x = -1$ to $x = \infty$, taking into account Eqns. (3.1),(3.2c)) yields

$$\varepsilon^2 \varphi_x(-1) = 1 \quad (3.2d)$$

The differential equation (3.2) can be solved through multiplying both sides by $d\varphi/dx$

$$\frac{d\varphi}{dx} \left(\frac{d}{dx} \left(\frac{d\varphi}{dx} \right) \right) = (-\tilde{A}e^{-\varphi}) \frac{d\varphi}{dx},$$

$$\frac{1}{2} \frac{d}{dx} \left(\left(\frac{d\varphi}{dx} \right)^2 \right) = \frac{d}{dx} (\tilde{A}e^{-\varphi}).$$

After integration we will obtain constant, that can be found from (3.2c)

$$\frac{1}{2} \left(\frac{d\varphi}{dx} \right)^2 = \tilde{A}e^{-\varphi} + const,$$

$$\frac{1}{2} \left(\frac{d\varphi}{dx} \right)^2 = \tilde{A}e^{-\varphi},$$

$$\frac{1}{\sqrt{2}} \frac{d\varphi}{dx} = \sqrt{\tilde{A}}e^{-\frac{\varphi}{2}},$$

$$e^{\frac{\varphi}{2}} = \sqrt{\frac{\tilde{A}}{2}}x + const,$$

Taking into account (3.2b)

$$\varphi = 2 \ln \left(\sqrt{\frac{\tilde{A}}{2}}(x+1) + 1 \right) \quad (3.3)$$

Substitution of (2.5) into the (2.4), yields

$$\tilde{A} \int_{-1}^{\infty} \frac{1}{\left(\sqrt{\frac{\tilde{A}}{2}}(x+1) + 1 \right)^2} dx = \frac{1}{\varepsilon^2},$$

$$\tilde{A} = \frac{1}{2\varepsilon^4},$$

The solution of the problem(2.2) reads:

$$\varphi = 2 \ln \left(\frac{1}{2\varepsilon^2}(x+1) + 1 \right) \quad (3.4a)$$

Except for the ε^2 scaling and its related discussion below, Eq. (2.3a) is the classical Gouy solution, [1]. As for its discussion, it follows from (2.3a) that

$$\varphi_x = \frac{2}{x + 1 + 2\varepsilon^2}. \quad (3.4b)$$

and, thus

$$\varphi_x \approx \frac{2}{x + 1}, \quad x + 1 \gg \varepsilon^2. \quad (3.5)$$

The charge density is given by expression

$$\rho = -\varepsilon^2 \varphi_{xx} = \frac{2\varepsilon^2}{(x + 1 + 2\varepsilon^2)^2} \quad (3.6a)$$

and, thus,

$$\rho = O(\varepsilon^{-2}), \quad \text{for } x + 1 = O(\varepsilon^{-2}) \quad (3.6b)$$

$$\rho \approx \frac{2\varepsilon^2}{(x + 1)^2}, \quad \text{for } x + 1 \gg \varepsilon^2. \quad (3.6c)$$

Integrating (3.6a) we may define the charge of a layer of width, $-1 < x < x_0$, adjacent to the wall, $x = -1$:

$$Q = \int_{-1}^{x_0} \frac{2\varepsilon^2 dx}{(x + 1 + 2\varepsilon^2)^2} = 1 - \frac{2\varepsilon^2}{x_0 + 1 + 2\varepsilon^2}. \quad (3.7)$$

Equation (3.7) implies that most of dissociated charge is concentrated near the charged surface, $x = -1$, in a thin layer with the thickness of the order of ε^2 . The amount of the charge distributed in the bulk ($\varepsilon^2 \ll x < \infty$) is negligible compared to this main part. However, this residual charge is sufficient to destroy the common picture of the diffusion layer split into the EDL and the electro-neutral bulk valid in the presence of and added salt with finite non-vanishing concentration in that sense that the rate of decay of ρ according to Eq. (3.6) is algebraic rather than exponential in the common EDL.

Figure 2 shows the “condensed” layer of dissociated particles near the surface. The same result can be obtained from Taylor series expansion of equation (3.6a) at $x = -1$.

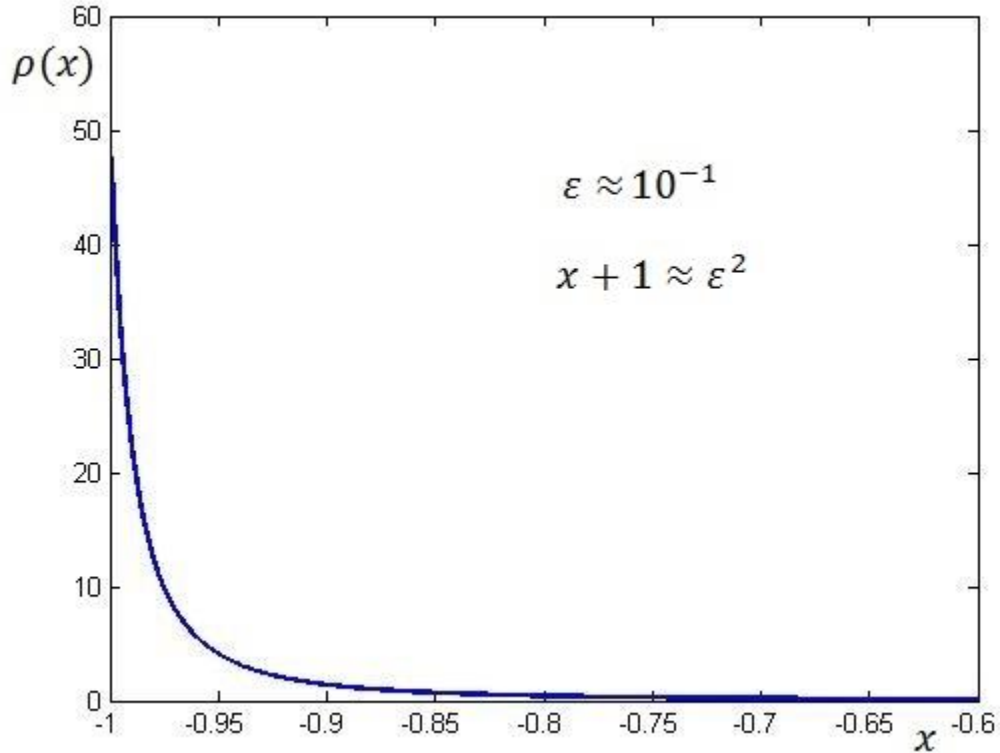


Figure 2: Density of dissociated charge near the surface.

It follows from equation (3.7) that the total charge inside the layer with the thickness of $2\epsilon^2$ ($x_0 + 1 = 2\epsilon^2$) is equal to $1/2$.

To conclude this section we reiterate, that, due to the absence of an intrinsic or macroscopic length scale for an infinite layer without an added salt at a finite concentration, ϵ in this analysis is arbitrary, and so the scaling of the interface boundary layer. In spite of this arbitrariness, this analysis is valuable because an

inner interface sublayer of width $O(\varepsilon^2)$, dominated by the dissociated charge, with a structure identical to that described above, will be recovered in Section 5, addressing a finite layer with a total amount of added ions comparable with that of ions dissociated from the wall.

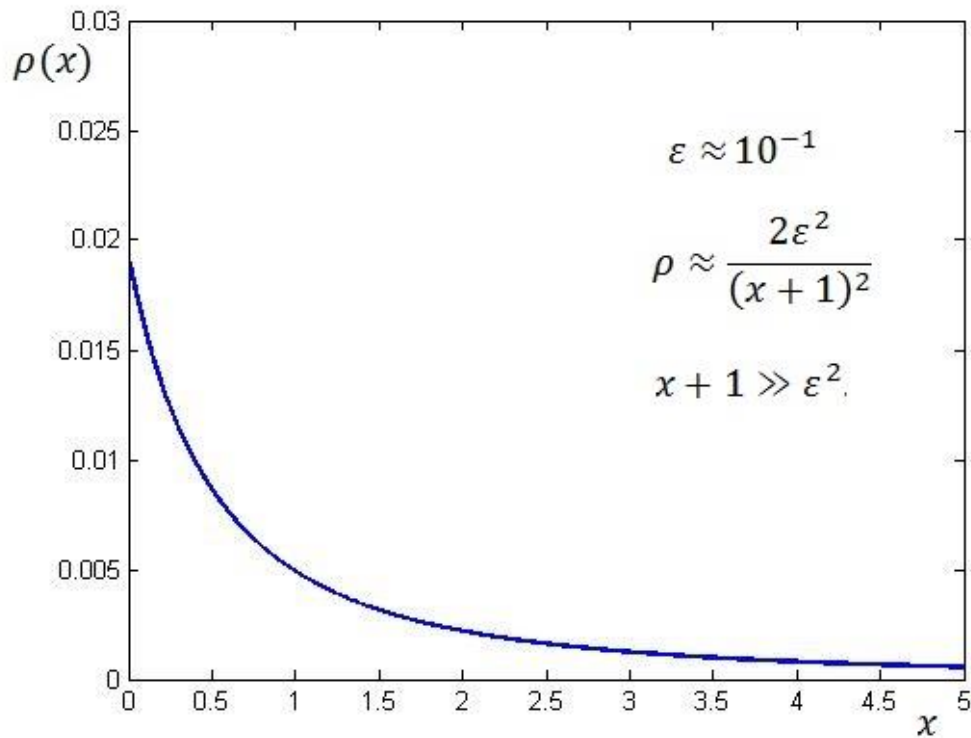


Figure 3: Density of dissociated charge far from the surface

CASE II: ADDED SALT, FINITE LAYER, $n_0 \gg 1$

In this case, $C_{\pm} \gg C'_+$, that is, therefore, the last term in equation (2.5a), which corresponds the density of particles dissociated from the surface becomes small and has to be handled asymptotically as a perturbation. For simplicity let us take the perturbation as

$$\frac{1}{n_0} = \varepsilon^2 \quad (4.1)$$

Thus, boundary value problem (2.5) can be written as

$$\tilde{\varepsilon}^2 \varphi_{xx} = \frac{1}{\int_{-1}^0 e^{\varphi} dx} e^{\varphi} - \frac{1}{\int_{-1}^0 e^{-\varphi} dx} e^{-\varphi} - \tilde{\varepsilon} \frac{1}{\int_{-1}^0 e^{-\varphi} dx} e^{-\varphi} \quad (4.2a)$$

$$\varphi_x(-1) = \frac{1}{\tilde{\varepsilon}}, \quad (4.2b)$$

$$\varphi_x(0) = 0, \quad (4.2c)$$

$$\varphi(0) = 0. \quad (4.2d)$$

Here $\tilde{\varepsilon}$ is the new dimensionless Debye length rescaled by n_0

$$\tilde{\varepsilon} = \frac{\varepsilon}{\sqrt{n_0}} \quad (4.3)$$

For aqueous electrolytes systems with $\tilde{\varepsilon}^2 \ll 1$, the electrolyte layer splits into the electro-neutral bulk, where the electric potential remains constant and EDL where the electric potential changes rapidly. In this case we may approximate the integrals in Eq. (4.2a) in the following fashion. According to (1.5d) the potential in electro-neutral bulk $\varphi_b \approx 0$. Thus each integral in (4.2a) can be expressed as a sum of the following two contributions:

$$\int_{-1}^0 e^{\varphi} dx = \int_{-1}^{-1+\tilde{\varepsilon}} e^{\varphi} dx + \int_{-1+\tilde{\varepsilon}}^0 e^{\varphi_b} dx \approx 1 + \mu_1 \tilde{\varepsilon}, \quad (4.3a)$$

$$\int_{-1}^0 e^{-\varphi} dx = \int_{-1}^{-1+\tilde{\varepsilon}} e^{-\varphi} dx + \int_{-1+\tilde{\varepsilon}}^0 e^{-\varphi_b} dx \approx 1 + \mu_2 \tilde{\varepsilon}, \quad (4.3b)$$

Here, μ_1 and μ_2 are order unity constants (evaluated in the end of this section) in the range $0 < \mu_1 < \exp(-V_0)$, $0 < \mu_2 < \exp(V_0)$. Here, V_0 is the unknown potential at the surface ($x = -1$). Substituting the results from (4.3) into (4.2) we obtain

$$\tilde{\varepsilon}^2 \varphi_{xx} = e^{\varphi} (1 - \mu_1 \tilde{\varepsilon}) - e^{-\varphi} (1 - \mu_2 \tilde{\varepsilon}) - \tilde{\varepsilon} e^{-\varphi} (1 - \mu_2 \tilde{\varepsilon}) \quad (4.4a)$$

$$\varphi_x(-1) = \frac{1}{\tilde{\varepsilon}}, \quad (4.4b)$$

$$\varphi_x(0) = 0, \quad (4.4c)$$

$$\varphi(0) = 0. \quad (4.4d)$$

Outer Problem

By applying EDL approximation we obtain for the leading order solution in outer region

$$e^{\varphi_0} - e^{-\varphi_0} = 0$$

thus

$$\varphi_0 = 0.$$

Inner Problem

In order to formulate the inner boundary value problem let us introduce the following inner variable

$$y = \frac{x+1}{\tilde{\varepsilon}} \quad (4.5)$$

Using (4.5) we approximate the solution to (4.4) by the solution to the inner equation

$$\varphi_{yy}^{in} = e^{\varphi^{in}} - e^{-\varphi^{in}} \quad (4.6a)$$

$$\varphi_y(0) = 1, \quad (4.6b)$$

$$\varphi_y \rightarrow 0, \quad y \rightarrow \infty \quad (4.6c)$$

$$\varphi \rightarrow 0 \quad (4.6d)$$

After multiplying both sides by $d\varphi/dx$ and integration we will obtain constant, that can be found from (4.4 c,d)

$$\frac{1}{2} \left(\frac{d\varphi^{in}}{dx} \right)^2 = e^{\varphi^{in}} + e^{-\varphi^{in}} - 2. \quad (4.7)$$

The inner solution reads

$$\varphi^{in} = 2 \ln \left(\frac{e^{-\frac{V_0}{2}} + 1 + \left(e^{-\frac{V_0}{2}} - 1 \right) e^{-\sqrt{2}y}}{e^{-\frac{V_0}{2}} + 1 - \left(e^{-\frac{V_0}{2}} - 1 \right) e^{-\sqrt{2}y}} \right). \quad (4.8)$$

Here V_0 is the electric potential at $y = 0$, which can be found from (4.7)
 $V_0 = \ln(2) = 0.6931$. The leading order solution itself for the problem (4.4) reads:

$$\varphi(x) = 2 \ln \left(\frac{e^{-\frac{V_0}{2}} + 1 + \left(e^{-\frac{V_0}{2}} - 1 \right) e^{-\sqrt{2}\frac{x+1}{\tilde{\epsilon}}}}{e^{-\frac{V_0}{2}} + 1 - \left(e^{-\frac{V_0}{2}} - 1 \right) e^{-\sqrt{2}\frac{x+1}{\tilde{\epsilon}}}} \right), \quad (4.9)$$

Accordingly for the charge density this solution yields

$$\begin{aligned} \rho = -\tilde{\epsilon}^2 \varphi_{xx} = & - \frac{4(e^{-V_0} - 1)e^{\sqrt{2}\frac{x+1}{\tilde{\epsilon}}}}{\left(e^{-\frac{V_0}{2}} - 1 - \left(e^{-\frac{V_0}{2}} + 1 \right) e^{\sqrt{2}\frac{x+1}{\tilde{\epsilon}}} \right)^2} \\ & - \frac{4(e^{-V_0} - 1)e^{\sqrt{2}\frac{x+1}{\tilde{\epsilon}}}}{\left(e^{-\frac{V_0}{2}} - 1 + \left(e^{-\frac{V_0}{2}} + 1 \right) e^{\sqrt{2}\frac{x+1}{\tilde{\epsilon}}} \right)^2} \end{aligned} \quad (4.10)$$

In this case, the effect of the charges dissociated from the wall upon the overall potential distribution in the solution is negligible due to the complete dominance of the “salt” ions. Electrolyte layer is divided into two parts: the electro-neutral bulk

and thin EDL. According to equation (4.3) the thickness of the EDL, that is, dimensionless Debye length, is proportional to $n_0^{-\frac{1}{2}}$ and, thus, increases with the decrease of the total amount of added ions n_0 , in precise agreement with the common picture of EDL known since the pioneering works of Gouy and Chapman [1], [2].

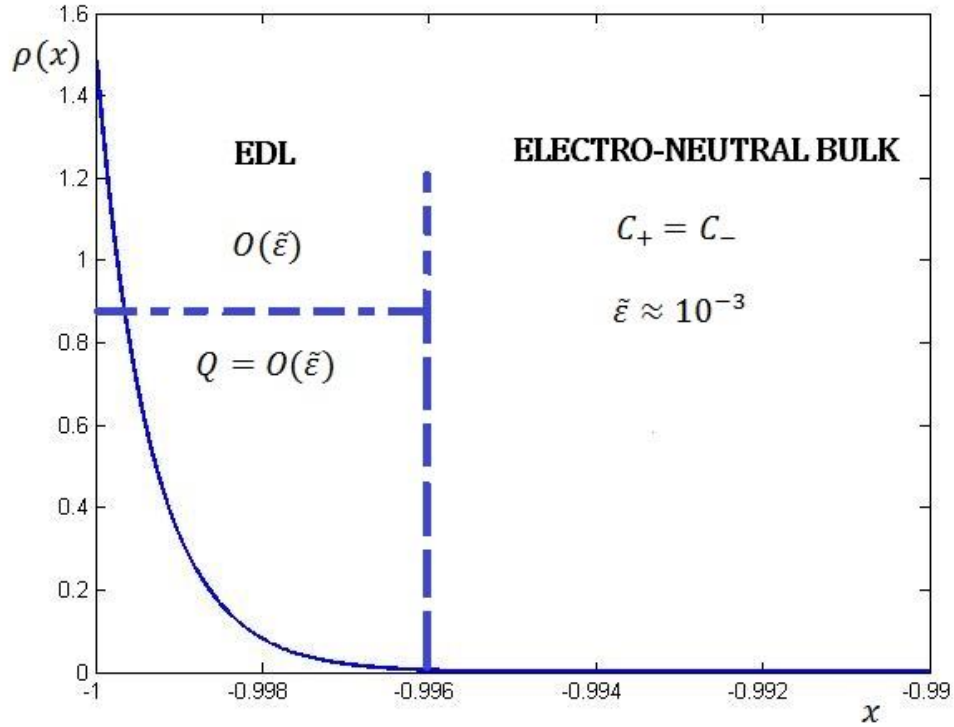


Figure 4: Density of ions.

To complete this section, we evaluate μ_1 and μ_2 . By substituting the leading order solution of (4.4) into (4.3), we obtain the equations for μ_1 and μ_2 in terms of $\tilde{\epsilon}$

$$\mu_1 = \frac{x + 1 - \frac{2\sqrt{2}\tilde{\epsilon}\left(e^{-\frac{V_0}{2}+1}\right)}{e^{-\frac{V_0}{2}+1} + \left(e^{-\frac{V_0}{2}-1}\right)e^{-\sqrt{2}\frac{x+1}{\tilde{\epsilon}}}}}{\tilde{\epsilon}} \Bigg|_{x=-1}^{x=0} - 1 \quad (4.11a)$$

$$\mu_2 = \frac{x + 1 - \frac{2\sqrt{2}\tilde{\varepsilon}(e^{-\frac{V_0}{2}} + 1)}{e^{-\frac{V_0}{2}} + 1 - \left(e^{-\frac{V_0}{2}} - 1\right)e^{-\sqrt{2}\frac{x+1}{\tilde{\varepsilon}}}}}{\tilde{\varepsilon}} \Bigg|_{x=-1}^{x=0} - 1 \quad (4.11b)$$

Taking into account (4.11) we can calculate the actual values of μ_1 and μ_2 .

$$\mu_1 \approx 0.58,$$

$$\mu_2 \approx -0.41,$$

The calculations show that the values of μ_1 and μ_2 don't depend from $\tilde{\varepsilon}$.

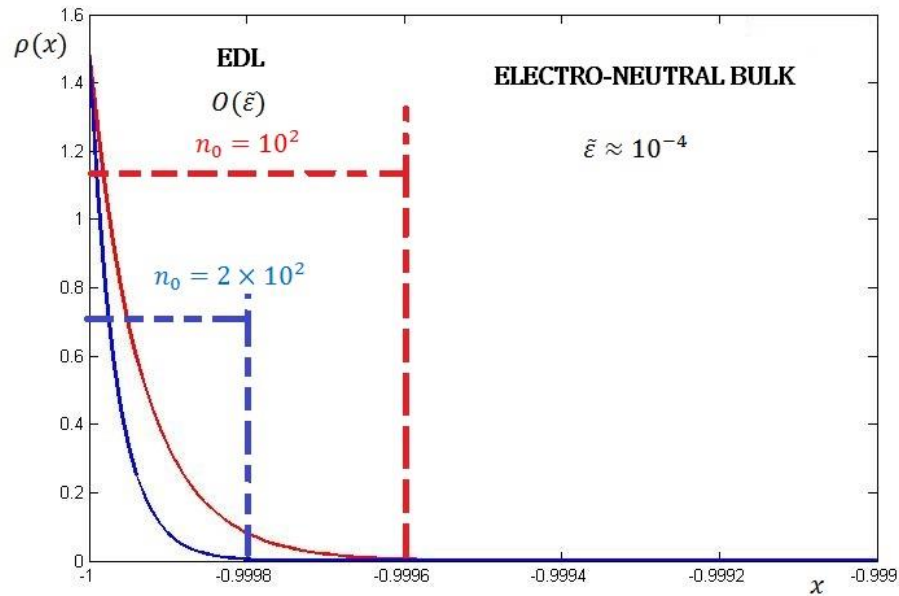


Figure 5: Charge density profiles for different salt concentrations.

**CASE III: DISSOCIATED CHARGE AND ADDED SALT BALANCE,
FINITE LAYER, $n = O(\sigma)$**

This is the most interesting case and essentially the main focus of our study. In this case the number of both types of ions, added and dissociated from the wall, is comparable and as a result the electric potential is effected by both types of charges. As we will show below, in this case, in addition to the microscopic ε -wide EDL and a macroscopic electro-neutral bulk present in accordance with the classical Gouy-Chapman picture of EDL a new very thin (ε^2 -wide) charged layer appears near the wall. Let us assume for simplicity $O(\sigma) = \sigma$. In this case, the boundary value problem (4.1) assumes the form

$$\tilde{\varepsilon}^2 \varphi_{xx} = \frac{1}{\int_{-1}^0 e^{\varphi} dx} e^{\varphi} - \frac{2}{\int_{-1}^0 e^{-\varphi} dx} e^{-\varphi}, \quad (5.1a)$$

$$\tilde{\varepsilon}^2 \varphi_x(-1) = 1, \quad (5.1b)$$

$$\varphi(-1) = 0, \quad (5.1c)$$

$$\varphi_x(0) = 0, \quad (5.1d)$$

Numerical Solution.

Numerical procedure

In this section we present the results of the numerical study of the model problem (5.1a – c). In what follows we address the case of equal mass of the dissolved and dissociated charges: $n_0 = 1$. This problem may be solved semi-analytically through solution of the equation (5.1a) in terms of elliptic Jacobi functions, with a subsequent numerical solution of the resulting system of two transcendental equations, or through a direct numerical solution by iteration scheme in which the

electric potential φ in the integrals is updated after each iteration step. We chose the latter approach. In our iterations we use the equation

$$\tilde{\varepsilon}^2 \varphi''_i = A_{i-1} e^{\varphi_i} - B_{i-1} e^{-\varphi_i}, \quad i = 1, 2..$$

Here

$$A_{i-1} = \frac{1}{\int_{-1}^0 e^{\varphi_{i-1}} dx}$$

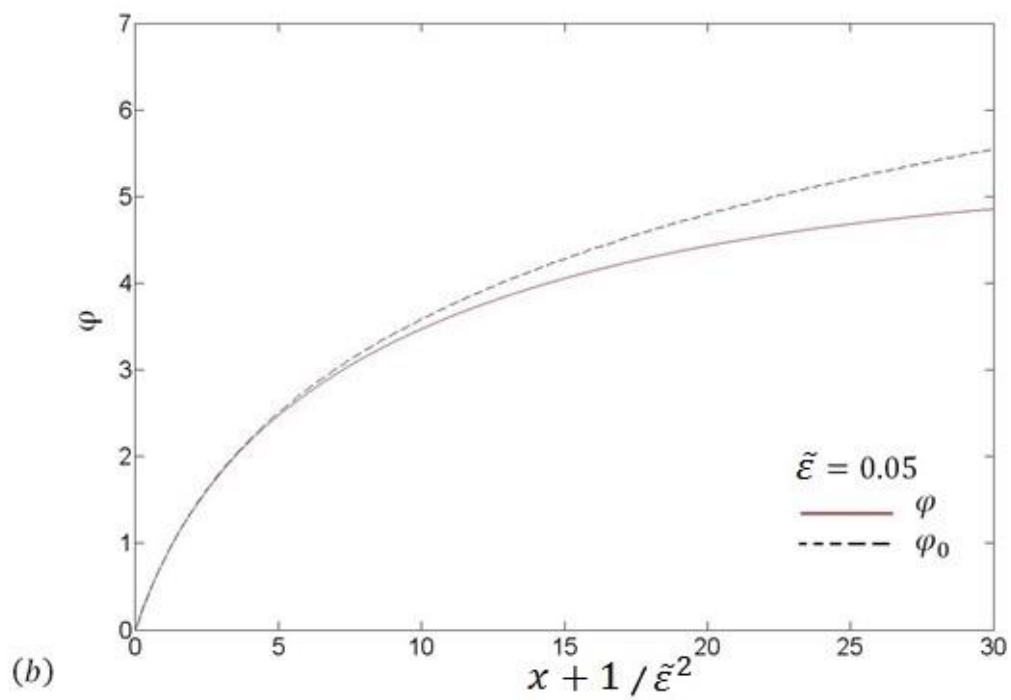
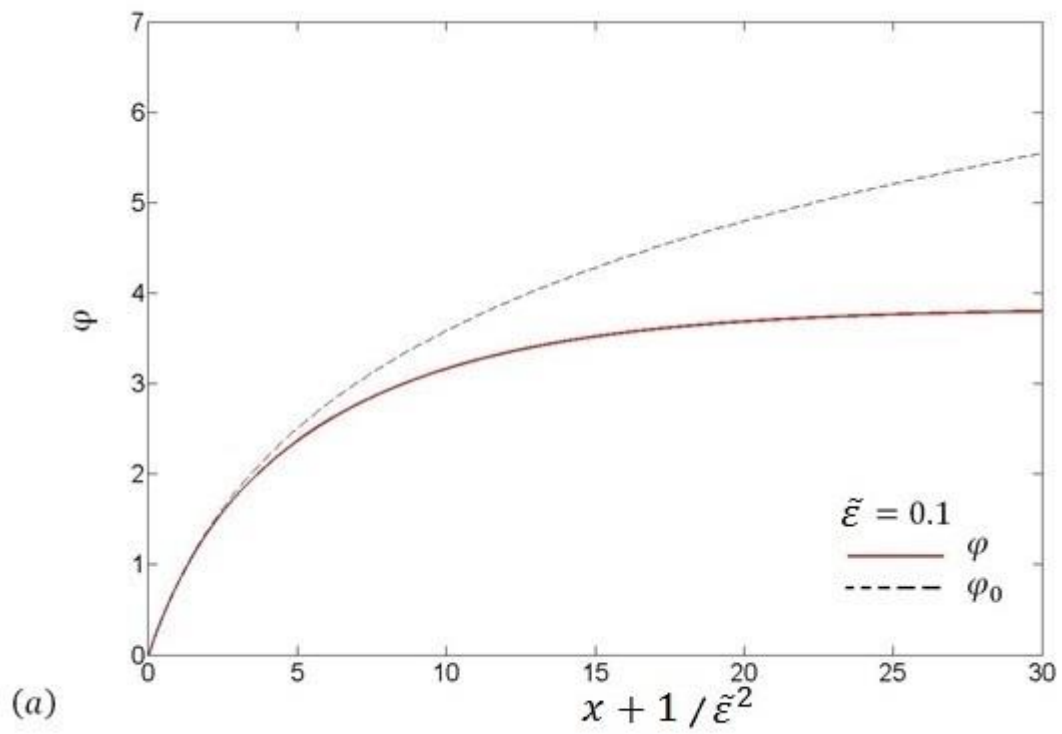
$$B_{i-1} = \frac{2}{\int_{-1}^0 e^{\varphi_{i-1}} dx}$$

For evaluation of the initial approximation for the integrals A_0 and B_0 we use the analytical solution (3.4a).

The accuracy of the proposed numerical solution is verified through convergence of A_{i-1} and B_{i-1} . Numerical solution to the problem (5.1) have been obtained for $\tilde{\varepsilon} = 0.1, 0.05, 0.02$ and $n_0 = 1$. For implementation of this iteration procedure we used MATLAB package bvp4c. The results obtained are presented below.

Results

In *Fig.6* we depict the profiles of the electric potential φ . It is observed that, in addition to the common $O(\tilde{\varepsilon})$ wide boundary layer, a novel charged sublayer appears near the surface, with the thickness of the order of $O(\tilde{\varepsilon}^2)$. This layer is dominated by the charges dissociated from the wall. The thickness of this layer relative to the thickness of the entire boundary layer increases upon the decrease of the $\tilde{\varepsilon}$ (*Fig.7*). The electric field in this layer algebraically vanishes as $x/\tilde{\varepsilon}^2 \rightarrow \infty$, similar to that of the classical Gouy solution for the no added electrolyte case in an infinite layer ([1], Case I, p.12 of this study).



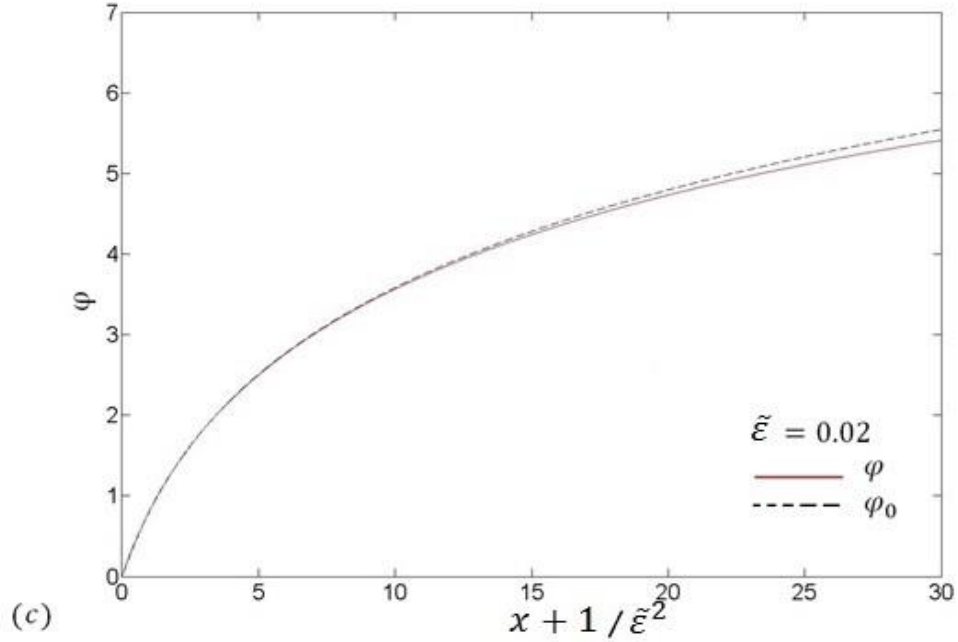


Figure 6: The profiles of the electric potential φ : for $\tilde{\varepsilon} = 0.1$ (a), $\tilde{\varepsilon} = 0.05$ (b), $\tilde{\varepsilon} = 0.02$ (c). Dashed line stands for the analytical approximation (φ_0 given by Eq 3.3). Solid line stands for numerical solution φ to the problem (5.1a – c).

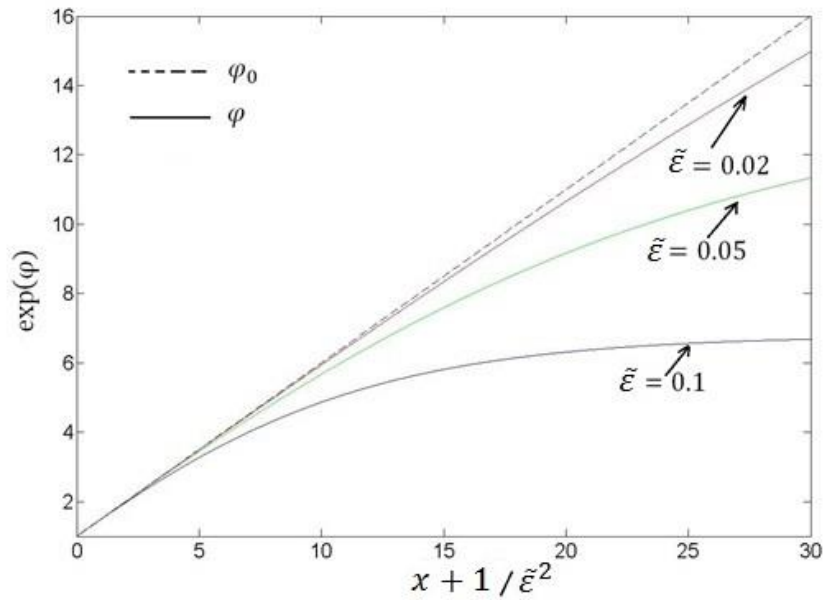
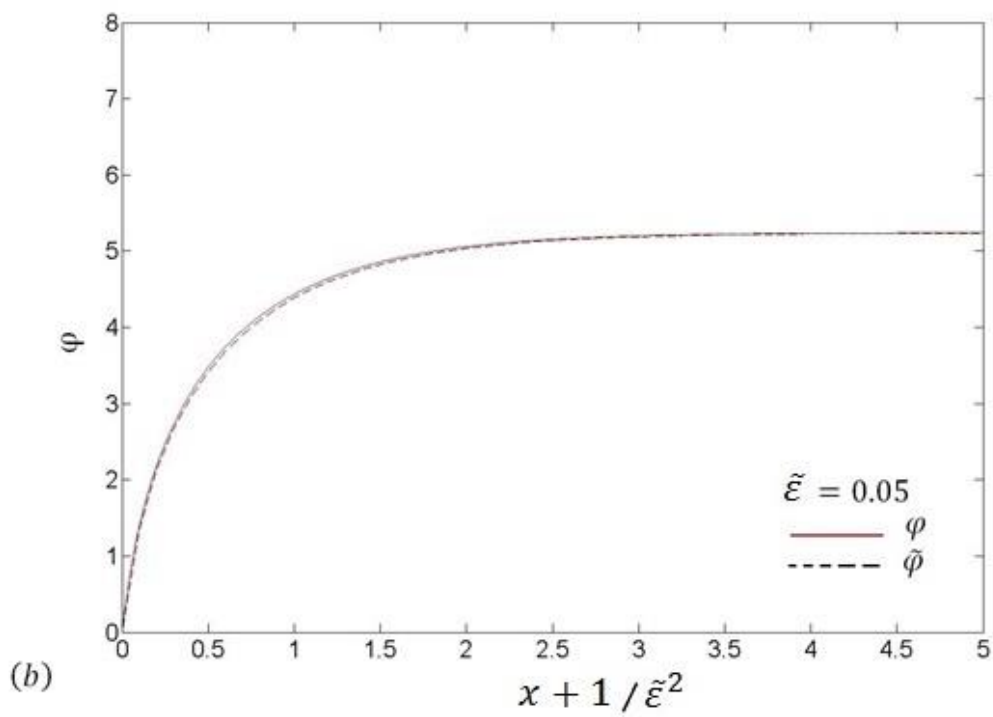
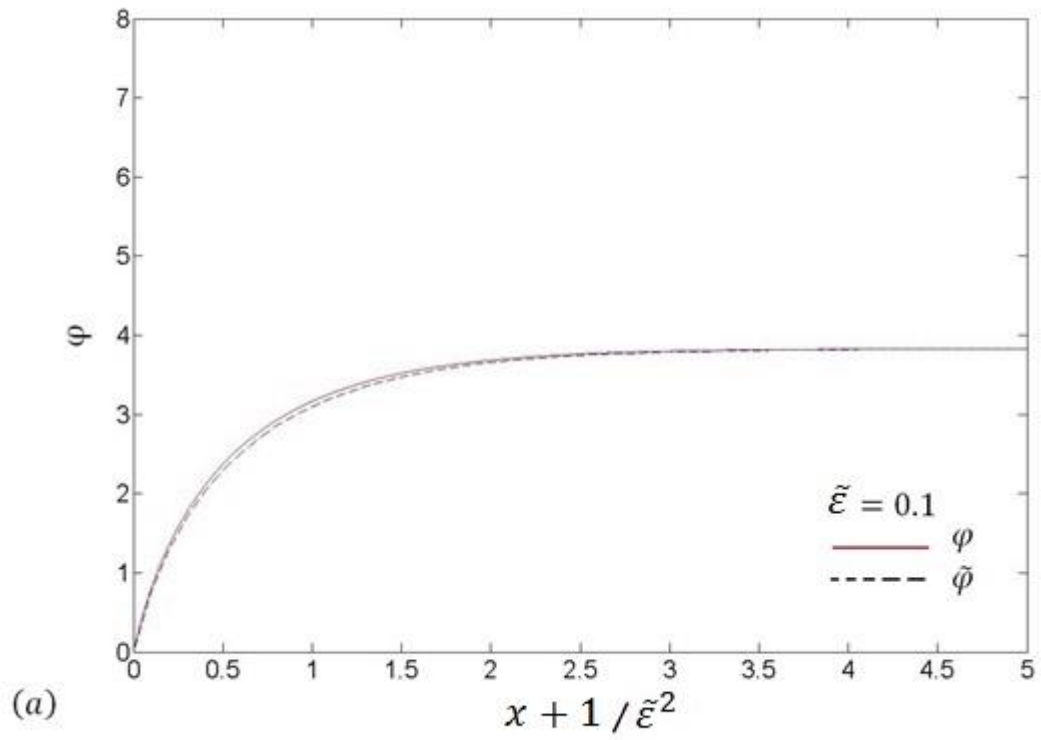


Figure 7: The profiles of the electric potential φ : for $\tilde{\varepsilon} = 0.1$, $\tilde{\varepsilon} = 0.05$, $\tilde{\varepsilon} = 0.02$. Dashed line stands for the analytical approximation (φ_0 given by Eq 3.3). Solid line stands for numerical solution φ to the problem (5.1a – c).



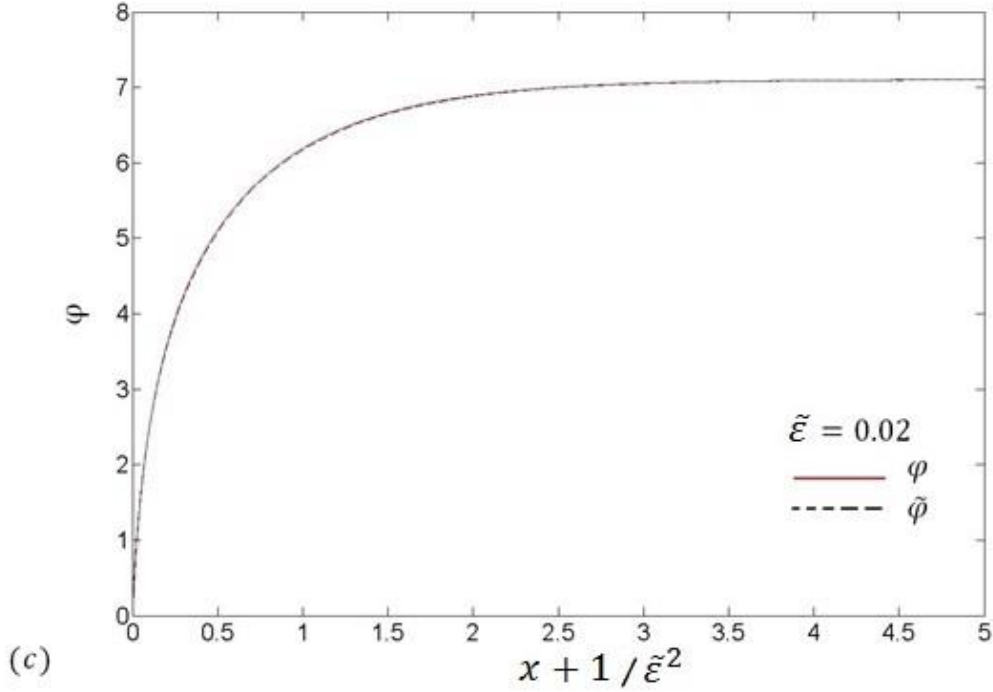


Figure8: The profiles of the electric potential φ : for $\tilde{\varepsilon} = 0.1(a)$, $\tilde{\varepsilon} = 0.05(b)$, $\tilde{\varepsilon} = 0.02(c)$. Dashed line stands for the analytical approximation ($\tilde{\varphi}$ given by Eq 2.9). Solid line stands for numerical solution φ to the problem (5.1a – c).

Next we address the asymptotic behavior of the solution to the problem (5.1 a – c) in the layer $y = O(\tilde{\varepsilon})$. In *Figs.8* we present the plots of numerically computed potential φ and its analytical approximation $\tilde{\varphi}$.

This portion of the boundary layer corresponds to the classical order $O(\tilde{\varepsilon})$ thick Gouy-Chapman EDL, discussed in CASE II (*Figs 8(a, b, c)*). This layer is dominated by the ions of the added salt. According to Eq. (5.1 b), the absolute thickness of this sublayer increases upon the decrease of the added salt concentration.

To summarize, if the dissolved wall charge is comparable with the total mass of added salt ions, the structure of the electrolyte layer changes dramatically: near the wall there appears a new $O(\tilde{\varepsilon}^2)$ thick sublayer which is dominated by the wall

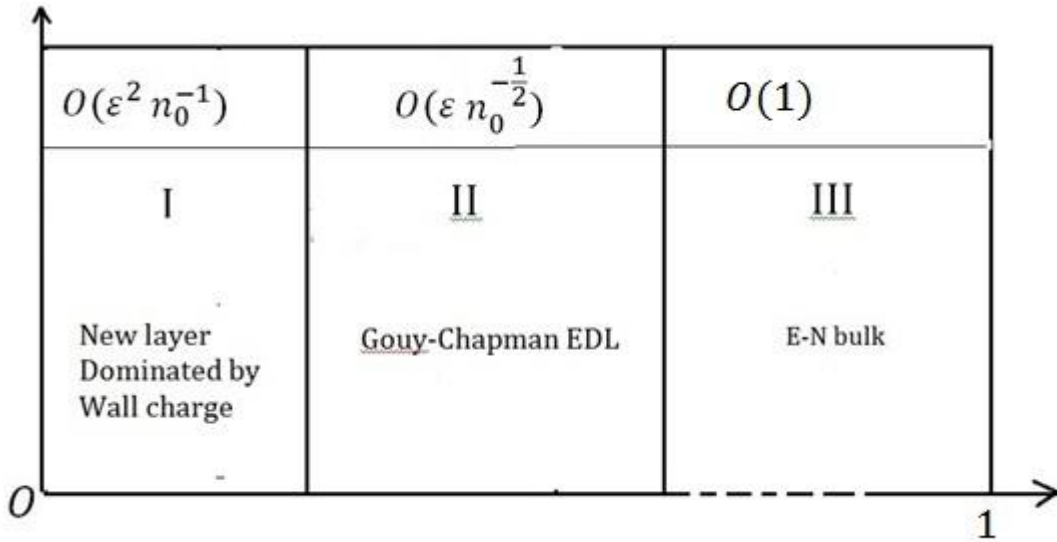


Figure 9: Structure of the electrolyte layer. I - fixed width layer dominated by wall charge; II - $O(\varepsilon)$ Gouy-Chapman layer ; III - wide E-N bulk.

charge only. The electric field decreases and vanishes algebraically towards the outer edge of this layer as it does in the classical Gouy solution of Section 3. In our analysis in this section, this sublayer is not masked by the excess salt ions, as it is in the asymptotic treatment of Section 5. This layer is followed (*Fig. 9*) by a much wider, $O(\varepsilon)$ thick, classical Gouy-Chapman layer in which the electric field decreases exponentially. This layer is followed by $O(1)$ - thick electro-neutral bulk with zero electric field. To the best of our knowledge, this fine structure emerging when the dissolved wall charge is comparable with the total mass of added salt ions has not been observed in the previous EDL studies and constitutes a novel information worthy of publication.

CONCLUSION

We formulated a mean field model for the equilibrium distribution of the ionic concentrations and electric potential in a closed ionic system consisting of two charged metal walls flanking a univalent electrolyte solution layer of finite width. The model is formulated in terms of Poisson Boltzmann (PB) equation with integral terms in it accounting for the closeness of the system and specifying the total amount of ions in it. We discussed in detail the solution of PB equation in three regimes: in the absence of an added salt, in the case where the amount of ions dissociated from wall, σ , is negligible compared to the amount of the ions of the added salt, nL , and in the case where σ and nL are of the same orders of magnitude. The solution for the first regime, by and large recovering the classical solution of Gouy in terms of the total mass of dissociated particles in per unit area, σ , sets the ground for interpretation of the numerical results for the main topic of our study: analysis of the intermediate regime when σ and nL are comparable.

The explicit solution of the PB equation obtained for this first regime allowed us to identify of the ultrathin sublayer of “condensed” charge near the interface appearing in the intermediate regime (CASE III). In this regime, the classical picture of the solution split into the $O(\tilde{\varepsilon})$ wide electric double layer and the electroneutral bulk breaks down, with the main part of dissociated particles concentrated in a $O(\tilde{\varepsilon}^2)$ compact sub layer, density of residual charge decays algebraically towards the adjacent $O(\tilde{\varepsilon})$ wide classical EDL recovered by the analysis of the CASE II. For this case, addressing the situation when the total amount of the ions of the added salt is high compared to that of ions dissociated from the wall, the smallness of the relevant control parameter $\tilde{\varepsilon}$ allowed us to efficiently approximate the values of the

phase integrals in the modified PB equation. This result reveals the relation of the results for the modified PB equation to those in the classical Gouy-Chapman theory through renormalization of the classical dimensionless Debye length into the one scaled by the mass of the added salt. The relative measure of the latter versus the mass of ions dissociated from the wall is provided by the parameter m_0 . To summarize, our numerical solution for the intermediate regime in CASE III discloses the existence near the interface of a novel ultrathin charged sublayer unobserved in previous studies of EDL. The typical width of this sublayer, largely dominated by the counterions dissociated from the interface is $O(\tilde{\varepsilon}^2)$, where

$$\tilde{\varepsilon}^2 = \frac{\varepsilon_r \varepsilon_0 RT}{F^2 L \sigma}.$$

is the squared dimensionless Debye length based on the dissociated ions.

The relative thickness of this sublayer versus the entire EDL increases upon the decrease of the surface charge σ .

It appears natural to ask the question whether this ultrathin sublayer is universally present at charged surface and is only obscured by the approximations of the straightforward asymptotic boundary layer analysis of the type presented in Section 4 of this study; or, alternatively, this layer is nothing more than a mathematical artifact of a detailed ionic mass balance in a closed system? Answer to this question could be provided by a detailed numerical investigation which could be a subject of our future study.

APPENDIX

```
clear;
A=1;B=1;n=1;sigma=1;

    epsilon=0.1;

    xm=linspace(0,1,1000);
    options = bvpset('Reltol',10^(-2));
    solinit=bvpinit(xm,[0 0]);
    sol=bvp4c(@test,@testbc,solinit,options,A,B,epsilon);
error=1;
it=1;
while error>0.001
    x=sol.x;
    fA=exp(sol.y(1,:));
    fB=exp(-sol.y(1,:));
    A=n/IntSimp2(x,fA);
    B=(n+sigma)/IntSimp2(x,fB);
    Bstore(:,it)=B;
    Astore(:,it)=A;
    if it>1
        error1=abs(Bstore(it)-Bstore(it-1));
        error2=abs(Astore(it)-Astore(it-1));
        error=max(error1,error2);
    end
    sol=bvp4c(@test,@testbc,sol,options,A,B,epsilon);

    it=it+1;
end
sol1=sol;
A1=A;
B1=B;
xo=linspace(0,1,100000);
sxint1=deval(sol1,xo,1);
    epsilon=0.01;

error=1;
it=1;
while error>0.001
    x=sol.x;
    fA=exp(sol.y(1,:));
    fB=exp(-sol.y(1,:));
    A=n/IntSimp2(x,fA);
    B=(n+sigma)/IntSimp2(x,fB);
    Bstore(:,it)=B;
    Astore(:,it)=A;
    if it>1
        error1=abs(Bstore(it)-Bstore(it-1));
        error2=abs(Astore(it)-Astore(it-1));
        error=max(error1,error2);
    end
    sol=bvp4c(@test,@testbc,sol,options,A,B,epsilon);

    it=it+1;
end
sol2=sol;
A2=A;
B2=B;
xo=linspace(0,1,100000);

sxint2=deval(sol2,xo,1);
epsilon=0.001;
```

```

error=1;
it=1;
while error>0.001
    x=sol.x;
    fA=exp(sol.y(1,:));
    fB=exp(-sol.y(1,:));
    A=n/IntSimp2(x,fA);
    B=(n+sigma)/IntSimp2(x,fB);
    Bstore(:,it)=B;
    Astore(:,it)=A;
    if it>1
        error1=abs(Bstore(it)-Bstore(it-1));
        error2=abs(Astore(it)-Astore(it-1));
        error=max(error1,error2);
    end
    sol=bvp4c(@test,@testbc,sol,options,A,B,epsilon);

    it=it+1;
end
xo=linspace(0,1,100000);
sol3=sol;
sxint3=deval(sol3,xo,1);

```

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