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STEADY STATE AND PSEUDO-TRANSIENT ELECTRIC POTENTIAL USING THE POISSON-BOLTZMANN EQUATION

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Abstract - A method for analysis of the electric potential profile in saline solutions was developed for systems with one or two infinite flat plates. A modified Poisson-Boltzmann equation, taking into account non-electrostatic interactions between ions and surfaces, was used. To solve the stated problem in the steady-state approach the finite-difference method was used. For the formulated pseudo-transient problem, we solved the set of ordinary differential equations generated from the algebraic equations of the stationary case. A case study was also carried out in relation to temperature, solution concentration, surface charge and salt-type. The results were validated by the stationary problem solution, which had also been used to verify the ionic specificity for different salts. The pseudo-transient approach allowed a better understanding of the dynamic behavior of the ion-concentration profile and other properties due to the surface charge variation.

Keywords: Electric Potential; Poisson-Boltzmann; Finite Difference.

INTRODUCTION

At the interface of the disperse and the dispersant phases of a colloidal system there are characteristic surface phenomena, like adsorption effects and an electric double layer that are very important to determine the physicochemical properties of the whole system (Lima *et al.*, 2008). In the classical approach, the Poisson-Boltzmann (PB) equation does not take into account the non-electrostatic interactions present between ions and surfaces. However, the modified PB equation used in this study enables the ionic specificity to be described, as verified in several colloidal systems.

Even though the classical form of the Poisson-Boltzmann equation presents limitations, an innumerable number of application are found in the literature. A good introduction and derivation can be found in Israelachvili (1995). Concerning application of the PB equation, excellent reviews are reported by Davis and McCammon (1990) and by Honig and Nicholls (1995). In particular, Shestakov *et al.* (2002) solved the nonlinear Poisson-Boltzmann equation using pseudo-transient continuation and the finite element

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*To whom correspondence should be addressed method to show the behavior of ions close to electrodes with changinged potential. Although a very good numerical technique was used, Shestakov *et al.* (2002) reported results that are limited for general electrolytes. The authors did not include ionic specificity (Hofmeister effect). Here, we include the dispersion interaction between each ion and the electrode wall (from Lifshitz theory as described in Ninham and Yaminsky, 1997) to take into account the difference between salt types. The Hamaker potentials are obtained elsewhere (Tavares *et al.*, 2004, Livia *et al.*, 2007).

The PB equation in 1-D form is a second order non-linear ordinary differential equation with Dirichlet and/or Neumann boundaries conditions. An analytical solution for this equation is only available for particular cases like when the system is composed of a single plate and the classical PB approach for symmetrical electrolyte solution is used (Lima *et al.*, 2007). In this study, the PB equation was solved for the classic and modified forms, for one or two flat plate systems, using the finite-difference method and a numeric approach, which is detailed in the second and third section of this paper. A pseudo-transient form of this equation is described in the fourth section. Finally, results and conclusions are presented in the last sections.

POISSON-BOLTZMANN EQUATION

In a liquid medium with electric charges, the basic form of the Laplace equation gives place to the Poisson equation, shown in Equation (1), which relates the vector field divergence to the charge density, ρ (Equation (2)).

$$-\varepsilon_0 \nabla \cdot \left(\varepsilon_w \nabla \phi(x) \right) = \rho(x) \tag{1}$$

$$\rho(x) = e \sum_i z_i \, c_i(x) \tag{2}$$

in which c_i is the concentration of ion *i*, e is the elementary charge, z_i is the valence of ion *i*, ε_0 the vacuum permittivity, and ε_w the water dielectric constant (Lima *et al.*, 2007).

From the chemical potential of each ion in solution, the Boltzmann distribution (Equation (3)) of the ions can be obtained.

$$c_i(x) = c_{i0} \exp\left[-\frac{E_i(x) - E_{io}}{k_B T} \right] \tag{3}$$

where c_{i0} is the concentration of ion *i* in the bulk solution, E_{i0} is the reference state potential energy for ion *i*, and E_i is the potential energy of ion *i* defined as the sum of the electrostatic potentials plus the dispersion interactions (U_i) between the ion i and the surface (non-electrostatic potentials). Considering that all potentials between ions and macro particles in an aqueous solution go asymptotically to zero in the bulk phase ($x \to \infty \Rightarrow E_{i0} = 0, \forall i$), Equation (3) becomes:

$$c_i(x) = c_{io} \exp\left[-\frac{z_i e \phi(x) + U_i(x)}{k_B T} \right] \tag{4}$$

Substituting Equation (4) in (2), gives (Equation (5)):

$$\rho(x) = e \sum z_i c_{io} \exp\left[-\frac{z_i e \phi(x) + U_i(x)}{k_B T} \right] \tag{5}$$

Substituting Equation (5) into Equation (1), gives the second-order non-linear modified PB equation:

$$\varepsilon_0 \nabla \cdot \left(\varepsilon_w \nabla \phi(x) \right) + e \sum z_i c_{io} \exp\left[-\frac{z_i e \phi(x) + U_i(x)}{k_B T} \right] = 0 \tag{6}$$

NUMERICAL SOLUTION OF THE POISSON-BOLTZMANN EQUATION

This section presents a pseudo-transient approach to calculate the electrical potential profile using a modified Poisson-Boltzmann equation in different conditions. The profile trends presented in the Results section, based on the data calculated from this approach, in some cases are all well known; however, these trends are confirmed and presented in a different way using 3D figures.

Two kinds of geometry have been studied. The problem domains for each case are:

$r_{ion} < x < \infty$ for one flat plate

$r_{ion} < x < L - r_{ion}$ for two parallel plates

in which r_{ion} is the ionic radius (here all ions have the same size), x is the independent variable and L is the distance between the two flat plates.

The Boundary Conditions

The 1-D form of the non-linear PB equation requires two boundary conditions. In this study two kinds of system are discussed: i) Systems with a charged surface, such as proteins not at their isoelectric point and, ii) Systems with a non-charged surface, such as the air/water interface. For an infinite flat plate, the first boundary condition (BC), valid for both systems (Equation (7)), admits that the electric field goes asymptotically to zero in the bulk phase ($x \rightarrow \infty$). Applying Gauss' law for charged surfaces, the second BC (Equation (8)) comes from the electric field generated by the surface charge density, σ (Moreira *et al.*, 2007):

$$\lim_{x \to \infty} \phi(x) = 0 \tag{7}$$

$$\left. \frac{d\phi(x)}{dx} \right|_{x=r_{ion}} = -\frac{\sigma}{\varepsilon_0 \varepsilon_w} \tag{8}$$

Equation (8) is also used for non-charged surfaces, at which $\sigma = 0$.

In the case of two parallel infinite flat plates, the first BC (Equation (9)) for both systems admits that the electric field profile has a symmetry condition in the mid-point of the domain ($x = L/2$).

$$\left. \frac{d\phi(x)}{dx} \right|_{x=L/2} = 0 \tag{9}$$

The second BC is also represented by Equation (8).

One Infinite Flat Plate – Dimensionless Form

For both geometries studied, the corresponding model equations were rewritten in dimensionless form in order to avoid scaling problems during the numerical resolution.

Defining the new independent variable y:

$$y = \exp(-kx) \;\; \forall \;\; 0 < y < \exp(-kr_{ion}) \tag{10}$$

The Debye-Length (k^{-1}) is defined by:

$$k^2 = \frac{e^2 \sum_i z_i^2 c_{i0}}{\varepsilon_o \varepsilon_w k_B T} \tag{11}$$

In which k_B is the Boltzmann constant and T is the temperature.

The new dependent variable (dimensionless electric potential) is defined as:

$$\varphi(y) = \frac{e\phi(y)}{k_B T} \tag{12}$$

and the ionic strength of the solution, is given by:

$$I = \frac{1}{2} \sum_i z_i^2 c_{io} \tag{13}$$

The dispersion interaction between each ion and the flat surface, in the Hamaker approach, is given by (Israellachvili, 1995):

$$\frac{U_i(x)}{k_B T} = -\frac{1}{k_B T} \frac{H_i}{x^3} = \frac{H_i k^3 / k_B T}{\ln(y)^3} \tag{14}$$

in which H_i is the dispersion coefficient, estimated here by the Lifshitz theory (for van der Waals interactions) (Israellachvili, 1995). Its dimensionless form, H_i^* is defined by:

$$H_i^* = \frac{H_i k^3}{k_B T} \tag{15}$$

For this geometry, the modified dimensionless form of the PB equation is given by:

$$y \frac{d\varphi(y)}{dy} + y^2 \frac{d^2\varphi(y)}{dy^2} + \frac{1}{2I} \sum_i z_i c_{i0} \exp\left[-z_i \varphi(y) - \frac{H_i^*}{\ln(y)^3} \right] = 0 \tag{16}$$

And the two dimensionless BC are represented by Equations (17) and (18):

$$\left. \varphi(y) \right|_{y=0} = 0 \tag{17}$$

$$\left. y \frac{d\varphi(y)}{dy} \right|_{y=\exp(-k\, r_{ion})} = \frac{\sigma k}{2eI} \tag{18}$$

Two Parallel Flat Plates – Dimensionless Form

In the case of two parallel flat plates, a similar procedure was performed; however, the independent variable was defined as:

$$y = kx \;\; \forall \;\; kr_{ion} < y < k\left(L - r_{ion}\right) \tag{19}$$

For this geometry, the modified dimensionless form of the PB equation is given by:

$$\frac{d^2\varphi(y)}{dy^2}+\frac{1}{2I}\sum_i z_i c_{i0}\exp\left[-z_i\varphi(y)+\frac{H_i^*}{y^3}\right]=0 \quad (20)$$

And the two dimensionless BC are represented by Equations (21) and (22):

$$\left.\frac{d\varphi(y)}{dy}\right|_{y=k\frac{L}{2}}=0 \quad (21)$$

$$\left.\frac{d\varphi(y)}{dy}\right|_{y=k\,r_{ion}}=-\frac{\sigma k}{2eI} \quad (22)$$

The Finite-Difference Method

As already mentioned, for the examples studied here, there are no analytical solutions. Therefore, the finite-difference method with second-order approximations and n equally-spaced discretization intervals was used to solve the problem. The equations used to calculate the derivative at the domain endpoints were generated from linear interpolation in $y_0 < y < y_1$ and $y_{n-1} < y < y_n$, respectively.

a) One Infinite Flat Plate – Steady State Condition

Applying the finite-difference method in Equations (16)-(18) ($j = 1,2,...,n-1$) gives:

$$\varphi_0 = 0 \quad (23)$$

$$\begin{aligned}0=&\frac{j}{2}\left(\varphi_{j+1}-\varphi_{j-1}\right)+j^2\left(\varphi_{j+1}-2\varphi_j+\varphi_{j-1}\right)\\&+\left(z_+c_{+0}\exp\left[-z_+\varphi_j-\frac{H_+{}^*}{\ln\left(y_j\right)^3}\right]\right.\\&\left.+z\_c_{-0}\exp\left[-z\_\varphi_j-\frac{H_-{}^*}{\ln\left(y_j\right)^3}\right]\right)\frac{1}{2I}\end{aligned} \quad (24)$$

$$\frac{\sigma k}{2Ine}=\left(\frac{1}{2}\varphi_{n-2}-2\varphi_{n-1}+\frac{3}{2}\varphi_n\right) \quad (25)$$

b) One Infinite Flat Plate – Pseudo-Transient Condition

To verify the effects on the electric potential profiles, caused by changes in surface charge, a pseudo-transient model of the modified PB was proposed. The pseudo-transient form of the modified PB equation is an extension form of Shestakov *et al.* (2002). Furthermore, verifying these changes, it was possible to corroborate the results found with the steady-state problem solution. The pseudo-transient problem was formulated by defining a dimensionless potential variation with respect to a dimensionless time, t (Shestakov *et al.*, 2002). The system of *n+1* algebraic equations, generated in the previous item, is turned into a system with two algebraic equations defined by the boundary conditions (Equations (23) and (25)), and *n-1* differential Equations (24) for the internal points ($j = 1,2,...,n-1$).

$$\begin{aligned}\frac{d\varphi_j}{dt}=&\frac{j}{2}\left(\varphi_{j+1}-\varphi_{j-1}\right)+j^2\left(\varphi_{j+1}-2\varphi_j+\varphi_{j-1}\right)\\&+\left(z_+c_{+0}\exp\left[-z_+\varphi_j-\frac{H_+{}^*}{\ln\left(y_j\right)^3}\right]\right.\\&\left.+z\_c_{-0}\exp\left[-z\_\varphi_j-\frac{H_-{}^*}{\ln\left(y_j\right)^3}\right]\right)\frac{1}{2I}\end{aligned} \quad (26)$$

c) Two Parallel Plates – Steady-State Condition

Applying the finite-difference method in Equations (20)-(22) ($j = 1,2,...,n-1$) gives:

$$\varphi_0=\frac{\sigma k\Delta y}{3eI}+\frac{4}{3}\varphi_1-\frac{1}{3}\varphi_2 \quad (27)$$

$$\begin{aligned}0=&\frac{\varphi_{j+1}-2\varphi_j+\varphi_{j-1}}{\Delta y^2}\\&+\left(z_+c_{+0}\exp\left[-z_+\varphi_j+\frac{H_+{}^*}{y_j{}^3}\right]\right.\\&\left.+z\_c_{-0}\exp\left[-z_j\varphi_j+\frac{H\_{}^*}{y_j{}^3}\right]\right)\end{aligned} \quad (28)$$

$$\varphi_n=-\frac{1}{3}\varphi_{n-2}+\frac{4}{3}\varphi_{n-1} \quad (29)$$

d) Two Parallel Plates – Pseudo-Transient Condition

In a similar way, using $\varphi = \varphi(t)$, the steady-state system of *n+1* algebraic equations is redefined by Equations (27) and (29), and *n-1* differential Equations (30) for the internal points ($j = 1,2,...,n-1$).

$$\frac{d\varphi_j}{dt}=\frac{\varphi_{j+1}-2\varphi_j+\varphi_{j-1}}{\Delta y^2}+\left(z_+c_{+0}\exp\left[-z_+\varphi_j+\frac{H_+^{\ *}}{y_j^{\ 3}}\right]+z_-c_{-0}\exp\left[-z_j\varphi_j+\frac{H_-^{\ *}}{y_j^{\ 3}}\right]\right)\frac{1}{2I} \tag{30}$$

To solve item (b) and item (d), the initial conditions ($\varphi_j(0)$) are obtained from the solution of the stationary problem for discharged surfaces.

To solve the proposed problem, a computational code was written in MATLAB, using internal *solvers* like *fsolve* and *ode45*.

RESULTS AND DISCUSSION

To establish the mesh size, an analysis of the convergence of the electric potential on the surface as a function of *n* was performed. It was verified that, for above 100 intervals, the difference between the surface electric potentials was less than 10^{-4} and the electric potential value in the limit of $x \to \infty$ converged asymptotically to zero. To validate the implemented algorithm, we compared our results with those presented in the recent literature for NaCl, considering the dispersion interaction (Moreira *et al.*, 2007). The base case was generated for NaCl solutions (1 M at 298.15K).

One Infinite Flat Plate – Steady State Condition

These results were generated for NaCl solutions (1 molar at 298.15 K). Figure 1 shows the electric potential profile generated by a discharged surface, Figure 2 (a) and (b) shows the electric potential profiles for surfaces with positive and negative charges, respectively. From these results, it is possible to say that the modified PB equation accounts for the influence of the non-electrostatic potential of each ion, that is, the ionic specificity given by the dynamic reorientation of the electronic cloud due to a nearby surface. This becomes evident in the electric potential value observed on the surface, which is not zero even when the surface is not charged. The latter result would not be obtained from the solution of the classical PB equation.

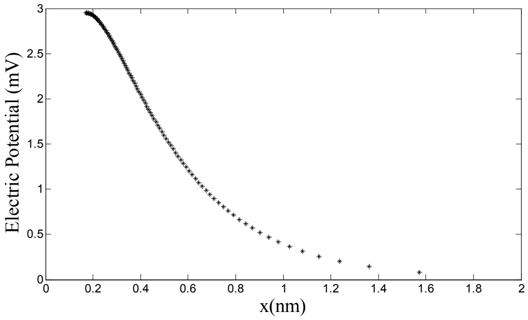
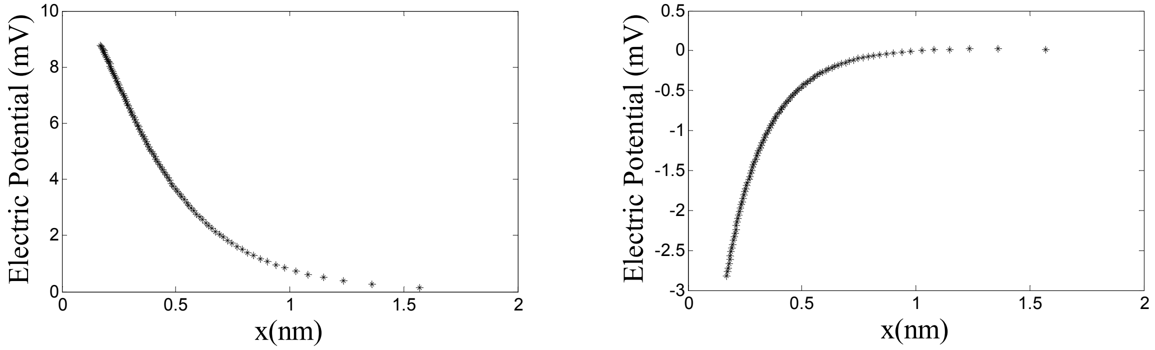


Figure 1: Electric potential profile for a discharged surface (Surface Charge Density =0 C/m^2).



(a) (b)

Figure 2: (a) Electric potential profile for a positively charged surface (Surface Charge Density =0.012 C/m^2). (b) Electric potential profile for a negatively charged surface (Surface Charge Density =- 0.012 C/m^2).

One Infinite Flat Plate – Pseudo-Transient Condition

Results obtained from the dimensionless pseudo-transient model for one infinite flat plate are shown in Figures 3 and 4 (1 molar NaCl solutions at 298.15 K). Based on these results it is possible to verify changes in the electric potential profile caused by changes in the surface charge.

It is important to emphasize that the electric potential on the surface is not zero, even when the surface has no charge (see Figure 1). This is not true when using the classical PB equation, as can be seen in Figure 5.

One Infinite Flat Plate – Case Study

Figures 6-10 show the electric potential profiles obtained by perturbations in the model parameters: solution temperature, solution concentration, surface charge and the salt type. These results were obtained by evaluating the steady-state model for different parameter values. Regarding the solution temperature, two opposite effects can be observed, a negative correlation (the potential decreases as the temperature increases) when there is charge on the surface (Figure 6), and a positive one (Figure 7) when the surface is discharged. We show calculations for a very large range of temperature (from 200 to 600 K). At very high pressure (i.e., 10^9 Pa), water is an incompressible liquid in this temperature range. Because the calculations are carried out in the McMillan-Mayer framework, results are independent of pressure. Other important point is about the dielectric constant. The dielectric constant decreases when temperature increases. However, we assume that the product $\varepsilon_o \varepsilon_w k_B T$ is independent of temperature.

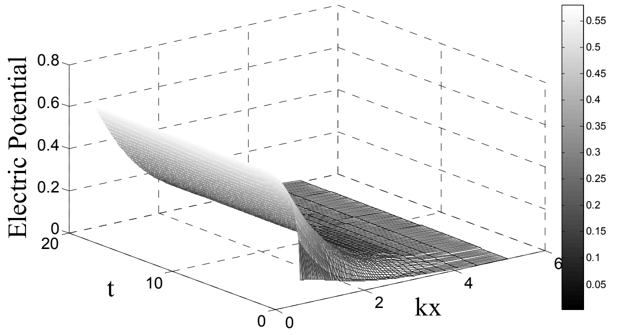


Figure 3: Dimensionless electric potential profile for increasing surface charge (σ_{initial}=0 C/m^2 and σ_{final}=0.012 C/m^2).

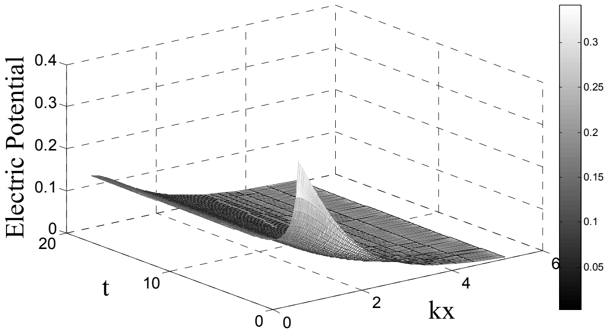


Figure 4: Dimensionless electric potential profile for decreasing surface charge (σ_{initial}=0.012 C/m^2 and σ_{final}=0 C/m^2).

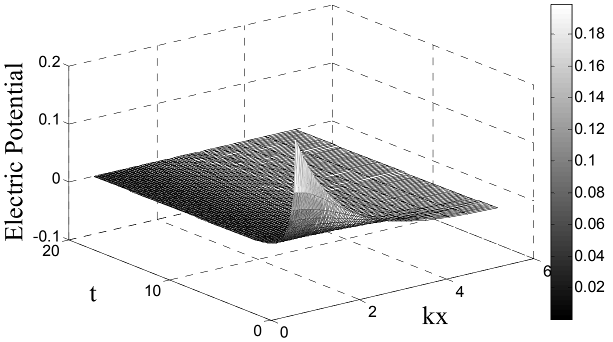


Figure 5: Dimensionless electric potential profile for decreasing surface charge (σ_{initial}=0.012 C/m^2 and σ_{final}= 0 C/m^2), considering only the electrostatic potential (classical PB equation).

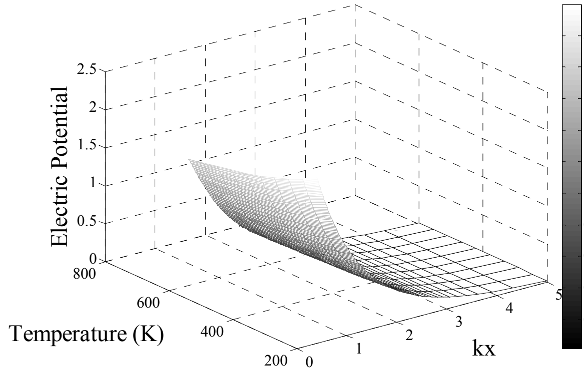


Figure 6: Dimensionless electric potential profile for temperatures between 200 and 600 K with charged surface (Surface Charge Density =0.06 C/m^2)

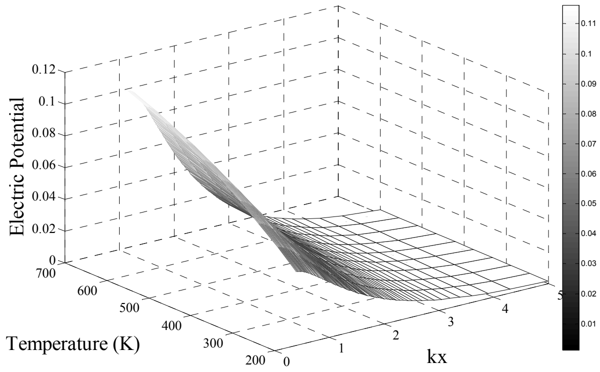


Figure 7: Dimensionless electric potential profile for temperatures between 200 and 600 K for a discharged surface (Surface Charge Density =0 C/m^2).

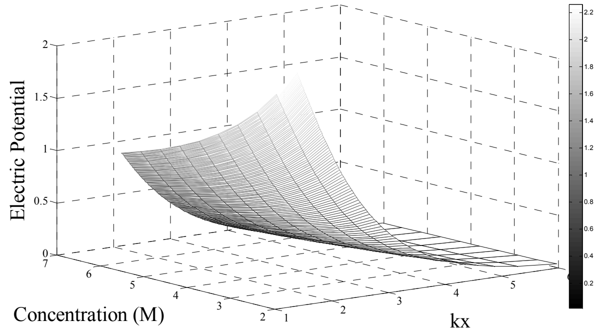


Figure 8: Dimensionless electric potential profile for concentrations between 2 and 6 molar with a charged surface (Surface Charge Density =0.06 C/m^2).

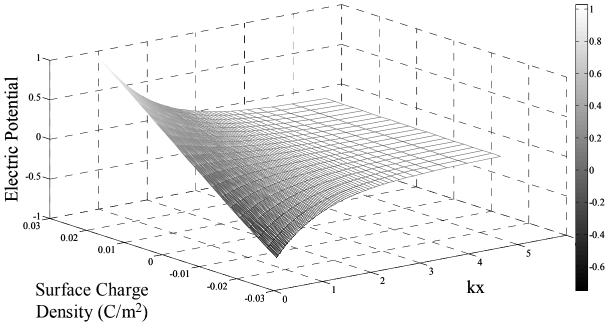
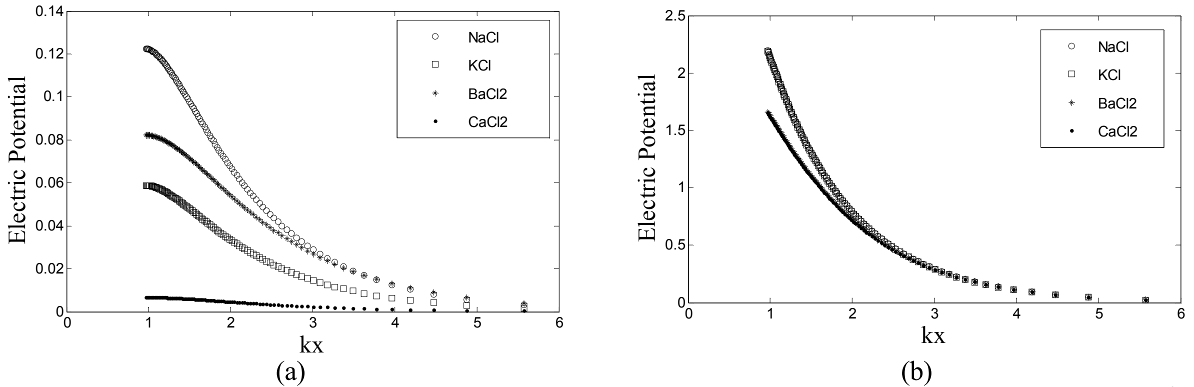


Figure 9: Dimensionless electric potential profile for surface charge densities between: -0.024 and 0.024 C/m^2.

Figures 6 - 9 were obtained for NaCl. The base case was done at 298 K and 1M. The results in Figures 10 (a) and (b) were obtained by evaluating the steady-state model for different salts (NaCl, KCl, $BaCl_2$ and $CaCl_2$) and concentration 1M. It is noteworthy that the ion specificity shown (Hofmeister effect) in Figure 10 (a) loses its influence in cases where the surface charge is high. For these cases, electrostatic effects outweigh the others and the valence of the ions in solution becomes more relevant (Figure 10 (b)). In conclusion, in Figure 10 (b), it is not possible do distinguish NaCl and KCl. In addition, results obtained for $BaCl_2$ and $CaCl_2$ are praticaly the same.



(a) (b)

Figure 10: (a) Dimensionless electric potential profiles for different salts (Surface Charge Density =0 C/m^2); (b) Dimensionless electric potential profiles for different salts (Surface Charge Density = 0.06 C/m^2).

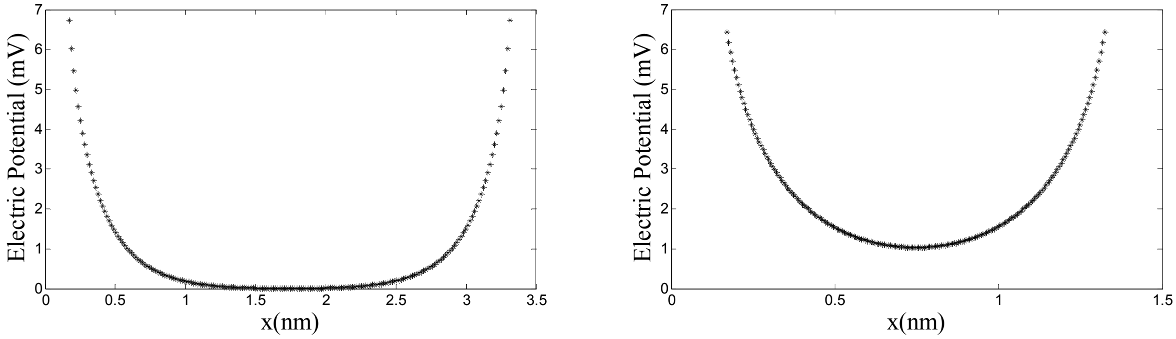
Two Parallel Plates – Steady-State Condition

These results were generated for NaCl solutions (1 molar at 298.15 K). Figures 11(a) and 11(b) show the results generated for the geometry with two charged parallel flat plates, where the influence of the distance (L) between the two plates on the electric potential profile can be seen.

A critical point was observed half way between the two plates; however, the potential value at this point is not necessarily zero and it increases (in magnitude) as the plates come closer to each other.

Two Parallel Plates – Pseudo-Transient Condition

The results obtained from the dimensionless pseudo-transient model for this geometry are shown in Figures 12 and 13. Based on these results, it is possible to verify changes in the electric potential profile due to changes in the surface charge.



(a) (b)

Figure 11: (a) Electric potential profile with $L = 3.5\ nm$ (Surface Charge Density =0.034 C/m^2); (b) Electric potential profile with $L = 1.5\ nm$ (Surface Charge Density =0.034 C/m^2).

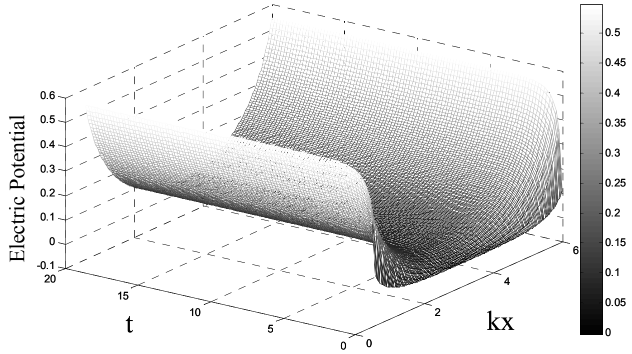


Figure 12: Effect of inversion of the surface charge density (σ) on the dimensionless electric potential profile with $L = 3\ nm$ (σ_{initial}=+0.024 C/m^2 and σ_{final}=-0.024 C/m^2).

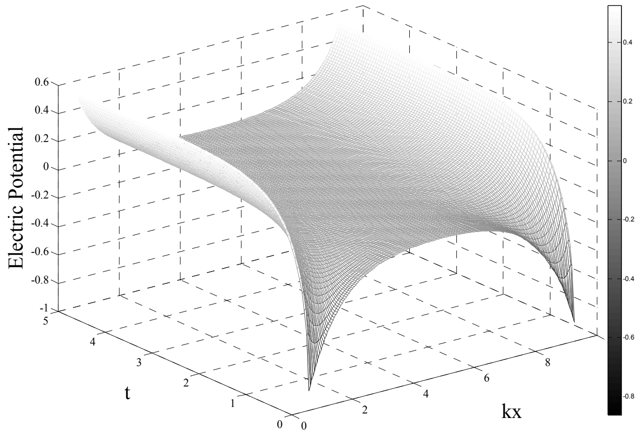


Figure 13: Effect of inversion of the charge on the electric potential profile with $L = 3\ nm$ (σ_{initial}= -0.06 C/m^2 and σ_{final}= 0.06 C/m^2).

Two Parallel Flat Plates – Case Study

Figures 14-17 show the profiles obtained by changes in: solution temperature, solution concentration, surface charge and type of salt used. Figures 14 - 16 were obtained for NaCl. The base case was done at 298 K and 1M. The results in Figure 17 were obtained by evaluating the steady-state model for different salts (NaCl, KCl, $BaCl_2$ and $CaCl_2$) and concentration 1M.

In a similar fashion, Figures 14, 15, 16 and 17 show the electric potential profiles obtained by changes in solution temperature, solution concentration, surface charge, and type of salt used. The results show that the electric potential is not necessarily zero in the middle of the domain, only the critical point condition is established by the problem boundary conditions. As shown in Figure 17, in cases where the surface charge is high, the influence of the electrostatic effects increases and the behavior of the physical properties is only modified by the valence of the ions present in the solution. Once more, in Figure 17, it is not possible to distinguish NaCl and KCl. Also, the results obtained for $BaCl_2$ and $CaCl_2$ are the same.

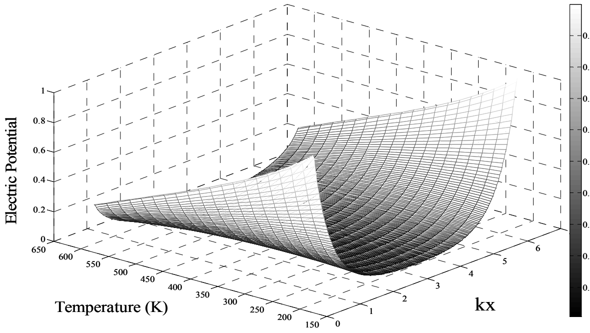


Figure 14: Dimensionless electric potential profile with temperatures between 200 and 600 K, with charged surface, and $L = 3\ nm$ (Surface Charge Density =0.06 C/m^2).

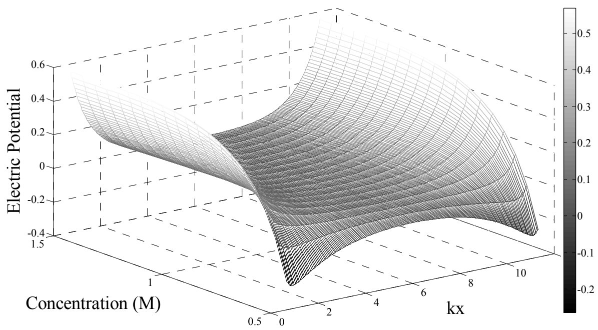


Figure 15: Dimensionless electric potential profile for concentrations between 0.5 and 1.5 molar, with charged surface and $L = 3\ nm$ (Surface Charge Density =0.06 C/m^2).

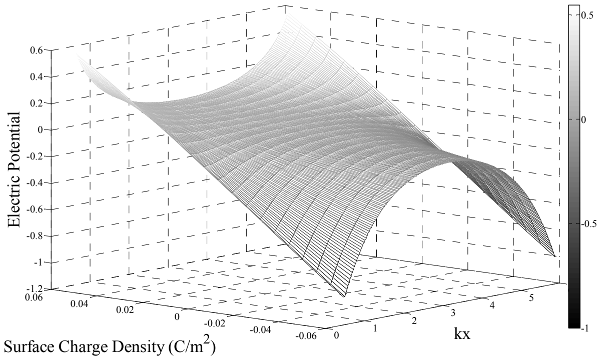


Figure 16: Dimensionless electric potential profile for surface charge density between -0.06 and 0.06 C/m^2 ($L = 2\ nm$).

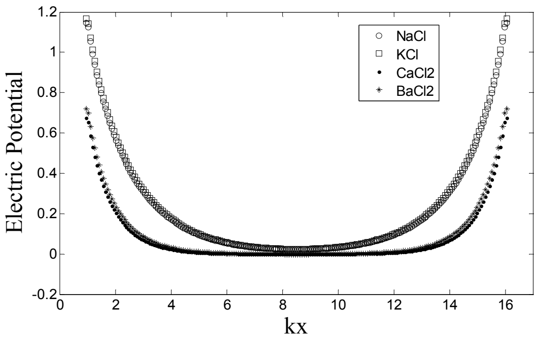


Figure 17: Dimensionless electric potential profile for different salts (Surface Charge Density = 0.06 C/m^2).

CONCLUSIONS

A modified Poisson-Boltzmann equation, taking into account non-electrostatic interactions between ions and surfaces was used to describe salt concentrations close to one or two infinite flat plates. To describe pseudo-transient behavior, a set of ordinary differential equations generated from algebraic equations and written in dimensionless variables was solved. This procedure permitted obtaining the dynamic behavior of the ion-concentration profile and other properties due to the surface charge variation.

The proposed method to solve the pseudo-transient Poisson-Boltzmann equation that accounted for salt type and divalent counterions can be used to describe electrochemical devices, such as electrodes with different surface-charge frequency. Sensitivity analysis was successfully carried out to verify the potential and ion concentrations close to the electrode in response to temperature, solution concentration, salt type, and surface charge.

NOTATION

c_i	ion concentration
c_{i0}	concentration of ion i in the reference state (bulk phase)
E_i	potential energy
E_{io}	potential energy in the reference state (bulk phase)
$e_i z_i$	charge of each ion
H	dispersion potential (Hamaker constant)
H^*	dimensionless dispersion parameter
I	ionic force in the bulk phase
i	Counter
k^{-1}	Debye-Length
k_B	Boltzmann constant
L	distance between two flat plates
r_{ion}	radius of the ion
T	temperature
t	dimensionless time
U	dispersion potential
x	position coordinate, independent variable
y	dimensionless independent variable
n	number of discretization intervals
Z	valence surface
Δy	interval size

Greek Letters

σ	surface charge density
ε	dielectric constant
ρ	charge volumetric density
ϕ	electric potential
φ	dimensionless electric potential

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