Transient Electrical Double Layer Dynamics in a Quiescent Fluid

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ABSTRACT

From the moment a liquid is put in contact with a solid, physico-chemical reactions occur at their interface. These reactions have been modeled over the years by preferential adsorption or corrosion. Whatever the model, they lead to a charge distribution called electrical double layer (EDL), formed by a charge layer at the solid wall, and a diffuse charge layer of opposite sign in the liquid. In this work we focus on the formation of the EDL when a plane wall is put in contact with a quiescent fluid. The governing equations and a semi-analytical solution are presented. A simpler solution can be found by assuming the instantaneous formation of the charge density profile. The semi-analytical solution presented in this work is compared to the former at different reaction rates leading to the conclusion that for fast enough wall reactions, the instantaneous charge density profile cannot be assumed.

Index Terms — **Electrical double layer, transient dynamics, Quiescent fluid.**

1 INTRODUCTION

ELECTRICAL double layers (EDL) have been studied for over a century due to the important role that they play in chemistry, biology, engineering and industrial processes. In particular, problems related to the petroleum industry or the electric power industry led to the study of the EDL in dielectric liquids [1-5]. In the petroleum or electric power industries, EDL related phenomena represent a problem due to charge buildup that can lead to explosions. On the other hand, in the last fifteen years there has been growing interest in electro kinetic phenomena related to microfluidics where the electrolyte is a solution of some salt in water. In this area of application, electrokinetics is used to induce movement of the fluid or to control mixing processes for instance. This led to the development of many electroosmotic pumps, driven by DC currents or AC currents, as well as mixer devices. Three comprehensive reviews on these subjects can be found in [6-8].

The use of AC electroosmotic pumps led to the study of the dynamics of the diffuse layer charge. Although the macroscopic theory of neutral electrolytes with quasi-equilibrium double layers is well developed [9-11], the transient formation of the EDL, or the response of an electrolyte to the application of a variable voltage or a sudden voltage are still subject of current research efforts [12-17].

The cited works related to transient EDL are focused mostly on the response of an electrolyte to an externally applied potential, with blocking electrodes and no chemical reactions in the bulk, or at the interface between the electrolyte and the electrodes. A detailed description can be found in [18]. With the exception of the analysis presented in [18], the cited works are numerical solutions to the linear or non-linear partial differential equations that govern EDL dynamics, or theoretical models based on electrical analogies where the EDL is modeled as combinations of resistors and capacitors. On the other hand, the transient formation of an EDL when a quiescent liquid is put in contact with a solid wall is of interest because the results can be extrapolated to the evolution of an EDL in the entrance region of a duct

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when the liquid is set in motion (this point is discussed further in the results section), which is rather complicated. A numerical solution to the full non-linear partial differential equations, with dissociation-recombination reactions in the liquid, and a reaction model at the interface (preferential adsorption), can be found in [19]. However, in order to obtain analytical solutions some simplifications are needed. For instance, some authors assume the reactions' kinetics to be too slow [20-24], or too fast [25-27] when compared to charge relaxation time. In this work, we present and solve the differential equation that governs the transient formation of an EDL when a liquid at rest is put in contact with a solid wall, in the case of weak space charge density (which allows for the linearization of the equation). In order to solve the differential equation, two approaches are used. The first one assumes that the transient solution is at all times proportional to the stationary solution, and that only the wall space-charge-density changes with time. We call this solution the "instantaneous profile" solution. The second approach does not rely on that assumption. The problem to solve is then more complicated and led us to a "semi-analytical" solution using Laplace transforms. The approach is similar to the one used in [18], but with different boundary conditions (we included a wall current due to reactions at the interface instead of a suddenly applied potential), and we were able to find the inverse transform in the form of an integral (the so-called semi-analytical solution). The results obtained with both methods are compared, and limits to the application of the former are established.

2 GOVERNING EQUATIONS

The transport of a charged species is given by diffusion, migration and convection. The flux density $\vec{\Gamma}_i$ of a charged species can be represented by:

$$\vec{\Gamma}_i = -D_i \vec{\nabla} n_i \mp n_i \frac{e_0 z_i D_i}{kT} \vec{\nabla}\phi + n_i \vec{u} \tag{1}$$

Where:

D_i	diffusion coefficient (m^2/s)
n_i	concentration of species i ($1/m^3$)
e_0	elementary charge ($1.6022\ 10^{-19}$ C)
z_i	species i valence
k	Boltzmann constant ($1.38\ 10^{-23}$ J/K)
T	temperature (K)
ϕ	electric potential (V)
$\vec{u}$	velocity vector (m/s)

The second term in equation (1) is negative for positive charge species, and positive for negative charge species.

The current density (A/m^2) due to this flux is, for a positive charge species:

$$\vec{i}_i = e_0 z_i \vec{\Gamma}_i \tag{2}$$

And for a negative charge species it is:

$$\vec{i}_i = -e_0 z_i \vec{\Gamma}_i \tag{3}$$

If we consider a fluid with l types of cations and m types of anions, the current density due to the flux of those l positive species is:

$$\vec{i_P} = -e_0 \sum_{i=1}^{l} z_i D_i \vec{\nabla} n_i - \frac{e_0^2}{kT} \sum_{i=1}^{l} z_i^2 D_i n_i \vec{\nabla}\phi + e_0 \sum_{i=1}^{l} z_i n_i \vec{u} \tag{4}$$

And the current density due to the flux of the m negative species is:

$$\vec{i_N} = e_0 \sum_{j=1}^{m} z_j D_j \vec{\nabla} n_j - \frac{e_0^2}{kT} \sum_{j=1}^{m} z_j^2 D_j n_j \vec{\nabla}\phi - e_0 \sum_{j=1}^{m} z_j n_j \vec{u} \tag{5}$$

In the absence of chemical reactions in the fluid, conservation equations are:

$$\vec{\nabla} \cdot \vec{i_P} + e_0 \sum_{i=1}^{l} z_i \frac{\partial n_i}{\partial t} = 0 \tag{6}$$

$$\vec{\nabla} \cdot \vec{i_N} - e_0 \sum_{j=1}^{m} z_j \frac{\partial n_j}{\partial t} = 0 \tag{7}$$

And finally the Poisson equation for the electric potential:

$$\Delta\phi = -\frac{e_0}{\varepsilon} \left(\sum_{i=1}^{l} z_i n_i - \sum_{j=1}^{m} z_j n_j \right) \tag{8}$$

It is possible to reduce this system into a binary one by making the hypothesis that all cations have the same valence z_P and that all anions have the same valence z_N.

We have to introduce a mean positive diffusion coefficient D_P and a number of cations n_P as follows:

$$D_P = \frac{\sum_{i=1}^{l} D_i n_i}{\sum_{i=1}^{l} n_i} = \frac{\sum_{i=1}^{l} D_i n_{i\infty}}{\sum_{i=1}^{l} n_{i\infty}}, \qquad n_P = \sum_{i=1}^{l} n_i \tag{9}$$

Where n_i can be obtained from the Boltzmann solution [28], in which $n_{i\infty}$ represents the ion concentration at the center of the fluid.

$$n_i = n_{i\infty} \exp\left(\frac{e_0 z_P \phi}{kT} \right) \tag{10}$$

The mean negative diffusion coefficient D_N and the anion concentration n_N can be defined in the same manner.

The binary system is then:

$$\begin{aligned}
&\vec{i_P} = -e_0 z_P D_P \vec{\nabla} n_P - n_P \frac{e_0^2 z_P^2 D_P}{kT} \vec{\nabla}\phi + e_0 z_P n_P \vec{u} \\
&\vec{i_N} = e_0 z_N D_N \vec{\nabla} n_N - n_N \frac{e_0^2 z_N^2 D_N}{kT} \vec{\nabla}\phi - e_0 z_N n_N \vec{u} \\
&\vec{\nabla} \cdot \vec{i_P} + e_0 z_P \frac{\partial n_P}{\partial t} = 0 \\
&\vec{\nabla} \cdot \vec{i_N} - e_0 z_N \frac{\partial n_N}{\partial t} = 0 \\
&\Delta\phi = -\frac{e_0}{\varepsilon} \left(z_P n_P - z_N n_N \right)
\end{aligned} \tag{11}$$

At this point we can introduce the variables ρ for the space charge density and σ for the conductivity of the liquid:

$$\begin{aligned}
&\rho = e_0 \left(z_P n_P - z_N n_N \right) \\
&\sigma = \frac{e_0^2}{kT} \left(D_P z_P^2 n_P + D_N z_N^2 n_N \right)
\end{aligned} \tag{12}$$

In order to simplify the system we assume that the positive and negative valences are the same: $z_P=z_N=z$. In this case, the problem's general equations are:

$$\begin{aligned}
&\vec{i}=-D_0\vec{\nabla}\left(\rho+\beta\sigma^*\right)-\frac{e_0 z D_0}{kT}\sigma^*\vec{\nabla}\phi+\rho\vec{u}\\
&\vec{i^*}=-D_0\vec{\nabla}\sigma^*-\frac{e_0 z D_0}{kT}\left(\rho+\beta\sigma^*\right)\vec{\nabla}\phi\\
&\qquad+\left[\left(1-\beta^2\right)\sigma^*-\beta\rho\right]\vec{u}\\
&\vec{\nabla}\cdot\vec{i}+\frac{\partial\rho}{\partial t}=0\\
&\vec{\nabla}\cdot\vec{i^*}+\left(1-\beta^2\right)\frac{\partial\sigma^*}{\partial t}-\beta\frac{\partial\rho}{\partial t}=0\\
&\Delta\phi=-\frac{\rho}{\varepsilon}
\end{aligned}\tag{13}$$

Where we have used the following definitions:

$$\sigma^*=\sigma\frac{kT}{e_0 z D_0}\quad D_0=\frac{2D_N D_P}{D_P+D_N}\quad \beta=\frac{D_P-D_N}{D_P+D_N}\tag{14}$$

$$\begin{aligned}
&\vec{i}=\vec{i_P}+\vec{i_N}\\
&\vec{i^*}=\vec{i_P}-\vec{i_N}
\end{aligned}\tag{15}$$

By replacing the current densities i and i^* in the conservation equation and then using the electric potential equation we get, for the case of a quiescent fluid (u=0):

$$\begin{aligned}
0=&-D_0\Delta\rho-\vec{\nabla}f\left(\rho,\sigma\right)\cdot\vec{\nabla}\phi+f\left(\rho,\sigma\right)\frac{\rho}{\varepsilon}\\
&+\frac{\partial\rho}{\partial t}-\frac{\beta kT}{e_0 z D_0}\frac{\partial f\left(\rho,\sigma\right)}{\partial t}
\end{aligned}\tag{16}$$

Where:

$$f\left(\rho,\sigma\right)=\left(1-\beta^2\right)\sigma-\beta\rho\Big/\left(\frac{kT}{e_0 z D_0}\right)\tag{17}$$

In order to solve this equation, we consider here the case of weak space charge density. This assumption leads to conductivity values very close to the mean conductivity σ and also to the following relation:

$$\left(1-\beta^2\right)\sigma>>\beta\frac{\rho e_0 z D_0}{kT}\Rightarrow\left(1-\beta^2\right)\sigma-\beta\frac{\rho e_0 z D_0}{kT}\approx\left(1-\beta^2\right)\sigma\tag{18}$$

Touchard [28] established three ranges in order to determine whether one is in the case of "weak space charge density (WSCD)", "mean space charge density (MSCD)" or "strong space charge density (SSCD)":

$$\beta\frac{\rho e_0 z D_0}{kT\sigma_0}\le 10^{-2}\left(1-\beta^2\right)\rightarrow WSCD\tag{19}$$

$$10^{-2}\left(1-\beta^2\right)<\beta\frac{\rho e_0 z D_0}{kT\sigma_0}\le 10^{2}\left(1-\beta^2\right)\rightarrow MSCD\tag{20}$$

$$10^{2}\left(1-\beta^2\right)<\beta\frac{\rho e_0 z D_0}{kT\sigma_0}\rightarrow SSCD\tag{21}$$

In the case of weak space charge density, the condition $f\left(\rho,\sigma\right)\approx\left(1-\beta^2\right)\sigma=const$ holds, and consequently (16) becomes:

$$0=-D_0\Delta\rho+\frac{\left(1-\beta^2\right)\sigma}{\varepsilon}\rho+\left(1+\beta^2\right)\frac{\partial\rho}{\partial t}\tag{22}$$

This equation is called the Debye-Falkenhagen equation [29]. In order to non-dimensionalize equation (22), we choose the following parameters: the liquid's conductivity σ, its dielectric constant ε, the mean diffusion coefficient D_0 and the space charge density at the wall for a completely developed EDL ρ_{wd}.

As we are considering a quiescent fluid between to plates, the problem is one-dimensional in space. Equation (22) then becomes:

$$0=-\frac{\partial^2\rho_+}{\partial x_+^2}+\left(1-\beta^2\right)\rho_+ +\left(1+\beta^2\right)\frac{\partial\rho_+}{\partial t_+}\tag{23}$$

Where:

$x_+=x\sqrt{\sigma/\varepsilon D_0}=x/\delta_0$ is the dimensionless spatial coordinate normal to the interface. δ_0 is the EDL's thickness.

$t_+=t/\tau_r=t\dfrac{\sigma}{\varepsilon}$ is the dimensionless time, and $\tau_r=\varepsilon/\sigma$ is EDL's relaxation time.

$\rho_+=\rho/\rho_{wd}$ is the dimensionless space charge density.

3 Solving the Partial Differential Equation

In this section we present two different approaches in order to solve equation (23). Their results are compared in the next section in order to determine the limits to their application.

3.1 Instantaneous Space Charge Profile Formation (Method A)

The first approach, based on the work of Touchard et al. [20] consists in assuming that the solution is, at every instant, proportional the stationary solution. In the stationary case the temporal derivative in equation (23) is null:

$$0=-\frac{\partial^2\rho_+}{\partial x_+^2}+\left(1-\beta^2\right)\rho_+\tag{24}$$

The general solution to this PDE is:

$$\begin{aligned}
\rho_+\left(x_+\right)=&C_1\sinh\left(\sqrt{1-\beta^2}.x_+\right)\\
&+C_2\cosh\left(\sqrt{1-\beta^2}.x_+\right)
\end{aligned}\tag{25}$$

For an EDL between to infinite plates separated by a distance $2a$ the stationary solution is:

$$\rho_+\left(x_+\right)=\frac{\cosh(\sqrt{1-\beta^2}.x_+)}{\cosh(\sqrt{1-\beta^2}.a_+)},\tag{26}$$

where the boundary condition $\rho_+\left(x_+=\pm a_+\right)=1$ has been used.

$a_+=a/\delta_0$ is the non-dimensional half distance between the plates.

As stated before, this first method (method A) assumes that the transient solution is proportional to the stationary solution

at all times:

$$\rho_+(x_+,t_+)=f(t_+)\frac{\cosh(\sqrt{1-\beta^2}.x_+)}{\cosh(\sqrt{1-\beta^2}.a_+)} \tag{27}$$

For the temporal boundary condition we assume that from the moment the liquid is put in contact with the solid a wall current density appears in the form:

$$i_{w+}=\frac{i_w\tau_r}{\rho_{wd}\delta_0}=\frac{\tau_r}{\delta_0}K[1-\rho_{w+}]=K_+[1-\rho_+(a_+,t_+)] \tag{28}$$

with $K_+=K\,\tau_r/\delta_0$ being the dimensionless reaction rate.

Considering an elementary volume of non-dimensional wall surface dA_+, the charge conservation equation can be written in integral form to give:

$$2i_{w+}dA_+=\int_{-a_+}^{a_+}\frac{\partial\rho_+}{\partial t_+}dx_+\,dA_+ \tag{29}$$

Replacing equations (27) and (28) in equation (29) and integrating the resulting differential equation we obtain:

$$f(t_+)=1-\exp\left(-\frac{K_+t_+\sqrt{1-\beta^2}}{\tanh(a_+\sqrt{1-\beta^2})}\right) \tag{30}$$

where the initial condition used is $f(t_+=0)=0$, which corresponds to a null space charge density at $t_+=0$. Finally, the dimensionless space charge density is:

$$\rho_+(x_+,t_+)=\left[1-\exp\left(-\frac{K_+t_+\sqrt{1-\beta^2}}{\tanh(a_+\sqrt{1-\beta^2})}\right)\right]\frac{\cosh(x_+\sqrt{1-\beta^2})}{\cosh(a_+\sqrt{1-\beta^2})} \tag{31}$$

If the distance between the two plates is large enough ($a_+>>1$), the one plate solution (with the origin for the space coordinate set at the interface, pointing towards the liquid) is valid:

$$\rho_+(x_+,t_+)=\left[1-\exp\left(-K_+t_+\sqrt{1-\beta^2}\right)\right]\exp\left(-x_+\sqrt{1-\beta^2}\right) \tag{32}$$

Both solutions are equivalent at large values of a_+.

3.2 NON-INSTANTANEOUS SPACE CHARGE PROFILE FORMATION (METHOD B)

In order to solve equation (23) without the hypothesis used in the previous case we apply the Laplace transform to the space charge density:

$$L\left[\rho_+(x_+,t_+)\right]=\theta(x_+,s) \tag{33}$$

Therefore, in the transformed domain equation (23) reads [30]:

$$0=-\frac{\partial^2\theta(x_+,s)}{\partial x_+^2}+(1-\beta^2)\theta(x_+,s) +(1+\beta^2)\left[s.\theta(x_+,s)-\rho_+(x_+,t_+=0)\right] \tag{34}$$

The initial condition is, again, null space charge density at $t_+=0$. Then, reorganizing the terms in (34) we obtain (35):

$$0=-\frac{\partial^2\theta(x_+,s)}{\partial x_+^2}+\left[(1-\beta^2)+(1+\beta^2)s\right]\theta(x_+,s) \tag{35}$$

The solution to this equation is, in the transformed domain:

$$\theta_+(x_+,s)=\Phi_1(s)\sinh\left(x_+\sqrt{(1-\beta^2)+s(1+\beta^2)}\right) +\Phi_2(s)\cosh\left(x_+\sqrt{(1-\beta^2)+s(1+\beta^2)}\right) \tag{36}$$

To simplify the equations below we will obtain the solution in the case of far away plates ($a_+>>1$), with the origin ($x_+=0$) of the space coordinate at the interface. In that case $\rho_+(x_+=\infty)=0$, and the solution becomes:

$$\theta_+(x_+,s)=\Phi_2(s)\exp\left(-x_+\sqrt{(1-\beta^2)+s(1+\beta^2)}\right) \tag{37}$$

At this point we must introduce the same boundary condition as before. That is, we assume that from the moment the liquid is put in contact with the solid a wall current density appears in the form:

$$i_{w+}=\frac{i_w\tau_r}{\rho_{wd}\delta_0}=\frac{\tau_r}{\delta_0}K[1-\rho_{w+}]=K_+[1-\rho_+(0,t_+)] \tag{38}$$

The conservation equation in integral form is, again:

$$i_{w+}dA_+=\int_0^{\infty}\frac{\partial\rho_+}{\partial t_+}dx_+\,dA_+ \tag{39}$$

And in the transformed domain it becomes:

$$\int_0^{\infty}\left[s\theta(x_+,s)-\rho_+(x_+,t_+=0)\right]dx_+=\frac{K_+}{s}-K_+\Phi_2(s) \tag{40}$$

Introducing the solution (37) and integrating leads to:

$$\Phi_2(s)=\frac{K_+\sqrt{(1-\beta^2)+s(1+\beta^2)}}{s^2+sK_+\sqrt{(1-\beta^2)+s(1+\beta^2)}} \tag{41}$$

After some rearranging and using the convolution theorem [30], the inverse Laplace transform of $\theta_+(x_+,s)$ is:

$$\boxed{\rho_+(x_+,t_+)=L^{-1}\left[\theta(x_+,s)\right]= \frac{1}{2}\frac{K_+d_+}{s_2-s_1}\int_0^t\left\{\frac{x_+d_+}{\sqrt{\pi}\xi^{3/2}}\exp\left[-c_+\xi-\frac{x_+^2d_+^2}{4\xi}\right]F(t_+-\xi)\right\}d\xi} \tag{42}$$

Where we have used:

$$c_+=\frac{1-\beta^2}{1+\beta^2}\quad d_+=\sqrt{1+\beta^2}$$
$$s_1=\frac{K_+^2d_+^2+\sqrt{K_+^4d_+^4+4K_+^2d_+^2c_+}}{2} \tag{43}$$
$$s_2=\frac{K_+^2d_+^2-\sqrt{K_+^4d_+^4+4K_+^2d_+^2c_+}}{2}$$

and,

$$F(t_+-\xi)=\sqrt{c_++s_2}\cdot \left\{\exp\left[s_2(t_+-\xi)\right]\left[1+erf\left(\sqrt{(c_++s_2)(t_+-\xi)}\right)\right]-1\right\} +\sqrt{c_++s_1}\cdot \left\{\exp\left[s_1(t_+-\xi)\right]erfc\left(\sqrt{(c_++s_1)(t_+-\xi)}\right)-1\right\} \tag{44}$$

The integral in equation (42) has to be calculated numerically. Equation (42) is then a semi-analytical solution to equation (23), for the boundary condition equation (39) and null space charge density at $t_+=0$.

4 RESULTS AND DISCUSSION

In this section we are going to compare the results of methods A and B.

We will consider the case of a dielectric liquid (transformer oil) with the following properties:

$\sigma = 5\times10^{-13}$ S/m, $D_0 = 4\times10^{-11}$ m^2/s, $\varepsilon = 1\times95\times10^{-11}$ F/m.

The value used for the diffusion coefficient is proposed in [31]. If heptane (which is also a dielectric liquid with low conductivity, but with lower viscosity) were used instead of transformer oil, the diffusion coefficient would be on the order of 1×10^{-9} m^2/s.

This values give a double layer thickness of δ_0=39.46 μm. For a distance $2a$=3 mm (this is the dimension between plates of the sensor described in [32-33]) between plates, a_+= 38, which allows largely for the use of the single plate solution.

The only two dimensionless parameters that influence the solution are K_+ and β. By definition -1 < β < 1, but it is squared in the solution so only values between 0 and 1 give different results. Higher values of β result in wider diffuse layers and longer equilibrium times. In practice small differences in the diffusion coefficients of positive and negative ions give values of β around 0. In this work we present results assuming that the cations' diffusion coefficient is the same to that of the anions. In that case β=0.

In those conditions, the only parameter to vary is the reaction rate K. We present here the results of both methods for $K_+ = K\,\tau_r/\delta_0$=0.001, 0.01, 0.1, 1, 10 and 100. This choice of K_+ values is due to the experimental values of K_+ obtained in previous work [34], which were in the range of 0.01-1. This dimensionless parameter represents the ratio of the reaction rate to the relaxation velocity δ_0/τ_r, due to migration-diffusion. Higher values of K_+ mean faster reactions.

The dimensionless time evolution of the dimensionless space charge density, calculated with methods A and B, is presented in Figures 1 and 2 for K_+=10, and in figures 3 and 4 for K_+=0.1.

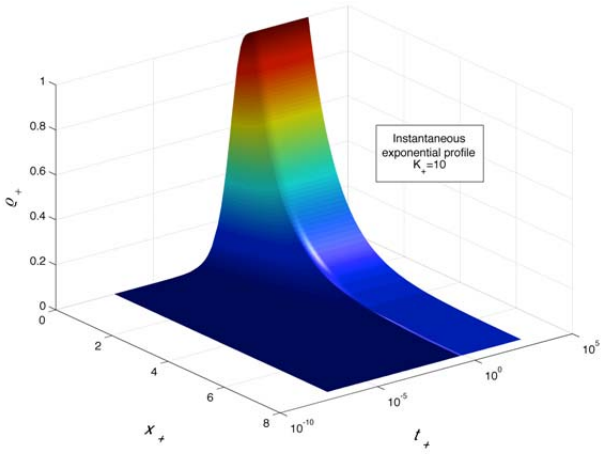

Figure 1. Dimensionless time evolution of the dimensionless space charge density for K_+=10, calculated with method A: instantaneous exponential profile (in color online).

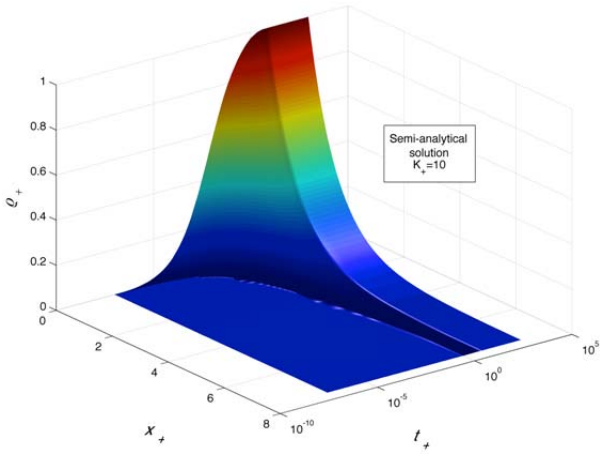

Figure 2. Dimensionless time evolution of the dimensionless space charge density for K_+=10, calculated with method B: semi-analytical solution (in color online).

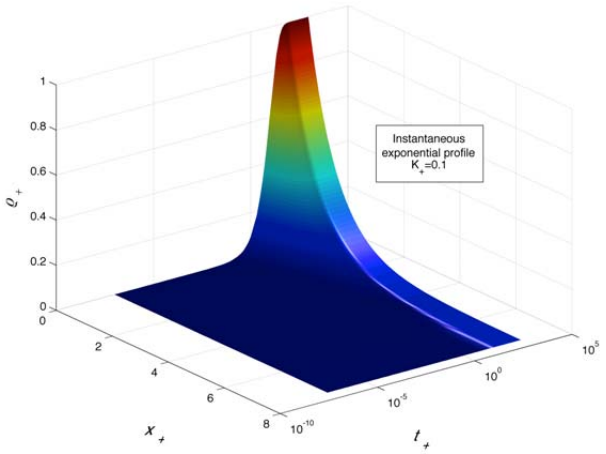

Figure 3. Dimensionless time evolution of the dimensionless space charge density for K_+=0.1, calculated with method A: instantaneous exponential profile (in color online).

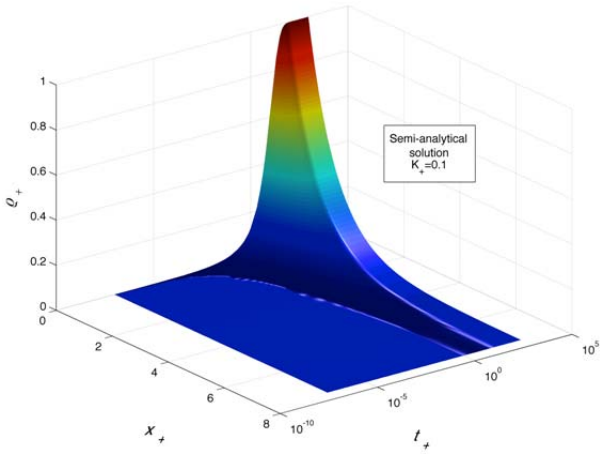

Figure 4. Dimensionless time evolution of the dimensionless space charge density for K_+=0.1, calculated with method B: semi-analytical solution (in color online).

In all four figures it can be observed that the completely developed space charge profiles calculated with both methods coincide for large values of t_+. This of course is an expected result because at large t_+ the time derivative in the differential equation vanishes. However, it is clear when comparing Figure 1 and Figure 2, and also Figure 3 and Figure 4, that during the formation methods A and B do not show the same behavior, the difference is more evident when comparing Figures 1 and 2. In these cases (K_+=10), charge production at the interface is too fast, and does not give enough time to those charges to relax in the diffuse layer. The space charge density profile calculated with method B shows that charges are closer to the interface, with higher values of the wall space charge density at every time. This is more clear when plotting the dimensionless space charge profile calculated with both methods at different dimensionless times, on the same plot, as presented in Figures 5, 6, 7 and 8 for dimensionless reaction rates K_+=10, 1, 0.1 and 0.01 respectively.

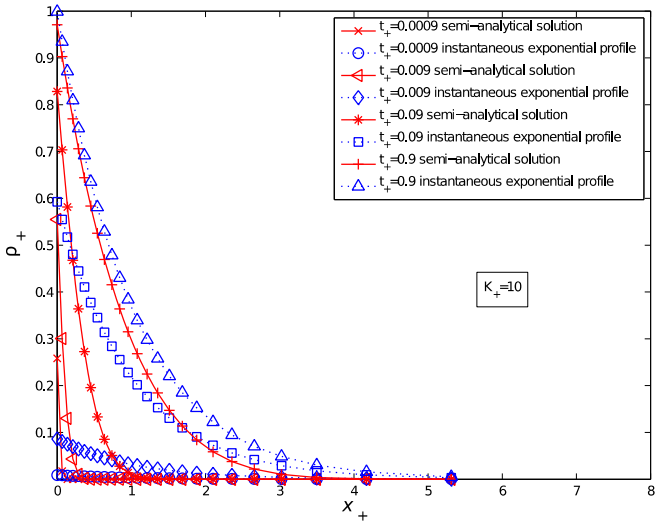

Figure 5. Dimensionless space-charge density (ρ_+) profiles for K_+=10, at four different dimensionless times, calculated with methods *A* and *B* (in color online).

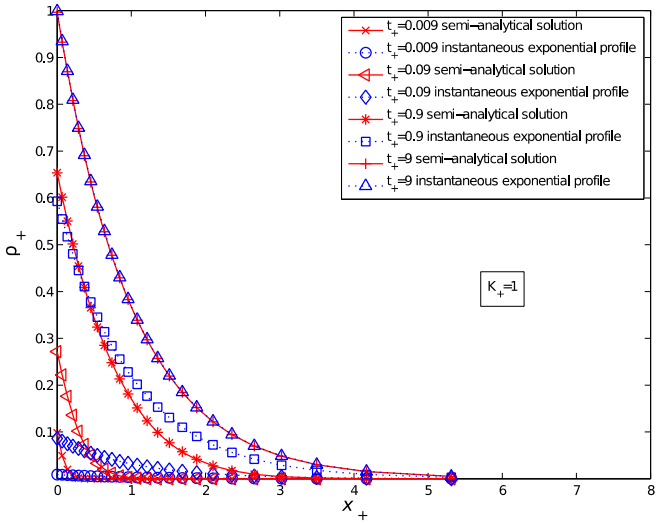

Figure 6. Dimensionless space-charge density (ρ_+) profiles for K_+=1, at four different dimensionless times, calculated with methods *A* and *B* (in color online).

In Figure 8 one can see that the reaction rate is slow enough for the charges to form an equilibrium profile at all presented times. In Figures 5 to 8, the maximum dimensionless time presented was chosen so that the instantaneous exponential profile had reached the stationary profile.

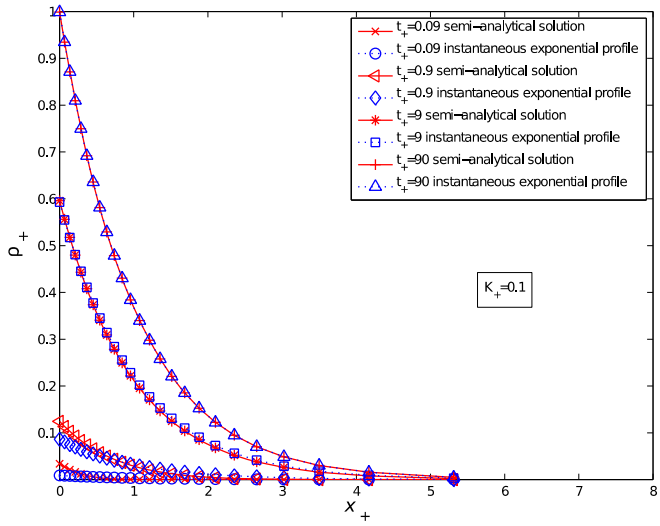

Figure 7. Dimensionless space charge density profiles for K_+=0.1, at four different dimensionless times, calculated with methods *A* and *B* (in color online).

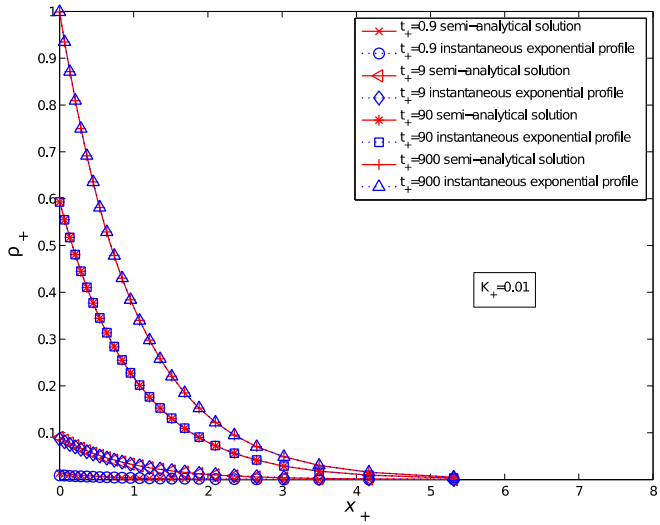

Figure 8. Dimensionless space charge density profiles for K_+=0.01, at four different dimensionless times, calculated with methods *A* and *B* (in color online).

Furthermore, Figure 9 and Figure 10 present the evolution of the dimensionless wall-space-charge density as a function of dimensionless time found with method A and method B, respectively. The bigger differences between both methods are found for times t_+<1. That is, for times smaller than the double layer relaxation time, in all cases. However, the slower the reaction, the more the relaxation time is negligible compared to the equilibrium time, and therefore the more the error made in assuming instantaneous formation of the profile will be acceptable. This result could be extrapolated to the formation of an EDL in the entrance region of a duct. If one assumes an instantaneous formation of the profile, the more the reaction is slow, the shorter

the length over which the charge profile is incorrectly assumed. This is important because in streaming electrification experiments, the streaming current is used to determine the space charge density at the wall, and if the duct's length is short, to extrapolate the value obtained to the fully developed EDL wall space charge. The procedure that is used is to assume a space charge profile at the exit and, because the flow used is laminar, it is then easy to obtain the wall space at the exit position [33]. If one uses the instantaneous profile hypothesis, but the reaction is too fast, then the profile at the exit does not correspond to the one assumed. The charges are placed in a region closer to the wall and the method underestimates the wall charge density.

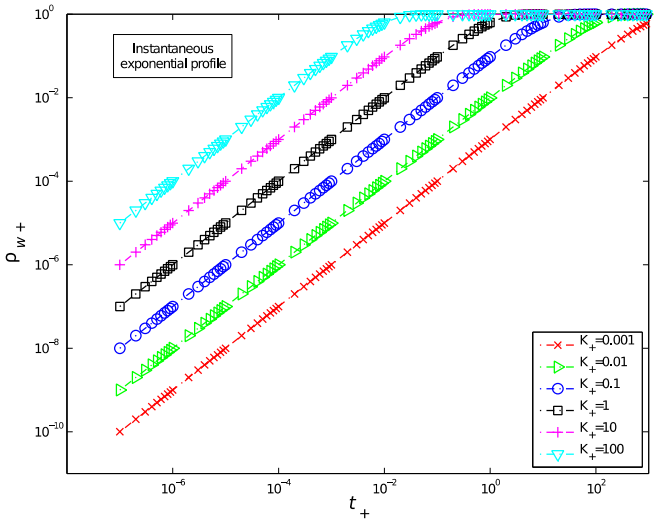

Figure 9. Dimensionless wall-space-charge-density calculated with method A (in color online).

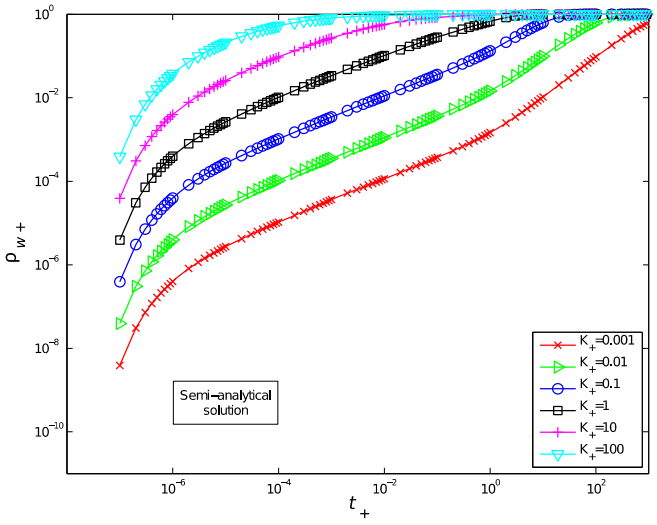

Figure 10. Dimensionless wall-space-charge-density calculated with method B (in color online).

Finally, it is shown in Figures 11 and 12 that the wall current density drops earlier in the case of faster reactions when using the semi-analytical solution. This difference is less and less clear for the slower reaction rates.

The results presented here are related to the analytical solution of the linearized partial differential equation that governs the transient formation of an EDL in the case of weak space charge density. The fully non-linear system of PDE needs to be solved numerically. A finite volumes numerical solution including adsorption and desorption at the wall, plus dissociation-recombination reactions in the liquid for this problem, and for the transient set in motion of the liquid in the duct can be found in [19].

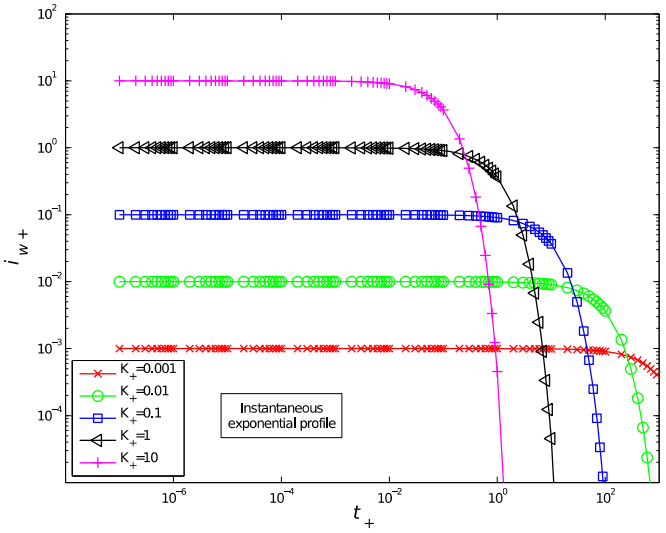

Figure 11. Dimensionless wall current density calculated with method A (in color online).

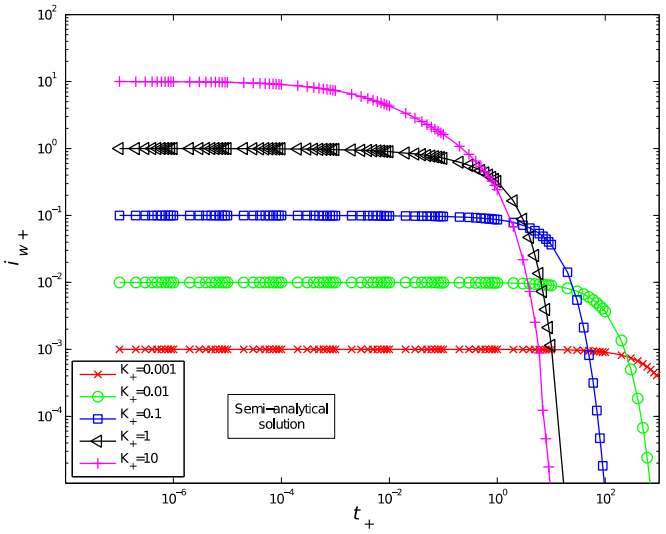

Figure 12. Dimensionless wall current density calculated with method B (in color online).

5 CONCLUSION

In this work we have presented and solved the differential equation that governs the formation of an Electrical Double Layer (EDL) when a liquid is put in contact with a solid wall. In order to solve this differential equation, two approaches were used. The first one assumed that the transient solution is at all times proportional to the stationary solution, and that only the wall space-charge-density changes with time. We called this solution the "instantaneous profile" solution. The second approach did not rely on that assumption. The problem to solve led us to a "semi-analytical" solution. The results obtained with both methods were compared, showing that the instantaneous profile solution should be used with caution when the non-dimensional reaction rate

$K_+>1$. For values of $K_+<0.1$ the differences on both results are relevant at the initial times only and those times are very small compared to the equilibrium time.

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