Analytical description of the ionic relaxation in the presence of surface adsorption

To cite this article: Giovanni Barbero *et al* 2024 *J. Phys. A: Math. Theor.* **57** 265005

View the article online for updates and enhancements.

Analytical description of the ionic relaxation in the presence of surface adsorption

Giovanni Barbero[1,2] ⓘ**, Yagub Aliyev**[3] ⓘ
and Antonio M Scarfone[2,*] ⓘ

[1] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy
[2] Istituto dei Sistemi Complessi del Consiglio Nazionale delle Ricerche (ISC-CNR) c/o Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy
[3] ADA-University, Ahmadbey Aghaoglu str. 61, Baku, 1008, Azerbaijan

E-mail: antoniomaria.scarfone@cnr.it

Abstract

The temporal evolution of the surface electric field in a cell in the presence of ionic adsorption is investigated. The analysis is performed in the framework of the Poisson–Nernst–Planck model, based on the conservation of particles and the equation of Poisson for the actual electric potential across the cell, assuming that only the ions of a given sign are mobile. The adsorption is described using a kinetic equation of Langmuir's type. The simple case of small adsorption is considered, in which the saturation effect can be neglected, and the fundamental equations of the model can be linearized. In this framework, the effective relaxation time describing the dynamics of the system is evaluated, as well as the profiles of the ions and the electric field. The case in which the sample is a half-space is first considered. A more realistic situation where the sample is a slab of thickness d, limited by two identical or different electrodes, is analyzed too. The difference in electric potential due to the adsorption phenomenon between the electrodes is determined. Our analysis shows that its

time dependence, when the electrodes have different adsorption properties, is not monotonic.

1. Introduction

When a liquid containing ions is in contact with a surface, some of the ions can be adsorbed by the surface [1]. In this case, if in thermodynamical equilibrium the liquid is locally and globally neutral, in the presence of the adsorption phenomenon, the liquid is locally charged close to the surface, and an electric field is present [2]. In this situation, the electric potential of the electrode differs from that in the bulk [3]. Our goal is to investigate the temporal evolution of the surface electric field in a cell in the presence of ionic adsorption. The analysis is performed in the framework of the Poisson–Nernst–Planck model, based on the conservation of particles and on the equation of Poisson for the actual electric potential across the cell [3–5]. The adsorption is described using a kinetic equation of Langmuir's type, involving the adsorption coefficient and the desorption time [6].

We will limit our analysis to the case of small adsorption, in which the saturation effect can be neglected [3, 7, 8], and the fundamental equations of the model can be linearized. In this framework, the solution of the dynamical problem can be separated into the equilibrium and transient components. A complete investigation of the difference of electric potential, in the equilibrium state, in a cell due to the adsorption-desorption phenomenon of ions at open circuit conditions, has been discussed in [3]. The analysis presented in [3] concerns a liquid containing positive and negative ions identical in all aspects, except the sign of the electric charge. They just differ from the adsorbing properties, which in the Langmuir approximation means that the adsorption coefficients and the desorption times for the positive and negative ions are different. Our aim is the description of the temporal evolution of the system toward the equilibrium state, and the determination of the main relaxation time in this multi-relaxation phenomenon, only briefly discussed in [3] and limited to a numerical analysis of the eigenvalue equation defining the relaxation times.

The goal of the paper is the investigation of the time evolution of the bulk density of ions and of the electric field in the presence of adsorption. Special attention is devoted to the difference of potential between the electrodes adsorbing ions limiting the cell, which is a quantity experimentally detectable. We limit our consideration to a system in which only the ions of a given sign are mobile, as in hydrogels containing ions [9, 10]. The application of the present model to other physical systems, such as electrolytic cells containing two or more groups of mobile ions or porous electrodes or membranes, requires considering the case of two mobile ions, with different diffusion coefficients, and generation-recombination effects. The work is under analysis and will be published elsewhere.

Our paper is organized as follows. The model and the physical problem are described in section 2. The case in which the sample can be considered semi-infinite is analyzed in section 3, where the equilibrium and transient components of the bulk density of ions, of the electric field, and of the surface density of adsorbed ions are evaluated. In that section we evaluate the relaxation time of the evolution of the system toward the equilibrium state, the electric potential of the electrode with respect to the bulk, and its time dependence. In section 4 a discussion on the case in which the sample is a symmetric slab is reported, whereas the asymmetric slab is considered in section 5. The analysis relevant to an asymmetric slab indicates that when the thickness of the sample is large with respect to the length of Debye, the sample can be

approximated by two half-spaces and that the difference of potential between the electrodes, with different adsorption properties, tends to its equilibrium value in a non-monotonic manner. Section 6 is devoted to the conclusions.

2. The problem

The model we consider is based on the equation of continuity for the ions and on the equation of Poisson relating the electric field to the electric charge density [11]. This model is widely used in the analysis of the experimental data obtained by means of the impedance spectroscopy technique [12]. It has been generalized to take into account anomalous diffusion and reaction terms in the medium under investigation [13–17]. We consider the simple case in which only the positive ions are mobile and the diffusion is described by Fick's law. We indicate by q the electric charge of the ions, D their diffusion coefficient in the considered matrix, ε the dielectric constant of the medium in which the ions are dispersed. We assume that in the absence of the adsorption phenomenon, the medium is globally and locally neutral, and indicates by n_0 the bulk density of positive and negative ions. In this situation, the effective electric field is identically zero in the sample. In the presence of adsorption, the mobile ions move to the adsorbing surface giving rise to a current density of particles $\boldsymbol{j}$, and the ionic distribution of the mobile ions, n, and the resulting electric field, $\boldsymbol{E}$, are perturbed. We indicate by σ the surface density of the adsorbed particles. The continuity equation for the mobile ions and the equation of Poisson are, respectively

$$\frac{\partial n}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{j}, \quad \text{and} \quad \boldsymbol{\nabla} \cdot \boldsymbol{E} = \frac{1}{\varepsilon} \rho, \tag{1}$$

where $\rho = q\,(n - n_0)$ is the bulk density of electric charge of ionic origin, n_0 is the bulk density of ions at the thermodynamic equilibrium, and the current density of particles $\boldsymbol{j}$ is

$$\boldsymbol{j} = -D\left(\boldsymbol{\nabla} n - \frac{qn}{k_{\mathrm{B}}T}\boldsymbol{E}\right), \tag{2}$$

in the Einstein–Smolucowski approximation [6]. In equation (2), k_{B} is Boltzmann's constant, and T is the absolute temperature. The boundary conditions relating the bulk and the surface density are [17]

$$\boldsymbol{j} \cdot \boldsymbol{u_n} = \frac{\mathrm{d}\sigma}{\mathrm{d}t}, \quad \text{and} \quad \boldsymbol{E} \cdot \boldsymbol{u_n} = q\,\frac{\sigma}{\varepsilon}, \tag{3}$$

where $\boldsymbol{u_n}$ is the unity vector to the limiting surface outward-directed.

For the sake of simplicity, we consider first the case in which the medium occupies the half-space $z \geqslant 0$, and the limiting surface is homogeneous. In such a situation, the mathematical problem is one-dimensional.

We assume that the adsorption phenomenon is well described by Langmuir's kinetic equation, where the rate of adsorption depends linearly on the bulk density of adsorbable particles just in front of the adsorbing surface, and the desorption of particles is linearly proportional to the surface density of adsorbed particles. Thus, in this framework, the evolution of the surface density of adsorbed particles σ is

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma(t) = \kappa_a n(t) - \frac{1}{\tau_a}\sigma(t), \tag{4}$$

where κ_a and τ_a are the adsorption coefficient and desorption time, respectively, and $n(t) \equiv n(0, t)$.

Kinetic equation (4) is valid in the limit of small adsorption, i.e. for σ very small with respect to the density of adsorption sites [8, 18]. The dimension of κ_a are *length/time* and $\ell = \kappa_a \tau_a$ is a length characteristic of the adsorption phenomenon under consideration.

The fundamental equations of the problem, in the linear approximation valid in the limit of small adsorption, are

$$\frac{\partial n}{\partial t} = D \left(\frac{\partial^2 n}{\partial z^2} - \frac{n_0 q}{k_B T} \frac{\partial E}{\partial z} \right) , \tag{5}$$

$$\frac{\partial E}{\partial z} = \frac{q}{\varepsilon} (n - n_0) . \tag{6}$$

Equations (5) and (6) have to be solved with the boundary conditions

$$E(0,t) = \frac{q}{\varepsilon} \sigma(t) \quad \text{and} \quad j(0,t) = -\frac{d}{dt} \sigma(t) , \tag{7}$$

in the case in which the sample is a half-space, where

$$j(0,t) = -D \left(\frac{\partial n}{\partial z} - \frac{n_0 q}{k_B T} E \right)_{z=0} . \tag{8}$$

We have furthermore

$$\lim_{z \to \infty} n(z,t) = n_0 , \quad \text{and} \quad \lim_{z \to \infty} E(z,t) = 0 , \tag{9}$$

indicating that very far from the adsorbing surface, the system is not perturbed.

In this problem, an intrinsic length $\Lambda = \sqrt{\varepsilon k_B T / (n_0 q^2)}$, and an intrinsic time $\tau_0 = \Lambda^2/D$, known as Debye's length and Debye's relaxation time, are present. We use now space dimensionless coordinate and time defined by $\zeta = z/\Lambda$, and $\tau = t/\tau_0$ and define the dimensionless quantities $\mathcal{N} = n/n_0$, $\mathcal{S} = \sigma/(n_0 \Lambda)$, and $\mathcal{E} = q \Lambda E/(k_B T)$.

As it is evident from the definition, $\mathcal{N}$ is the bulk density of particles measured in terms of n_0, $\mathcal{S}$ is the surface density of adsorbed particles measured in $n_0 \Lambda$, the surface density of particles in the Debye surface layer, and $\mathcal{E}$ is the electric field measured in terms of v_{th}/Λ, where $v_{th} = k_B T/q$ is the thermal electric voltage.

In terms of $\mathcal{N}$ and $\mathcal{E}$, equations (5) and (6) can be rewritten as

$$\frac{\partial \mathcal{N}}{\partial \tau} = \frac{\partial^2 \mathcal{N}}{\partial \zeta^2} - \frac{\partial \mathcal{E}}{\partial \zeta} , \tag{10}$$

$$\frac{\partial \mathcal{E}}{\partial \zeta} = \mathcal{N} - 1 , \tag{11}$$

and the boundary conditions (7), taking into account (8), becomes

$$\mathcal{S}(\tau) = \mathcal{E}(0,\tau) , \quad \frac{d\mathcal{S}}{d\tau} = \left(\frac{\partial \mathcal{N}}{\partial \zeta} - \mathcal{E} \right)_{\zeta=0} . \tag{12}$$

The two boundary conditions (12) are equivalent each to other, as shown in the appendix.

Finally, the kinetic equation, in terms of reduced quantities, is

$$\frac{d}{d\tau} \mathcal{S}(\tau) = a\mathcal{N}(\tau) - \frac{1}{b} \mathcal{S}(\tau) , \tag{13}$$

where $a = \kappa_a \tau_0 / \Lambda$, $b = \tau_a / \tau_0$ and $\mathcal{N}(\tau) \equiv \mathcal{N}(0, \tau)$.[4] From the definition of a it is evident that in the problem under consideration, there is an intrinsic adsorption coefficient given by Λ / τ_0.

In the following, we look for a solution to the problem of the type

$$\mathcal{H}(\zeta, \tau) = \mathcal{H}_{\mathrm{eq}}(\zeta) + \mathcal{H}_{\mathrm{tr}}(\zeta, \tau) , \tag{14}$$

where $\mathcal{H} \equiv \mathcal{N}$, $\mathcal{E}$, or $\mathcal{S}$, and the subscripts 'eq' and 'tr' refer to the equilibrium and transient components.

We assume that the adsorption phenomenon begins at $\tau = 0$. In this case, we have the obvious initial conditions

$$\mathcal{N}(\zeta, 0) = 1 , \quad \mathcal{E}(\zeta, 0) = 0, \quad \mathcal{S}(0) = 0 . \tag{15}$$

Furthermore, for $\tau \to \infty$ the system has to be described by the equilibrium components, and hence

$$\lim_{\tau \to \infty} \mathcal{H}(\zeta, \tau) = \mathcal{H}_{\mathrm{eq}}(\zeta) , \tag{16}$$

for all ζ. It follows that the transient components have to be such that

$$\begin{aligned} \mathcal{N}_{\mathrm{tr}}(\zeta, 0) &= 1 - \mathcal{N}_{\mathrm{eq}}(\zeta) , \\ \mathcal{E}_{\mathrm{tr}}(\zeta, 0) &= -\mathcal{E}_{\mathrm{eq}}(\zeta) , \\ \mathcal{S}_{\mathrm{tr}}(0) &= -\mathcal{S}_{\mathrm{eq}} , \end{aligned} \tag{17}$$

derived by (15), and

$$\lim_{\tau \to \infty} \mathcal{H}_{\mathrm{tr}}(\zeta, \tau) = 0 , \tag{18}$$

for all ζ, derived by (16).

Finally, the system for $\zeta \to \infty$ is not perturbed, and hence

$$\lim_{\zeta \to \infty} \mathcal{N}(\zeta, \tau) = 1 , \quad \text{and} \quad \lim_{\zeta \to \infty} \mathcal{E}(\zeta, \tau) = 0 . \tag{19}$$

These conditions imply, in particular,

$$\lim_{\zeta \to \infty} \mathcal{N}_{\mathrm{eq}}(\zeta) = 1 , \quad \text{and} \quad \lim_{\zeta \to \infty} \mathcal{E}_{\mathrm{eq}}(\zeta) = 0 , \tag{20}$$

and, consequently

$$\lim_{\zeta \to \infty} \mathcal{N}_{\mathrm{tr}}(\zeta, \tau) = 0, \quad \text{and} \quad \lim_{\zeta \to \infty} \mathcal{E}_{\mathrm{tr}}(\zeta, \tau) = 0 . \tag{21}$$

In the following, we will consider the equilibrium and transient components separately.

3. Half space

We consider first the half-space limit, in which the sample occupies the region $\zeta \geqslant 0$ and the adsorbing surface is in $\zeta = 0$.

---

[4] Assuming $\varepsilon \sim 80\varepsilon_0$, $n_0 \sim 10^{22} \, \mathrm{m}^{-3}$, and $D \sim 10^{-9} \, \mathrm{m}^2 \, \mathrm{s}^{-1}$, corresponding to a moderate concentration of ions in water, we get $\Lambda \sim 10^{-7} \, \mathrm{m}$, and $\tau_0 \sim 10^{-5} \, \mathrm{s}$. Since $\tau \sim 1 \, \mathrm{s}$, [19], $b \gg 1$.

3.1. Equilibrium components

The equilibrium components are solutions of the system of ordinary differential equations

$$\frac{d^2 \mathcal{N}_{eq}}{d\zeta^2} - \frac{d\mathcal{E}_{eq}}{d\zeta} = 0 , \tag{22}$$

$$\frac{d\mathcal{E}_{eq}}{d\zeta} = \mathcal{N}_{eq}(\zeta) - 1 , \tag{23}$$

derived by equations (10) and (11). A simple calculation, taking into account (20), gives

$$\mathcal{N}_{eq}(\zeta) = \mathcal{A}_{eq} e^{-\zeta} + 1 , \tag{24}$$

$$\mathcal{E}_{eq}(\zeta) = -\mathcal{A}_{eq} e^{-\zeta} , \tag{25}$$

where $\mathcal{A}_{eq}$ is an integration constant to be determined by the boundary conditions (12). The surface density of adsorbed particles, in the equilibrium state, $\mathcal{S}_{eq}$, from (13), is given by

$$\mathcal{S}_{eq} = ab\mathcal{N}_{eq} , \tag{26}$$

where $\mathcal{N}_{eq} \equiv \mathcal{N}_{eq}(0)$.

In this framework, the second boundary condition (12) is identically satisfied, and the first gives $\mathcal{A}_{eq} = -ab/(1+ab)$.

Therefore, the equilibrium components are

$$\mathcal{N}_{eq}(\zeta) = 1 - \frac{ab}{1+ab} e^{-\zeta} , \tag{27}$$

$$\mathcal{E}_{eq}(\zeta) = \frac{ab}{1+ab} e^{-\zeta} , \tag{28}$$

and

$$\mathcal{S}_{eq} = \frac{ab}{1+ab} , \tag{29}$$

in dimensionless form.

3.2. Transient components

The transient components are solutions of the partial differential equations

$$\frac{\partial \mathcal{N}_{tr}}{\partial \tau} = \frac{\partial^2 \mathcal{N}_{tr}}{\partial \zeta^2} - \frac{\partial \mathcal{E}_{tr}}{\partial \zeta} , \tag{30}$$

$$\frac{\partial \mathcal{E}_{tr}}{\partial \zeta} = \mathcal{N}_{tr} . \tag{31}$$

The transient component of the surface density of the adsorbed is given by

$$\frac{d}{d\tau} \mathcal{S}_{tr}(\tau) = a\mathcal{N}_{tr}(\tau) - \frac{1}{b} \mathcal{S}_{tr}(\tau) . \tag{32}$$

Substituting (31) into (30), we get

$$\frac{\partial \mathcal{N}_{tr}}{\partial \tau} = \frac{\partial^2 \mathcal{N}_{tr}}{\partial \zeta^2} - \mathcal{N}_{tr} . \tag{33}$$

The transient components have to satisfy the initial conditions (17) and the boundary conditions, at the interface $\zeta = 0$, given by

$$\mathcal{S}_{\text{tr}}(\tau) = \mathcal{E}_{\text{tr}}(0, \tau) \ , \quad \frac{d\mathcal{S}_{\text{tr}}}{d\tau} = \left(\frac{\partial \mathcal{N}_{\text{tr}}}{\partial \zeta} - \mathcal{E}_{\text{tr}} \right)_{\zeta=0} . \tag{34}$$

We look for a solution of the type

$$\mathcal{N}_{\text{tr}}(\zeta, \tau) = \phi(\zeta) \, e^{-\tau/\mathcal{T}} \ ,$$
$$\mathcal{E}_{\text{tr}}(\zeta, \tau) = \psi(\zeta) \, e^{-\tau/\mathcal{T}} \ , \tag{35}$$
$$S_{\text{tr}}(\tau) = \mathcal{C} \, e^{-\tau/\mathcal{T}} \ ,$$

where $\mathcal{T}$ is the relaxation time we are looking for, and $\mathcal{C}$ a constant to be determined. As usual in relaxation problems, it is important the longest relaxation time [20]. In this section, we will limit our consideration to $\mathcal{T} \gg 1$, in dimensionless units, that corresponds to the case in which the actual relaxation time, in absolut units, is very large with respect to τ_0. A full analysis of the relaxation phenomenon is discussed in the next section, where the sample is assumed in the shape of a slab.

A simple calculation gives

$$\phi(\zeta) = \mathcal{A}_{\text{tr}} e^{-\beta\zeta} \ , \tag{36}$$

$$\psi(\zeta) = -\frac{\mathcal{A}_{\text{tr}}}{\beta} \, e^{-\beta\zeta} \ , \tag{37}$$

so that

$$\mathcal{N}_{\text{tr}}(\zeta, \tau) = \mathcal{A}_{\text{tr}} e^{-\beta\zeta - \tau/\mathcal{T}} \ , \tag{38}$$

$$\mathcal{E}_{\text{tr}}(\zeta, \tau) = -\frac{\mathcal{A}_{\text{tr}}}{\beta} \, e^{-\beta\zeta - \tau/\mathcal{T}} \ , \tag{39}$$

where $\beta = \sqrt{1 - 1/\mathcal{T}}$.

From the kinetic equation (32) and the first boundary condition (34) we finally get

$$\mathcal{C} = \frac{a}{1/b - 1/\mathcal{T}} \mathcal{A}_{\text{tr}} \ , \quad \text{and} \quad \mathcal{C} = -\frac{1}{\beta} \mathcal{A}_{\text{tr}} \ , \tag{40}$$

from which it follows the compatibility condition

$$\beta = \frac{1}{a} \left(\frac{1}{\mathcal{T}} - \frac{1}{b} \right) \ . \tag{41}$$

This last relation shows that the relaxation time is such that $1 \leqslant \mathcal{T} \leqslant b$. When β is given by (41) the second boundary condition (34) is identically verified.

Since it is expected that $\mathcal{T} \gg 1$, then $\beta \sim 1$, and from (41) we obtain for the longest relaxation time the approximated expression

$$\mathcal{T} = \frac{b}{1 + ab} \ , \tag{42}$$

where a and b are the dimensionless absorption coefficient and desorption time. Taking into account that $a = \kappa_a \tau_0 / \Lambda$, and $b = \tau_a / \tau_0$, where $\kappa_a, \tau_a, \Lambda$ and τ_0 are, respectively, the adsorption coefficient, the desorption time, the length of Debye, and the Debye relaxation time, in

absolute units, the relaxation time $\mathcal{T}_a = \tau_0 \mathcal{T}$ is given by

$$\mathcal{T}_a = \frac{\tau_a}{1 + \kappa_a \tau_a / \Lambda} . \tag{43}$$

In the limit $\kappa_a \tau_a \ll \Lambda$, $\mathcal{T}_a \sim \tau_a$. This means that the evolution of the system just depends on the desorption time. In other words, the system follows adiabatically the variation of the adsorption phenomenon of the surfaces [21]. In the other limit where $\kappa_a \tau_a \gg \Lambda$, $\mathcal{T}_a \sim \Lambda / \kappa_a$, and the bulk plays an important role in the relaxation.

In the approximation $\beta \sim 1$ the transient components are given by

$$\mathcal{N}_{\text{tr}}(\zeta, \tau) \sim \mathcal{A}_{\text{tr}} e^{-\zeta - \tau / \mathcal{T}} , \tag{44}$$

$$\mathcal{E}_{\text{tr}}(\zeta, \tau) \sim -\mathcal{A}_{\text{tr}} e^{-\zeta - \tau / \mathcal{T}} , \tag{45}$$

and

$$\mathcal{S}_{\text{tr}}(\tau) \sim -\mathcal{A}_{\text{tr}} e^{-\tau / \mathcal{T}} . \tag{46}$$

From the initial condition (17), $\mathcal{A}_{\text{tr}} = -\mathcal{A}_{\text{eq}}$.

The approximated solution of the problem is then

$$\mathcal{N}(\zeta, \tau) = 1 - \frac{ab}{1 + ab} e^{-\zeta} \left(1 - e^{-\tau / \mathcal{T}} \right) ,$$

$$\mathcal{E}(\zeta, \tau) = \frac{ab}{1 + ab} e^{-\zeta} \left(1 - e^{-\tau / \mathcal{T}} \right) , \tag{47}$$

$$\mathcal{S}(\tau) = \frac{ab}{1 + ab} \left(1 - e^{-\tau / \mathcal{T}} \right) .$$

We observe that for $\tau \to \infty$ the transient components vanish, as expected, and for $\tau = 0$ the initial conditions are verified. Furthermore, the spatial dependencies of $\mathcal{N}$ and $\mathcal{E}$ are localized on a surface layer of the order of 1, corresponding to the length of Debye.

3.3. Electrode electric potential

From (47) the dimensionless electric potential profile $\mathcal{V}(\zeta, \tau)$ is found to be

$$\mathcal{V}(\zeta, \tau) = \frac{ab}{1 + ab} e^{-\zeta} \left(1 - e^{-\tau / \mathcal{T}} \right) , \tag{48}$$

assuming that the potential vanishes at the spatial infinity: $\lim_{\zeta \to \infty} \mathcal{V}(\zeta, \tau) \to 0$.

As stated above, the potential changes near the electrode in a surface layer whose thickness is of the order of the Debye length. From equation (48), it follows that the potential of the electrode at $\zeta = 0$, with respect to $\zeta \to \infty$, in the equilibrium state, is

$$\mathcal{V}_0 = \frac{ab}{1 + ab} . \tag{49}$$

Let us consider now a cell in the shape of a slab of thickness $d \gg \Lambda$, limited by two adsorbing electrodes that we denote as 1 and 2. In this situation, the sample can be considered as formed by two half-spaces. That is, the perturbations due to the adsorption effects are localized close to the two electrodes and propagate into the bulk over a length of Debye. The voltage difference between the two electrodes is

$$\Delta \mathcal{V}(\tau) = \mathcal{V}_{01} \left(1 - e^{-\tau / \mathcal{T}_1} \right) - \mathcal{V}_{02} \left(1 - e^{-\tau / \mathcal{T}_2} \right) , \tag{50}$$
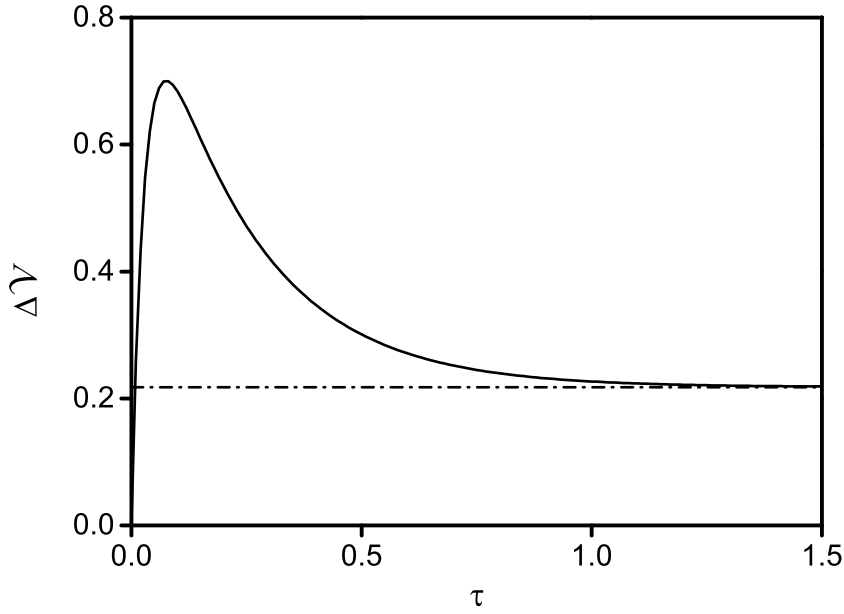
Figure 1. Time dependence of the potential difference, in units $v_{\text{th}} = k_B T/q$, between the electrodes of a cell in the shape of a slab of thickness $d \gg \Lambda$. The horizontal dash-dotted line represents the equilibrium value $\Delta \mathcal{V}_{\text{eq}}$. The numerical values of the parameters are $n_0 = 10^{22} \, \text{m}^{-3}$, $\varepsilon = 6 \cdot \varepsilon_0$, $D = 10^{-9} \, \text{m}^2 \, \text{s}^{-1}$, for which $\Lambda \sim 10^{-8} \, \text{m}$ and $\tau_0 \sim 10^{-6} \, \text{s}$. The adsorbing parameters of the two surfaces are $\kappa_{a_1} = 10^{-6} \, \text{m} \, \text{s}^{-1}$, $\tau_{a_1} = 5 \, \text{s}$, $\kappa_{a_2} = 10^{-7} \, \text{m} \, \text{s}^{-1}$, $\tau_{a_2} = 1 \, \text{s}$, for which $\mathcal{T}_{a1} = 2.8 \cdot 10^{-2} \, \text{s}$ and $\mathcal{T}_{a2} = 22 \cdot 10^{-2} \, \text{s}$.

where $\mathcal{T}_k = b_k/(1 + a_k b_k)$, and $\mathcal{V}_{0k} = a_k b_k/(1 - a_k b_k)$, with $k = 1, 2$. It tends, at equilibrium, to

$$\Delta \mathcal{V}_{\text{eq}} = \mathcal{V}_{01} - \mathcal{V}_{02} = \frac{a_1 b_1}{1 + a_1 b_1} - \frac{a_2 b_2}{1 + a_2 b_2} \, , \tag{51}$$

and vanishes when the two adsorbing surfaces are identical. Remark that the quantity $\Delta \mathcal{V}(\tau)$ tends to $\Delta \mathcal{V}_{\text{eq}}$ in a non-monotonic manner. It has an extremum for $\tau \equiv \tau^*$, given by

$$\tau^* = -\frac{\mathcal{T}_1 \mathcal{T}_2}{\mathcal{T}_1 - \mathcal{T}_2} \log \left(\frac{\mathcal{V}_{01} \mathcal{T}_2}{\mathcal{V}_{02} \mathcal{T}_1} \right) \, , \tag{52}$$

and the value of the extremum is given by

$$\Delta \mathcal{V}_{\text{extr}} = \Delta \mathcal{V}_{\text{eq}} - \frac{\mathcal{V}_{01} \mathcal{T}_2}{\mathcal{V}_{02} \mathcal{T}_1} \left(\exp \left(\frac{\mathcal{T}_2}{\mathcal{T}_1 - \mathcal{T}_2} \right) - \exp \left(\frac{\mathcal{T}_1}{\mathcal{T}_1 - \mathcal{T}_2} \right) \right) \, . \tag{53}$$

The time dependence of $\Delta \mathcal{V}(\tau)$ is shown in figure 1.

4. Symmetric slab

Let us consider the case in which the sample is in the shape of a slab of thickness d, limited by two identical adsorbing surfaces. It is useful to use a Cartesian reference frame with the ζ-axis perpendicular to the limiting surfaces, placed at $\zeta = \pm M$, where $M = d/(2\Lambda)$. In this case, the expected profile of the ionic bulk density is an even function of ζ, i.e. $\mathcal{N}(\zeta) = \mathcal{N}(-\zeta)$, whereas

the electric field is an odd function of ζ, i.e. $\mathcal{E}(\zeta) = -\mathcal{E}(-\zeta)$. Finally, the surface density of adsorbed particles is the same on the two limiting surfaces. We look again for a solution to the problem of the type (14), where the equilibrium and transient components are solutions of equations (22) and (23), and the transient components of equations (30) and (31).

4.1. Equilibrium components

From the kinetic equation at the interface we get, for $\mathcal{S}_{eq}$ the expression $\mathcal{S}_{eq} = ab\mathcal{N}_{eq}(\pm M)$. Furthermore, from equations (22) and (23) we have, taking into account the symmetry of the problem

$$\mathcal{N}_{eq}(\zeta) = 1 + \mathcal{A}_{eq}\cosh(\zeta) \ , \tag{54}$$

$$\mathcal{E}_{eq}(\zeta) = \mathcal{A}_{eq}\sinh(\zeta) \ , \tag{55}$$

where $\mathcal{A}_{eq}$ is an integration constant to be determined by the boundary conditions

$$\mathcal{S}(\tau) = \mp\mathcal{E}(\pm M, \tau) \ , \quad \frac{d\mathcal{S}}{d\tau} = \pm\left(\frac{\partial\mathcal{N}}{\partial\zeta} - \mathcal{E}\right)_{\zeta=\pm M} \ . \tag{56}$$

A simple calculation gives

$$\mathcal{A}_{eq} = -\frac{ab}{\sinh(M) + ab\cosh(M)} \ . \tag{57}$$

The equilibrium components of the solution of the problem are

$$\begin{aligned}
\mathcal{N}_{eq}(\zeta) &= 1 - \frac{ab}{\sinh(M) + ab\cosh(M)}\cosh(\zeta) \ , \\
\mathcal{E}_{eq}(\zeta) &= -\frac{ab}{\sinh(M) + ab\cosh(M)}\sinh(\zeta) \ , \\
\mathcal{S}_{eq} &= \frac{ab}{1 + ab\coth(M)} \ .
\end{aligned} \tag{58}$$

Note that in the limit of $d \to \infty$, that implies $M \to \infty$, from (58) we obtain (29), as expected.

4.2. Transient components

The transient components for the bulk density and electric field are still solutions of equations (30) and (31), and the surface density of adsorbed particles satisfies the kinetic equation (32). The conditions at the limiting surfaces, at $\zeta = \pm M$, are now

$$\mathcal{S}_{tr}(\tau) = \mp\mathcal{E}_{tr}(\pm M, \tau) \ , \quad \frac{d\mathcal{S}_{tr}}{d\tau} = \pm\left(\frac{\partial\mathcal{N}_{tr}}{\partial\zeta} - \mathcal{E}_{tr}\right)_{\zeta=\pm M} \ , \tag{59}$$

and the initial conditions (18) and (21).

We look again for the transient components, solutions of the type (35), and accounting for the symmetry of the problem, we obtain now

$$\mathcal{N}_{tr}(\zeta, \tau) = \mathcal{A}_{tr}\cosh(\beta\zeta)\,e^{-\tau/\mathcal{T}} \ , \tag{60}$$
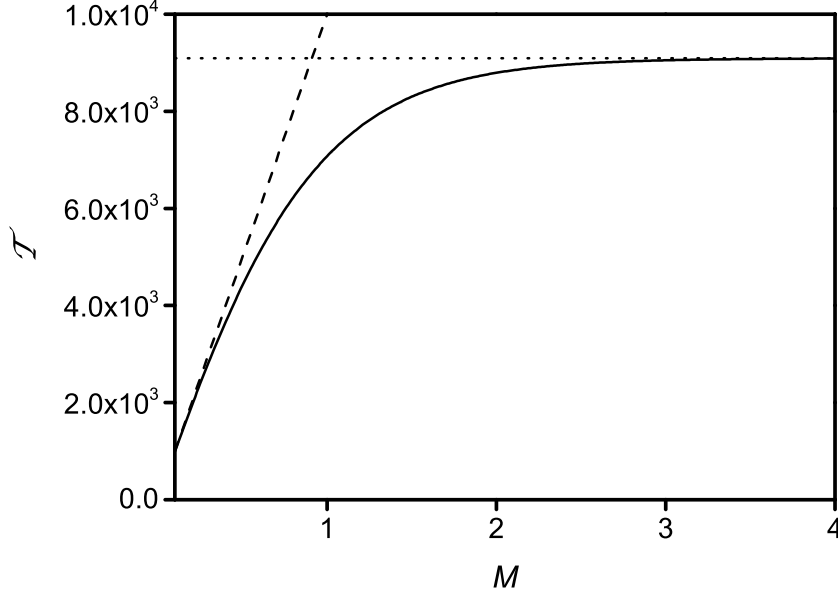
Figure 2. Thickness dependence of the relaxation time $\mathcal{T}$, in units of τ_0, versus the thickness of the sample $M = d/(2\Lambda)$. The full line is the numerical solution of equation (63), the dashed line depicts the approximation $\mathcal{T} = M/a$ valid for small M, while the dotted line depicts the asymptotic value $\mathcal{T} = b/(1 + ab)$ valid for $M \to \infty$. The curves are drawn for $\Lambda = 10^{-7}$ m, $\kappa_a = 10^{-6}$ m s^{-1}, $\tau_a = 1$ s, for ions with diffusion coefficient in the solution $D = 10^{-9}$ m^2 s^{-1}. In this case, $\tau_0 = 10^{-5}$ s, and the dimensionless parameters of the adsorption are $a = 10^{-4}$ and $b = 10^5$. Note that already for $M = 5$ the expression for the relaxation time obtained in the half-space approximation works well.

$$\mathcal{E}_{\mathrm{tr}}(\zeta, \tau) = \frac{\mathcal{A}_{\mathrm{tr}}}{\beta} \sinh(\beta\zeta) e^{-\tau/\mathcal{T}} , \tag{61}$$

where, again, $\beta = \sqrt{1 - 1/\mathcal{T}}$. Finally, from the kinetic equation and the expression for $\mathcal{N}_{\mathrm{tr}}(\zeta, \tau)$ given by (60), we get

$$\mathcal{S}_{\mathrm{tr}}(\tau) = \frac{a\,\mathcal{A}_{\mathrm{tr}}}{1/b - 1/\mathcal{T}} \cosh(\beta M) e^{-\tau/\mathcal{T}} . \tag{62}$$

From the first boundary condition (59) and equation (62), we obtain the compatibility condition

$$\beta \coth(\beta M) = \frac{1}{a}\left(\frac{1}{\mathcal{T}} - \frac{1}{b}\right) , \tag{63}$$

that defines the relaxation times. Note that in the case where $M \to \infty$, from equation (63) we recover equation (41). When equation (63) is satisfied, the second boundary condition (34) is identically satisfied.

In the limit of $M \to 0$, from equation (63) it follows that $\mathcal{T} \sim M/a$, and for $M \to \infty$, $\mathcal{T} \to b/(1 + ab)$. In figure 2 we show, in log-log scale, the dependence of the relaxation time, in units of τ_0, versus the thickness of the sample $M = d/(2\Lambda)$, obtained solving equation (63), and
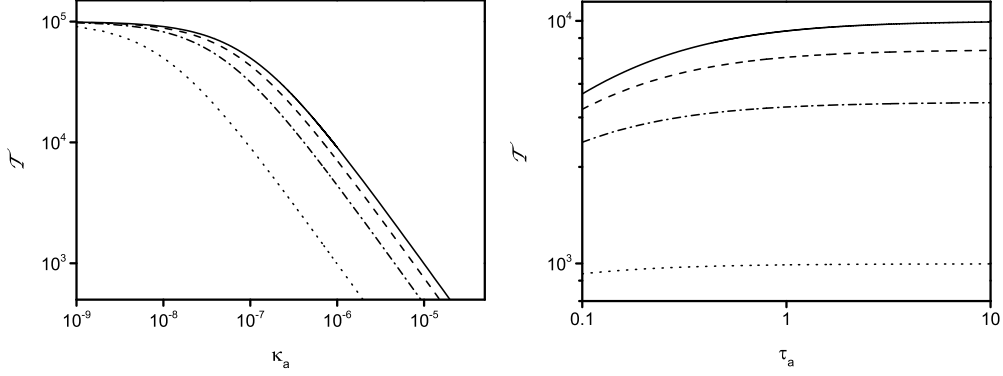
Figure 3. (Left panel). Relaxation time $\mathcal{T}$, in units of τ_0, versus the adsorption coefficient κ_a, in the range $10^{-9}\,\mathrm{m\,s^{-1}} \leqslant \kappa_a \leqslant 10^{-4}\,\mathrm{m\,s^{-1}}$, for $M=1$ (dashed), $M=0.5$ (dash-dotted), $M=0.1$ (dotted), and $\tau_a=1\,\mathrm{s}$. The full line is the asymptotic curve $\mathcal{T}=b/(1+ab)$ valid for $M\to\infty$. (Right panel). Relaxation time $\mathcal{T}$, in units of τ_0, versus the desorption time τ_a, in the range $0.1\,\mathrm{s} \leqslant \tau_a \leqslant 10\,\mathrm{s}$, for $M=1$ (dashed), $M=.5$ (dash-dotted), $M=0.1$ (dotted) and $\kappa_a=10^{-6}\,\mathrm{m\,s^{-1}}$. The full line is again the asymptotic curve $\mathcal{T}=b/(1+ab)$ valid for $M\to\infty$. The other parameters as in figure 2.

the approximate expressions valid for small M, and for large M, got numerically. The critical thickness separating the two regimes of small and large thickness is $M^*=ab/(1+ab)$, or in absolute units, $d^*=2\kappa_a\tau_a/(1+\kappa_a\tau_a/\Lambda)$.

In figure 3 it is shown the dependence of the relaxation time $\mathcal{T}$ on κ_a, in a, and on τ_a, in b. In the limit of large $\mathcal{T}$, $\beta\sim 1$ and the transient components are well approximated by

$$
\begin{aligned}
\mathcal{N}_{\mathrm{tr}}(\zeta,\tau) &= \mathcal{A}_{\mathrm{tr}}\cosh(\zeta)\,e^{-\tau/\mathcal{T}}\,, \\
\mathcal{E}_{\mathrm{tr}}(\zeta,\tau) &= \mathcal{A}_{\mathrm{tr}}\sinh(\zeta)\,e^{-\tau/\mathcal{T}}\,, \\
\mathcal{S}_{\mathrm{tr}}(\tau) &= \frac{a\mathcal{A}_{\mathrm{tr}}}{1/b-1/\mathcal{T}}\cosh(M)\,e^{-\tau/\mathcal{T}}\,.
\end{aligned}
\tag{64}
$$

In this approximation, from the initial conditions $\mathcal{N}_{\mathrm{tr}}(\zeta,0)=1-\mathcal{N}_{\mathrm{eq}}(\zeta)$ it follows that $\mathcal{A}_{\mathrm{tr}}=-\mathcal{A}_{\mathrm{eq}}$, where $\mathcal{A}_{\mathrm{eq}}$ is given by equation (57).

It is of some importance to note that equation (63) has now also solutions for $\mathcal{T}<1$. In this case equation (63) must be rewritten as

$$
\gamma\cot(\gamma M)=\frac{1}{a}\left(\frac{1}{\mathcal{T}}-\frac{1}{b}\right)\,,
\tag{65}
$$

where $\gamma=\sqrt{1/\mathcal{T}-1}$ is a real number. Equation (65) has infinite solutions $\mathcal{T}_m$, and for each mode m of the transient components $\mathcal{N}_{\mathrm{tr},m}$ we have

$$
\mathcal{N}_{\mathrm{tr},m}(\zeta,\tau)=\mathcal{A}_{\mathrm{tr},m}\varphi_m(\zeta)\,e^{-\tau/\mathcal{T}_m}\,,
\tag{66}
$$

where $\varphi_m(\zeta)=\cos(\gamma_m\zeta)$. The complete transient components are given by

$$
\mathcal{N}_{\mathrm{tr}}(\zeta,\tau)=\sum_m \mathcal{A}_{\mathrm{tr},m}\varphi_m(\zeta)\,e^{-\tau/\mathcal{T}_m}\,.
\tag{67}
$$

The set of eigenfunctions $\varphi_m(\zeta)$ can be orthogonalized by means of the Smith technique, and the coefficients $\mathcal{A}_{\mathrm{tr},m}$ determined by means of the initial conditions $\mathcal{N}_{\mathrm{tr}}(\zeta,0)=1-\mathcal{N}_{\mathrm{eq}}(\zeta)$,

where the equilibrium component $\mathcal{N}_{\mathrm{eq}}(\zeta)$ is given by the first equation of (58). In the case of interest, a is a small number, and b is rather large. In this framework from equation (65), $\gamma_m \sim m\pi/M$, where $m = 0, 1, 2, \ldots$, and the corresponding relaxation times are of the order of $\mathcal{T}_m = 1/[1 + (m\pi/M)^2]$. It follows that the eigenfunctions of the problem are $\varphi_m(\zeta) = \cos(m\pi\zeta/M)$, with $-M \leqslant \zeta \leqslant M$, that form a set of orthogonal functions in the range of variability of ζ. We stress that the dimensionless relaxation times smaller than 1, correspond to relaxation times smaller than τ_0. The corresponding modes are fundamental to satisfy the initial boundary conditions. However, in relaxation phenomena is important the longest relaxation time, is rather large with respect to τ_0. In this case equation (63) indicates that $1 \leqslant \mathcal{T} \leqslant b$, i.e. the relaxation time is in the range τ_0, τ_a, and rather close to the desorption time.

5. Asymmetric slab

In this case, the adsorbing surfaces are different. We indicate by a_k and b_k, with $k = 1, 2$, the dimensionless absorption coefficients and desorption times of the surfaces at $\zeta = -M$ and $\zeta = M$, respectively.

5.1. Equilibrium components

In this situation from the kinetic equations we get, the equilibrium components of the surface densities of adsorbed particles on the two limiting surfaces $\mathcal{S}_{\mathrm{tr},1} = a_1 b_1 \mathcal{N}_{\mathrm{eq}}(-M)$, and $\mathcal{S}_{\mathrm{tr},2} = a_2 b_2 \mathcal{N}_{\mathrm{eq}}(M)$.

The solutions of the ordinary differential equations (22) and (23) are, for the present case

$$\mathcal{N}_{\mathrm{eq}}(\zeta) = 1 + \mathcal{A}_{\mathrm{eq}} \cosh(\zeta) + \mathcal{B}_{\mathrm{eq}} \sinh(\zeta) , \tag{68}$$

$$\mathcal{E}_{\mathrm{eq}}(\zeta) = \mathcal{A}_{\mathrm{eq}} \sinh(\zeta) + \mathcal{B}_{\mathrm{eq}} \cosh(\zeta) . \tag{69}$$

The first boundary conditions (56) give now

$$\mathcal{A}_{\mathrm{eq}} = -\frac{(a_1 b_1 + a_2 b_2) \cosh(M) + 2 a_1 b_1 a_2 b_2 \sinh(M)}{(a_1 b_1 + a_2 b_2) \cosh(2M) + (1 + a_1 b_1 a_2 b_2) \sinh(2M)} , \tag{70}$$

$$\mathcal{B}_{\mathrm{eq}} = \frac{(a_1 b_1 - a_2 b_2) \sinh(M)}{(a_1 b_1 + a_2 b_2) \cosh(2M) + (1 + a_1 b_1 a_2 b_2) \sinh(2M)} . \tag{71}$$

In the symmetric case, $a_1 = a_2 = a$ and $b_1 = b_2 = b$, so that we get for $\mathcal{A}_{\mathrm{eq}}$ expression (57) and $\mathcal{B}_{\mathrm{eq}} = 0$, as expected.

5.2. Transient components

We look for transient components of the bulk density of ions and of the electric field of the functional form

$$\mathcal{N}_{\mathrm{tr}}(\zeta, \tau) = \phi_1(\zeta) e^{-\tau/\mathcal{T}_1} + \phi_2(\zeta) e^{-\tau/\mathcal{T}_2} , \tag{72}$$

$$\mathcal{E}_{\mathrm{tr}}(\zeta, \tau) = \psi_1(\zeta) e^{-\tau/\mathcal{T}_1} + \psi_2(\zeta) e^{-\tau/\mathcal{T}_2} , \tag{73}$$

and for the surface density of adsorbed particles on the limiting surfaces

$$\mathcal{S}_{\mathrm{tr},k} = \mathcal{C}_{k1} e^{-\tau/\mathcal{T}_1} + \mathcal{C}_{k2} e^{-\tau/\mathcal{T}_2} , \tag{74}$$

with $k = 1, 2$, where $\mathcal{T}_k$ are the relaxation times of the systems while $\phi_k(\zeta)$ and $\psi_k(\zeta)$ are solutions of the partial differential equations (30) and (31).

From the kinetic equations at the interfaces, we get

$$\left(\frac{1}{b_1} - \frac{1}{\mathcal{T}_k}\right) \mathcal{C}_{1k} = a_1 \, \phi_k(-M) \ , \tag{75}$$

$$\left(\frac{1}{b_2} - \frac{1}{\mathcal{T}_k}\right) \mathcal{C}_{2k} = a_2 \, \phi_k(M) \ , \tag{76}$$

whereas from the first boundary conditions (34) it follows that

$$\mathcal{C}_{1k} = \psi_k(-M) \ , \quad \text{and} \quad \mathcal{C}_{2k} = -\psi_k(M) \ . \tag{77}$$

From equations (75)–(77) we get the compatibility conditions

$$\psi_k(-M) = \frac{a_1}{1/b_1 - 1/\mathcal{T}_k} \, \phi_k(-M) \ , \tag{78}$$

$$\psi_k(M) = -\frac{a_2}{1/b_2 - 1/\mathcal{T}_k} \, \phi_k(M) \ . \tag{79}$$

Proceeding as in the symmetric case we obtain

$$\phi_k(\zeta) = \mathcal{A}_k \cosh(\beta_k \zeta) + \mathcal{B}_k \sinh(\beta_k \zeta) \ , \tag{80}$$

$$\psi_k(\zeta) = \frac{1}{\beta_k} \left([\mathcal{A}_k \sinh(\beta_k \zeta) + \mathcal{B}_k \cosh(\beta_k \zeta)\right) \ , \tag{81}$$

where $\beta_k = \sqrt{1 - 1/\mathcal{T}_k}$. Since, as underlined above, the relaxation times are expected to be of the order of 1 s whereas τ_0 is of the order of μs, the dimensionless relaxation time $\mathcal{T}_k \gg 1$, and hence $\beta_k \sim 1$.

Therefore, functions $\phi_k(\zeta)$ and $\psi_k(\zeta)$ can be approximated in

$$\phi_k(\zeta) = \mathcal{A}_k \cosh(\zeta) + \mathcal{B}_k \sinh(\zeta) \ , \tag{82}$$
$$\psi_k(\zeta) = \mathcal{A}_k \sinh(\zeta) + \mathcal{B}_k \cosh(\zeta) \ . \tag{83}$$

In this approximation equations (78) and (79) give

$$-\tanh(M) + \mathcal{R}_1 = \frac{a_1}{1/b_1 - 1/\mathcal{T}_1} \left(1 - \mathcal{R}_1 \tanh(M)\right) \ , \tag{84}$$

$$-\tanh(M) - \mathcal{R}_1 = \frac{a_2}{1/b_2 - 1/\mathcal{T}_1} \left(1 + \mathcal{R}_1 \tanh(M)\right) \ , \tag{85}$$

$$-\tanh(M) + \mathcal{R}_2 = \frac{a_1}{1/b_1 - 1/\mathcal{T}_2} \left(1 - \mathcal{R}_2 \tanh(M)\right) \ , \tag{86}$$

$$-\tanh(M) - \mathcal{R}_2 = \frac{a_2}{1/b_2 - 1/\mathcal{T}_2} \left(1 + \mathcal{R}_2 \tanh(M)\right) \ , \tag{87}$$

respectively, where $\mathcal{R}_k = \mathcal{B}_k/\mathcal{A}_k$.

From equations (84)–(87) it follows that the relaxation times $\mathcal{T}_k$ are the solutions of the equations

$$-\frac{b_1 \tanh(M) - (a_1 b_1 + \tanh(M)) \mathcal{T}_k}{\mathcal{T}_k - b_1 (1 - a_1 \mathcal{T}_k \tanh(M))} = \frac{b_2 \tanh(M) - (a_2 b_2 - \tanh(M)) \mathcal{T}_k}{\mathcal{T}_k - b_2 (1 - a_2 \mathcal{T}_k \tanh(M))} . \tag{88}$$

The expressions for $\mathcal{T}_k$ obtained by equation (88) are rather complicated. However, in the limit of $M \to \infty$, i.e. for $\tanh(M) \to 1$, they give $\mathcal{T}_k \to b_k/(1 + a_k b_k)$. In the same limit, from (88) we get $\mathcal{R}_1 \to -1$ and $\mathcal{R}_2 \to 1$.

It follows that

$$\phi_k(\zeta) = \mathcal{A}_1 \left(\cosh(\zeta) + (-1)^k \sinh(\zeta) \right) , \tag{89}$$

$$\psi_k(\zeta) = \mathcal{A}_1 \left(\sinh(\zeta) + (-1)^k \cosh(\zeta) \right) . \tag{90}$$

The transient component of the bulk density of ions is then given by

$$\mathcal{N}_{\mathrm{tr}}(\zeta, \tau) = \mathcal{A}_1 (\cosh(\zeta) - \sinh(\zeta)) e^{-\tau/\mathcal{T}_1} + \mathcal{A}_2 (\cosh(\zeta) + \sinh(\zeta)) e^{-\tau/\mathcal{T}_2} . \tag{91}$$

Taking into account the initial condition, $\mathcal{N}_{\mathrm{tr}}(\zeta, 0) = 1 - \mathcal{N}_{\mathrm{eq}}(\zeta)$ and equation (68) we get

$$\mathcal{A}_1 = -\frac{\mathcal{A}_{\mathrm{eq}} + \mathcal{B}_{\mathrm{eq}}}{2}, \quad \mathcal{A}_2 = -\frac{\mathcal{A}_{\mathrm{eq}} - \mathcal{B}_{\mathrm{eq}}}{2} \tag{92}$$

where the expressions of $\mathcal{A}_{\mathrm{eq}}$ and $\mathcal{B}_{\mathrm{eq}}$ have been reported in equations (70) and (71).

In this framework, from equation (74), taking into account equation (77), we get the transient components of the surface densities of the adsorbed particles in

$$\mathcal{S}_{\mathrm{tr},k}(\tau) = \mathcal{C}_{kk} e^{-\tau/\mathcal{T}_k} , \tag{93}$$

indicating that the two adsorbing surfaces relax with the relaxation times $\mathcal{T}_k$.

In the particular case of a symmetric slab from equation (91) we get $\mathcal{A}_1 = \mathcal{A}_2$.

5.3. Half space approximation

The goal of this subsection is to show that in the limit of large M, i.e. $d \gg \Lambda$, the asymmetric slab can be approximated by a system formed by two half-spaces each of them related to the two adsorbing surfaces. As we have seen in section 3, in the approximation of $\beta \sim 1$, the transient component of bulk density profile is given by $\mathcal{N}_{\mathrm{tr}}(\zeta, \tau) = \phi(\zeta) \exp(-\tau/\mathcal{T})$, where

$$\phi(\zeta) = \mathcal{A}_{\mathrm{tr}} e^{-\zeta} , \tag{94}$$

in the case in which the adsorbing surface is in $\zeta = 0$. If the surface is in $\zeta = -M$ equation (94) has to be written in

$$\phi_1(\zeta) = \mathcal{A}_{\mathrm{tr},1} e^{-(M+\zeta)} = \mathcal{A}_{\mathrm{tr},1} e^{-M} (\cosh(\zeta) - \sinh(\zeta)) , \tag{95}$$

holding for $\zeta > -M$.

The same consideration holds for the transient component related to the surface at $\zeta = M$, whose spatial dependence is

$$\phi_2\left(\zeta\right) = \mathcal{A}_{\text{tr},2}\, e^{-(M-\zeta)} = \mathcal{A}_{\text{tr},2} e^{-M}\left(\cosh\left(\zeta\right) + \sinh\left(\zeta\right)\right) , \tag{96}$$

holding for $\zeta < M$.

It follows that the total spatial dependence of the transient component of the bulk density of ions is

$$\begin{aligned}
\mathcal{N}_{\text{tr}}\left(\zeta,\tau\right) &= \mathcal{A}_{\text{tr},1}\, e^{-M}\left(\cosh\left(\zeta\right) - \sinh\left(\zeta\right)\right) e^{-\tau/\mathcal{T}_1} \\
&\quad + \mathcal{A}_{\text{tr},2}\, e^{-M}\left(\cosh\left(\zeta\right) + \sinh\left(\zeta\right)\right) e^{-\tau/\mathcal{T}_2} .
\end{aligned} \tag{97}$$

Solution (97) coincides with equation (91). Hence, we can conclude that in the limit of large M the system can be approximated by two half-spaces, as we have done before to evaluate the time dependence of the difference of electric potential in a cell.

6. Conclusions

The behavior of an electrolytic cell limited by adsorbing surfaces has been analyzed. The equilibrium and transient components of the bulk density of ions, of the electric field, and of the surface density of adsorbed particles have been evaluated in the framework of the Poisson–Nernst–Planck model. The simple case in which the sample occupies the half-space $\zeta \geqslant 0$ has been considered. After that, the more realistic case in which the sample is a slab of finite thickness, symmetric or not, has been investigated. The time dependence of the difference of potential between the two adsorbing electrodes tends to its equilibrium value in a non-monotonic manner.

Some attention has been put on the case in which the sample is a slab. Our analysis indicates that when the thickness of the sample is large with respect to the length of Debye, the sample is well approximated by two half spaces, each of them limited by an adsorbing surface whose adsorption parameters coincide with those of the given sample.

Data availability statement

No new data were created or analysed in this study.

Acknowledgments

Appendix

The goal of this appendix is to show that the boundary conditions (12) are equivalent. In fact, from equation (11), by a derivation with respect to τ we get

$$\frac{\partial^2 \mathcal{E}}{\partial \tau\, \partial \zeta} = \frac{\partial \mathcal{N}}{\partial \tau} , \tag{A.1}$$

that for equation (10), and taking into account the continuity of $\mathcal{E}$, can be rewritten as

$$\frac{\partial}{\partial \zeta} \left[\frac{\partial \mathcal{E}}{\partial \tau} + \left(-\frac{\partial \mathcal{N}}{\partial \zeta} + \mathcal{E} \right) \right] = 0 \,, \tag{A.2}$$

from which it follows that the quantity

$$\frac{\partial \mathcal{E}}{\partial \tau} + \left(-\frac{\partial \mathcal{N}}{\partial \zeta} + \mathcal{E} \right) = f(\tau) \,, \tag{A.3}$$

is position independent. It just represents the total electric current, in which the first contribution is the displacement current, and the second one is the conduction current. If the sample occupies the half-space $\zeta \geqslant 0$, in the limit $\zeta \to \infty$, we have $\mathcal{N} \to 1$ and $\mathcal{E} \to 0$. Consequently $f(\tau) = 0$. In the case of a symmetric slab, for symmetry reasons, the bulk density of ions has an extremum in the middle of the sample, where the electric field vanishes, and again $f(\tau) = 0$. In the case of an asymmetric slab, with the ansatz (80), we get also $f(\tau) = 0$. This can be easily understood by taking into account that, in the case considered in our analysis where only one type of ions is mobile, the electric field has different signs on the two adsorbing surfaces, and that the bulk density of ions has an extremum inside the bulk. Let us call ζ^* the ζ-coordinate of the extremum of $\mathcal{N}$. The curvature of the field vanishes for $\zeta = \zeta^*$, where $\mathcal{E}(\zeta^*, \tau) = 0$. Even in this case, we obtain from expression (A.3) that $f(\tau) = 0$. It follows that

$$\frac{\partial \mathcal{E}}{\partial \tau} = \frac{\partial \mathcal{N}}{\partial \zeta} - \mathcal{E} \,, \tag{A.4}$$

and in particular

$$\left(\frac{\partial \mathcal{E}}{\partial \tau} \right)_{\zeta=0} = \left(\frac{\partial \mathcal{N}}{\partial \zeta} - \mathcal{E} \right)_{\zeta=0} \,. \tag{A.5}$$

As a consequence, boundary conditions (12) are equivalent. The same conclusion holds for the symmetric and asymmetric slabs considered in our analysis.

ORCID iDs

Giovanni Barbero ⓘ https://orcid.org/0000-0002-2282-9536
Yagub Aliyev ⓘ https://orcid.org/0000-0003-1698-4297
Antonio M Scarfone ⓘ https://orcid.org/0000-0001-6699-5889

References

[1] Garrod C 1995 *Statistical Mechanics and Thermodynamics* (Oxford University Press)
[2] Barbero G and Olivero D 2002 *Phys. Rev.* E **65** 031701
[3] Bousiadi S and Lelidis I 2018 *Phys. Lett.* A **382** 127
[4] Macdonald J R 1953 *Phys. Rev.* **92** 4
[5] Trukhan E M 1963 *Sov. Phys. Solid State* **4** 2560 (Engl. transl.)
[6] Atkins P W 2000 *Physical Chemistry* (Oxford University Press)
[7] Maximus B, De Ley E, De Meyere A and Pauwels H 1991 Ion transport in SSFLCD's *Ferroelectrics* **121** 103
[8] Barbero G and Evangelista L R 2006 *Adsorption Phenomena and Anchoring Energy in Nematic Liquid Crystals* (Taylor & Francis)
[9] Ivan K, Kirschner N, Wittmann M, Simon P L, Jakab V, Noszticzius Z, Merkin J H and Scott S K 2002 *Phys. Chem. Chem. Phys.* **4** 1339
[10] Alexe-Ionescu A L, Atasiei R, Dascalu C, Freire F C M and Barbero G 2011 *Appl. Phys. Lett.* **98** 064101

[11] Lelidis I, Alexe-Ionescu A L and Barbero G 2014 *J. Phys. Chem. C* **128** 949
[12] Orazem M E and Tribollet B 2017 *Electrochemical Impedance Spectroscopy* (Wiley)
[13] Lenzi E K, Yednak C A R and Evangelista L R 2010 *Phys. Rev.* E **81** 011116
[14] Santoro P A, de Paula J L, Lenzi E K and Evangelista L R 2011 *Chem. Phys.* **135** 114704
[15] Lenzi E K, de Paula J L, Silva F R G B and Evangelista L R 2013 *J. Phys. Chem.* **117** 23685
[16] Lenzi E K, Lenzi M K, Silva F R G B, Gonçalves G, Rossato R, Zola R S and Evangelista L R 2014
     J. Electroanal. Chem. **712** 82
[17] Landau L D and Lifchitz E M 1960 *Electrodynamics of Continuous Media* (Pergamon)
[18] Masel R I 1996 *Principles of Adsorption and Reaction on Solid Surfaces* (Wiley-Interscience)
[19] Alexe-Ionescu A L, Zaccagnini P, Lamberti A, Pirri C F and Barbero G 2019 *Electrochim. Acta*
     323 134700
[20] Landau L D and Lifchitz E I 1959 *Fluid Mechanics* (Pergamon)
[21] Barbero G, Evangelista L R, Lenzi E K and Scarfone A M 2024 Charge storage and potential
     difference generation in ion adsorbing cells *Eur. Phys. J.* B (accepted)