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Electrode potential and selective ionic adsorption

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ABSTRACT

A simple description of the electrode potential based on the selective ionic adsorption is proposed. It is shown that if the adsorption–desorption coefficients entering in the Langmuir kinetic equation for the adsorption at the limiting surfaces are not identical, a difference of potential between the electrode and the bulk of the solution exists. In the case where the thickness of the sample is large with respect to the length of Debye, this difference of potential depends only on the adsorption–desorption coefficients and on the length of Debye of the ionic solution.

1. Introduction

The detection of bioelectrical signals (Electrocardiogram ECG, Electroencephalogram EEG, Electromyogram EMG, electrical impedance tomography) from the skin surface implies electrical contacts with the skin. This contact must be stable in time and in the presence of hair and relative micro-movements. This is usually obtained by interposing a conductive gel between a metal surface (electrode) and the skin therefore generating an electrode–gel–skin interface with electronic conduction in the metal and ionic conduction in the gel and skin. The phenomena taking place at the metal–gel and gel–skin interfaces are poorly known. Commercially available gels are the results of empirically tested recipes rather than of scientific investigations and design of their electrical properties. The importance of knowing and controlling the properties of this interface derives from the following:

1. a need to have contact impedances that are low and stable in time and possibly resistive (independent from frequency in the bandwidth of the bioelectric signal of interest) [1];
2. a need to have impedances of multiple contacts similar to each other in order to avoid unequal partitions of common mode voltage through the electrode-skin impedance and the amplifier input impedance. Unequal impedances would transform a portion of the common mode voltage into a differential voltage at the input of differential amplifiers and introduce power line interference into the bioelectric signal of interest [2];
3. a need to understand and control the physical mechanisms that generate noise, DC and low frequency voltage fluctuations at the interfaces.

The conductive gel is obtained by mixing an electrolyte solution with a polymer substance such as hydroxyethylcelluose. The issue of metal electrolyte interface is addressed in this work.

When a metal electrode is placed in an electrolyte solution an electrical potential difference is generated between the metal and the solution. This difference depends on the nature of the electrode and on the electrolyte solution. Many phenomena contribute to generate voltage differences and noise at the interface [3–5]. Our aim is to show that a possible mechanism generating such potential is the unbalance of the adsorption–desorption coefficients of the positive and negative ions on the electrode surface.

The presented model is based on the equation of Langmuir for the adsorption–desorption of the ions on the electrode [6]. We assume that the electrolyte can be considered as a dispersion of point-like ionic charges. The density of ions is assumed so small that the ionic recombination can be neglected [7]. In this framework, the number of ions is constant in time. The adsorption energy is identified with the electrostatic interaction energy of a given ion with its electrical image in the electrode, in such a manner that different adsorption energy implies different dimensions of the positive ion from the negative one. In this situation, in the absence of the adsorbing limiting surfaces, the electrolyte is locally and globally neutral. When the electrodes are immersed in the solution, due to the selective ionic adsorption, the surface density of adsorbed positive ions differs from that of the negative ions [8]. Consequently, in the bulk, the electrolyte is locally charged with a given sign, and the electric field is no longer identically zero. Our aim is to evaluate, in the equilibrium situation, the distribution of ions and of the electrical potential. In Section 2

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we present the fundamental equations of the problem, and describe the physical system under investigation. The evaluation of the difference of potential between the electrode and the solution is reported in Section 3. The temporal evolution of the system when the electrodes are immersed in the electrolyte is discussed in Section 4, where the relaxation times governing the evolution are determined. The main result of our Letter are presented in Section 5, devoted to the conclusions.

2. Formulation of the problem

Let us consider a sample in the shape of a slab of thickness d and surface area S. The electrolyte under consideration is assumed to be an isotropic dielectric liquid containing ions. The bulk density of ions in thermodynamical equilibrium, N, is supposed to be very small with respect to the bulk density of the molecules of the liquid, N_0, in such a manner that the ionic recombination can be neglected [7,9]. In the presence of an electric field the ions move, under the effect of the net electrical force, and for diffusion. We indicate by n_p and n_m the actual densities of positive and negative ions, and by V the electrical potential in the sample. The net bulk density of current for the positive, $\mathbf{J}_p$, and negative, $\mathbf{J}_m$, ions are

$$\begin{aligned} \mathbf{J}_p &= -D_p\big[\nabla n_p + (q/K_BT)\nabla V\big], \\ \mathbf{J}_m &= -D_m\big[\nabla n_m - (q/K_BT)\nabla V\big], \end{aligned} \tag{1}$$

where D_p and D_m are the diffusion coefficients for the positive and negative ions, q is the modulus of the ionic charge, and K_BT is the thermal energy. The fundamental equations governing the evolution of n_p, n_m and V are

$$n_{p,t} = -\nabla\cdot\mathbf{J}_p, \qquad n_{m,t} = -\nabla\cdot\mathbf{J}_m, \tag{2}$$

representing the equation of continuity for the two type of ions, and

$$\nabla^2 V = -(q/\varepsilon)(n_p - n_m), \tag{3}$$

which is the equation of Poisson, relating the actual potential, V, to the net charge, $q(n_p - n_m)$. In Eq. (2) the comma means derivation, $g_{,x} = \partial g/\partial x$. The bulk partial differential equations (2), (3), in the case where the limiting surfaces adsorb the ions, have to be solved with the boundary conditions

$$\mathbf{J}_p\cdot\mathbf{v} = \sigma_{p,t}, \qquad \mathbf{J}_m\cdot\mathbf{v} = \sigma_{m,t}, \tag{4}$$

where $\mathbf{v}$ is the geometrical normal to the limiting surface outward directed and σ_p and σ_m the surface densities of the positive and negative ions adsorbed on the surface. In the approximation of Langmuir, the rapidity of adsorbed particles is given by

$$\begin{aligned} \sigma_{p,t} &= \kappa_p n_p - (1/\tau_p)\sigma_p, \\ \sigma_{m,t} &= \kappa_m n_m - (1/\tau_m)\sigma_m, \end{aligned} \tag{5}$$

where κ and τ are the adsorption and desorption coefficients, respectively. Eq. (5) hold in the hypothesis that: (i) all the adsorption sites are equivalent, (ii) the surface is uniform, (iii) only one monolayer of adsorbed particles is possible, and (iv) the probability of a particle being adsorbed is independent of the surface density of particles already adsorbed. These assumptions are reasonable in the limit of small density of ions in thermodynamical equilibrium. If ℓ_p and ℓ_m are typical dimensions of the positive and negative ions, the limit of small adsorption implies that $\sigma_p \ll 1/\ell_p^2$ and $\sigma_m \ll 1/\ell_m^2$. Since in the equilibrium state n_p and n_m are smaller than N, the absorption–desorption coefficients have to be such that $\kappa_p\tau_p \ll 1/(N\ell_p^2)$ and $\kappa_m\tau_m \ll 1/(N\ell_m^2)$, as we assume from now on.

Other approximations for the adsorption kinetic equation have been proposed, and analyzed in the past by Delahay et al. [10–12].

In the following we limit our analysis to the case where the sample is in the shape of a slab of thickness d, whose limiting surfaces, identical in all the aspects, are located at $z = \pm d/2$. In this framework, the bulk differential equations read

$$\begin{aligned} n_{p,t} &= D_p\big[n_{p,z} + (q/K_BT)n_pV_{,z}\big]_{,z}, \\ n_{m,t} &= D_m\big[n_{m,z} - (q/K_BT)n_mV_{,z}\big]_{,z}, \end{aligned} \tag{6}$$

and

$$V_{,zz} = -(q/\varepsilon)(n_p - n_m), \tag{7}$$

that have to be solved with the boundary conditions

$$J_p = \pm\sigma_{p,t}, \quad \text{and} \quad J_m = \pm\sigma_{m,t} \tag{8}$$

at $z = \pm d/2$. The conservation of the number of particles requires that

$$\begin{aligned} &\int_{-d/2}^{d/2} n_p\,dz + 2\sigma_p = Nd, \\ &\int_{-d/2}^{d/2} n_m\,dz + 2\sigma_m = Nd. \end{aligned} \tag{9}$$

Usually the adsorption at the surface is small. By writing the actual bulk density of ions as $n_p = N + \delta n_p$ and $n_m = N + \delta n_m$, it means that the presence of the limiting surfaces is responsible for a small variation of the bulk density of ions with respect to the value, N, corresponding to the thermodynamical equilibrium. In other words, $\delta n_p \ll N$, and $\delta n_m \ll N$. Consequently, V can be considered as an infinitesimal quantity of the same order of δn_p or δn_m. In this approximation the equations governing the problem under investigation are linear, and can be rewritten as

$$\begin{aligned} \delta n_{p,t} &= D_p\big[\delta n_{p,z} + (qN/K_BT)V_{,z}\big]_{,z}, \\ \delta n_{m,t} &= D_m\big[\delta n_{m,z} - (qN/K_BT)V_{,z}\big]_{,z}, \end{aligned} \tag{10}$$

and

$$V_{,zz} = -(q/\varepsilon)(\delta n_p - \delta n_m). \tag{11}$$

For further considerations it is useful to introduce the quantities

$$\begin{aligned} &\mathcal{P} = \frac{\delta n_p}{N}, \qquad \mathcal{M} = \frac{\delta n_m}{N}, \qquad \mathcal{U} = \frac{qV}{K_BT}, \\ &\mathcal{S}_p = \frac{\sigma_p}{N}, \quad \text{and} \quad \mathcal{S}_m = \frac{\sigma_m}{N}. \end{aligned} \tag{12}$$

Using Eqs. (12), the fundamental equations of the problem are

$$\begin{aligned} \mathcal{P}_{,zz} &= D_p[\mathcal{P}_{,z} + \mathcal{U}_{,z}]_{,z}, \\ \mathcal{M}_{,zz} &= D_m[\mathcal{M}_{,z} - \mathcal{U}_{,z}]_{,z} \end{aligned} \tag{13}$$

and

$$\mathcal{U}_{,zz} = -\frac{1}{2\lambda^2}(\mathcal{P} - \mathcal{M}), \tag{14}$$

where $\lambda = \sqrt{\varepsilon K_BT/(2Nq^2)}$ is the length of Debye. With these symbols the bulk densities of current are

$$\begin{aligned} J_p &= -ND_p(\mathcal{P}_{,z} + \mathcal{U}_{,z}), \\ J_m &= -ND_m(\mathcal{M}_{,z} - \mathcal{U}_{,z}) \end{aligned} \tag{15}$$

and the boundary conditions of the problem, as it follows from Eq. (8), are

$$-D_p(\mathcal{P}_{,z}+\mathcal{U}_{,z})=\pm\mathcal{S}_{p,t},$$

$$-D_m(\mathcal{M}_{,z}-\mathcal{U}_{,z})=\pm\mathcal{S}_{m,t} \tag{16}$$

at $z=\pm d/2$. The conservation of the number of particles, expressed by Eq. (9), with the new reduced variables reads

$$\int_{-d/2}^{d/2}\mathcal{P}\,dz+2\mathcal{S}_p=0,$$

$$\int_{-d/2}^{d/2}\mathcal{M}\,dz+2\mathcal{S}_m=0. \tag{17}$$

We will solve first Eqs. (13), (15) with the boundary conditions (16) in the state of equilibrium, in order to evaluate the difference of potential between the electrode and the bulk. After that temporal evolution of the system will be considered.

3. Difference of potential between the electrode and the bulk

In the state of equilibrium, the variables characterizing the system depend only on the coordinate z. We indicate with p, m, s_p, s_m, and u the quantities of interest in this case. These are solutions of the bulk equations

$$p_{,z}+u_{,z}=H_p, \qquad m_{,z}-u_{,z}=H_m \tag{18}$$

and

$$u_{,zz}=-\frac{1}{2\lambda^2}(p-m) \tag{19}$$

where H_p and H_m are two integration constants. The boundary conditions of the equations of equilibrium are

$$p_{,z}+u_{,z}=0, \qquad m_{,z}-u_{,z}=0. \tag{20}$$

From Eqs. (18), (20) it follows that $H_p=H_m=0$, and hence

$$p+u=R_p, \qquad m-u=R_m \tag{21}$$

where R_p and R_m are two new integration constants. By means of Eq. (21) it is possible to rewrite Eq. (19) as

$$u_{,zz}+\frac{1}{\lambda^2}u=-\frac{R}{\lambda^2} \tag{22}$$

where $R=(1/2)(R_p-R_m)$, whose solution, even in z for the symmetry of the problem, is

$$u=A\cos(z/\lambda)-R, \tag{23}$$

where A is an integration constant to be determined. The bulk densities of ions, as it follows from Eq. (21), are

$$p=R-A\cosh(z/\lambda),$$

$$m=R+A\cosh(z/\lambda). \tag{24}$$

In the state of equilibrium, from the kinetic equations at the surfaces, Eq. (5), we get that the surface densities of adsorbed particles are $\sigma_p=\kappa_p\tau_p n_p(d/2)$ and $\sigma_m=\kappa_m\tau_m n_m(d/2)$, that in terms of the reduced variables read

$$s_p=\kappa_p\tau_p\big[1+p(d/2)\big], \quad \text{and} \quad s_m=\kappa_m\tau_m\big[1+m(d/2)\big]. \tag{25}$$

By substituting Eqs. (24), (25) into Eq. (17) we get

$$(d+2\kappa_p\tau_p)R-2(\lambda\sinh\delta+\kappa_p\tau_p\cosh\delta)A=-2\kappa_p\tau_p,$$

$$(d+2\kappa_m\tau_m)R+2(\lambda\sinh\delta+\kappa_m\tau_m\cosh\delta)A=-2\kappa_m\tau_m \tag{26}$$

where $\delta=d/(2\lambda)$. If $\kappa_p\tau_p=\kappa_m\tau_m=\kappa\tau$ from Eq. (26) it follows that $A=0$ and

$$R=-2\frac{\kappa\tau}{d+2\kappa\tau}, \tag{27}$$

as expected. In this case the adsorbing surfaces are at the same potential as the bulk of the solution because there is not selective ionic adsorption. In the general case, where $\kappa_p\tau_p\neq\kappa_m\tau_m$ from Eq. (26) we obtain

$$A=(\kappa_p\tau_p-\kappa_m\tau_m)\gamma d,$$

$$R=-2\gamma\left\{\lambda(\kappa_p\tau_p+\kappa_m\tau_m)\sinh\delta+2\kappa_p\tau_p\kappa_m\tau_m\cosh\delta\right\} \tag{28}$$

where

$$\frac{1}{\gamma}=2d\lambda\sinh\delta+\{d\cosh\delta+2\lambda\sinh\delta\}(\kappa_p\tau_p+\kappa_m\tau_m)$$

$$+4\kappa_p\tau_p\kappa_m\tau_m\cosh\delta. \tag{29}$$

The difference of potential between the electrode and the bulk is, in the limit of $\lambda\ll d$, given by

$$\delta u_V=\frac{\kappa_p\tau_p-\kappa_m\tau_m}{2\lambda+(\kappa_p\tau_p+\kappa_m\tau_m)}. \tag{30}$$

If $\lambda\ll\kappa_p\tau_p+\kappa_m\tau_m$ from Eq. (30) we get

$$\delta u_V=\frac{\kappa_p\tau_p-\kappa_m\tau_m}{\kappa_p\tau_p+\kappa_m\tau_m}, \tag{31}$$

independent of the properties of the solution. In the other limit, where $\lambda\gg\kappa_p\tau_p+\kappa_m\tau_m$ we obtain

$$\delta u_V=\frac{\kappa_p\tau_p-\kappa_m\tau_m}{2\lambda}. \tag{32}$$

In this case $\delta u_V\propto\sqrt{N}$, as it follows from the definition of λ. Under the hypothesis that only the positive ions are adsorbed and $\lambda\ll\kappa_p\tau_p$, from Eq. (31) it follows $\delta u_V=1$. Of course, a difference of potential larger than 1, i.e. in absolute units larger than K_BT/q, in this situation is possible, but our analysis based on the linear equation of the problem is no longer valid. In this case, the difference of potential is not a small quantity and the problem has to be solved by considering the non-linear differential equations (6), (7) with the boundary conditions (8). However, in electrodes used in biomedical applications when the electrode potentials are smaller than the thermal voltage our approximated analysis works well. A more rigorous analysis is under study.

4. Evolution of the system toward the equilibrium state

To investigate the temporal evolution of the system toward the state of equilibrium we proceed in the standard manner by separating the dynamical coordinates in the equilibrium and transient components as follows [13]

$$\mathcal{P}(z,t)=p(z)+P(z,t), \qquad \mathcal{S}_p(t)=s_p+S_p(t),$$

$$\mathcal{M}(z,t)=m(z)+M(z,t), \qquad \mathcal{S}_m(t)=s_m+S_m(t),$$

$$\mathcal{U}(z,t)=u(z)+U(z,t) \tag{33}$$

where $p(z)$, $m(z)$, s_p, s_m and $u(z)$ correspond to the state of equilibrium, and have been determined in the previous section, whereas $P(z,t)$, $M(z,t)$, $S_p(t)$, $S_m(t)$, and $U(z,t)$ represent the transient components of the solution, and will be determined in the present section. Since, by definition,

$$\lim_{t\to\infty}\mathcal{P}(z,t)=p(z) \tag{34}$$

it follows that

$$\lim_{t\to\infty}P(z,t)=0. \tag{35}$$

Furthermore, for $t=0$, before the adsorption–desorption phenomenon begins, $n_p(z,0)=N$, and hence $\mathcal{P}(z,0)=0$, and

$$P(z,0)=-p(z). \tag{36}$$

For what concerns the surface density of particles we have

$$\lim_{t\to\infty} S_p(t) = 0, \tag{37}$$

and

$$S_p(0) = -s_p. \tag{38}$$

Similar considerations hold for $M(z,t)$, $S_m(t)$ and $U(z,t)$. The transient components are solutions of the partial differential equations obtained by Eqs. (13), (15)

$$\begin{aligned} P_{,t} &= D_p(P_{,zz} + U_{,zz}), \\ M_{,t} &= D_m(M_{,zz} - U_{,zz}) \end{aligned} \tag{39}$$

and

$$U_{,zz} = -\frac{P - M}{2\lambda^2} \tag{40}$$

that have to be solved with the temporal boundary conditions

$$P(z,0) = -p(z), \qquad M(z,0) = -m(z), \qquad U(z,0) = -u(z) \tag{41}$$

and

$$\lim_{t\to\infty} P(z,t) = 0, \qquad \lim_{t\to\infty} M(z,t) = 0, \qquad \lim_{t\to\infty} U(z,t) = 0, \tag{42}$$

and with the spatial boundary conditions

$$\begin{aligned} -D_p(P_{,z} + U_{,z}) &= \pm\frac{dS_p}{dt}, \\ -D_m(M_{,z} - U_{,z}) &= \pm\frac{dS_m}{dt} \end{aligned} \tag{43}$$

at $z = \pm d/2$, where

$$\begin{aligned} \frac{dS_p}{dt} &= \kappa_p P - \frac{1}{\tau_p} S_p, \\ \frac{dS_m}{dt} &= \kappa_m M - \frac{1}{\tau_m} S_m \end{aligned} \tag{44}$$

in the approximation of Langmuir.

To determine the temporal evolution of the system we look for a solution of the problem of the type

$$\big[P(z,t), M(z,t), U(z,t)\big] = \big[\psi_p(z), \psi_m(z), \psi_u(z)\big]\exp(-at), \tag{45}$$

where $a > 0$ in order to satisfy the conditions (35) and similar for $M(z,t)$ and $U(z,t)$. By substituting the ansatz (45) into Eqs. (39), (40) we get

$$-a\psi_p = D_p(\psi_p'' + \psi_u), \qquad -a\psi_m = D_m(\psi_m'' - \psi_u'') \tag{46}$$

and

$$\psi_u'' = -\frac{1}{2\lambda^2}(\psi_p - \psi_m), \tag{47}$$

where $y' = dy/dz$. By substituting Eq. (47) into Eqs. (46) we obtain

$$\begin{aligned} &\psi_p'' - \frac{1}{2\lambda^2}\left(1 - 2a\frac{\lambda^2}{D_p}\right)\psi_p + \frac{1}{2\lambda^2}\psi_m = 0, \\ &\psi_m'' - \frac{1}{2\lambda^2}\left(1 - 2a\frac{\lambda^2}{D_m}\right)\psi_m + \frac{1}{2\lambda^2}\psi_p = 0. \end{aligned} \tag{48}$$

For the symmetry of the problem we look for a solution of Eqs. (48) of the type

$$\big[\psi_p(z), \psi_m(z)\big] = (C_p, C_m)\cosh(\mu z), \tag{49}$$

where C_p and C_m are two constants, and $1/\mu$ is a parameter to be determined. With this ansatz, Eqs. (48) can be rewritten as

$$\begin{aligned} &\left\{\mu^2 - \frac{1}{2\lambda^2}\left(1 - 2a\frac{\lambda^2}{D_p}\right)\right\}C_p + \frac{1}{2\lambda^2}C_m = 0, \\ &\frac{1}{2\lambda^2}C_p + \left\{\mu^2 - \frac{1}{2\lambda^2}\left(1 - 2a\frac{\lambda^2}{D_m}\right)\right\}C_m = 0. \end{aligned} \tag{50}$$

System (50) has a solution different from the trivial one only if μ is a solution of the characteristic biquadratic equation

$$\left\{\mu^2 - \frac{1}{2\lambda^2}\left(1 - 2a\frac{\lambda^2}{D_p}\right)\right\}\left\{\mu^2 - \frac{1}{2\lambda^2}\left(1 - 2a\frac{\lambda^2}{D_m}\right)\right\} - \frac{1}{4\lambda^2} = 0. \tag{51}$$

We indicate the solutions of Eq. (51) by $\pm\mu_1$ and $\pm\mu_2$. From the first equation of (50) it follows that

$$C_m = k\big(\mu^2\big)C_p, \tag{52}$$

where

$$k\big(\mu^2\big) = -2\lambda^2\left\{\mu^2 - \frac{1}{2\lambda^2}\left(1 - 2a\frac{\lambda^2}{D_p}\right)\right\}. \tag{53}$$

The solutions $\psi_p(z)$ and $\psi_m(z)$ we are looking for are then

$$\begin{aligned} \psi_p(z) &= C_1\cosh(\mu_1 z) + C_2\cosh(\mu_2 z), \\ \psi_m(z) &= k_1 C_1\cosh(\mu_1 z) + k_2 C_2\cosh(\mu_2 z), \end{aligned} \tag{54}$$

where $k_1 = k(\mu_1^2)$ and $k_2 = k(\mu_2^2)$. By substituting Eqs. (54) into Eq. (47) we get

$$\psi_u''(z) = -\frac{1}{2\lambda^2}\big\{(1 - k_1)C_1\cosh(\mu_1 z) + (1 - k_2)C_2\cosh(\mu_2 z)\big\}. \tag{55}$$

For the symmetry of the problem $\psi_u(z) = \psi_u(-z)$, and from the differential equation (55) we obtain

$$\begin{aligned} \psi_u(z) = A - \frac{1}{2\lambda^2}\bigg\{&\frac{1 - k_1}{\mu_1^2}C_1\cosh(\mu_1 z) \\ &+ \frac{1 - k_2}{\mu_2^2}C_2\cosh(\mu_2 z)\bigg\}. \end{aligned} \tag{56}$$

Let us consider now Eq. (44) when $P(z,t)$ is given by Eq. (45). In this case a simple calculation gives

$$S_p(t) = \alpha_p\exp(-t/\tau_p) + \beta_p\exp(-at) \tag{57}$$

where

$$\beta_p = \frac{\kappa_p\tau_p}{1 - a\tau_p}\psi_p(d/2). \tag{58}$$

A similar calculation gives

$$S_m(t) = \alpha_m\exp(-t/\tau_m) + \beta_m\exp(-at) \tag{59}$$

where

$$\beta_m = \frac{\kappa_m\tau_m}{1 - a\tau_m}\psi_m(d/2). \tag{60}$$

By substituting Eqs. (57), (59) into the boundary conditions (43) we get $\alpha_p = \alpha_m = 0$ and

$$\begin{aligned} D_p(\psi_p' + \psi_m') &= a\frac{\kappa_p\tau_p}{1 - a\tau_p}\psi_p, \\ D_m(\psi_p' - \psi_m') &= a\frac{\kappa_m\tau_m}{1 - a\tau_m}\psi_m \end{aligned} \tag{61}$$

at $z = \pm d/2$. By substituting into Eq. (54) we have the homogeneous system in C_1 and C_2

$$a_{11}C_1 + a_{12}C_2 = 0, \qquad a_{21}C_1 + a_{22}C_2 = 0 \tag{62}$$

where the coefficients are given by

$$
\begin{aligned}
a_{11} &= \mu_1\left(1-\frac{1-k_1}{2\lambda^2\mu_1^2}\right)\sinh(\mu_1 d/2) \\
&\quad -\frac{a}{D_p}\frac{\kappa_p\tau_p}{1-a\tau_p}\cosh(\mu_1 d/2), \\
a_{12} &= \mu_2\left(1-\frac{1-k_2}{2\lambda^2\mu_2^2}\right)\sinh(\mu_2 d/2) \\
&\quad -\frac{a}{D_p}\frac{\kappa_p\tau_p}{1-a\tau_p}\cosh(\mu_2 d/2), \\
a_{21} &= \mu_1\left(k_1-\frac{1-k_1}{2\lambda^2\mu_1^2}\right)\sinh(\mu_1 d/2) \\
&\quad -k_1\frac{a}{D_m}\frac{\kappa_m\tau_m}{1-a\tau_m}\cosh(\mu_1 d/2), \\
a_{22} &= \mu_2\left(k_2-\frac{1-k_2}{2\lambda^2\mu_2^2}\right)\sinh(\mu_2 d/2) \\
&\quad -k_2\frac{a}{D_m}\frac{\kappa_m\tau_m}{1-a\tau_m}\cosh(\mu_2 d/2).
\end{aligned}
\tag{63}
$$

According to elementary algebra, system (62) has a non-trivial solution only if the parameter a appearing in the ansatz (45) is such that

$$
a_{11}a_{22}-a_{12}a_{21}=0. \tag{64}
$$

Eq. (64) determines the relaxation times of the system when the selective adsorption phenomenon is responsible for the difference of potential between the electrode and the bulk of the electrolytic solutions. For the linearity of Eqs. (40), (41) the complete solution of the problem is a superposition of the solution associated to each relaxation time of the type

$$
\begin{aligned}
P(z,t) &= \sum_{a_i}\psi_p(a_i;z)\exp(-a_i t), \\
M(z,t) &= \sum_{a_i}\psi_m(a_i;z)\exp(-a_i t), \\
U(z,t) &= \sum_{a_i}\psi_u(a_i;z)\exp(-a_i t)
\end{aligned}
\tag{65}
$$

where $\psi(a_i;z)$, $\psi_m(a_i;z)$, and $\psi_u(a_i;z)$ are given by Eqs. (54), (56) and a_i is the ith solution of the eigenvalues equation (64). The constants $C_1(a_i)$ and $C_2(a_i)$ are determined by the temporal boundary conditions (41). The evolution toward the equilibrium state, described by $p(z)$, $m(z)$, and $u(z)$ is a multi-relaxation process.

5. Conclusion

We have shown that the selective ionic adsorption by solid electrodes in contact with electrolytic solutions is responsible for a difference of potential between the electrode and the bulk of the solution. Our analysis has been performed in the limit of small adsorption, where the approximation of Langmuir works well. In this limit the bulk ionic density variations induced by the adsorption phenomenon are small, and the fundamental equations of the problem are linear. In this framework, the difference of potential between the electrode and the bulk is of the order of $K_B T/q$. We have also considered the evolution of the system toward the equilibrium state, when the electrodes are in contact with the electrolytic solution, and shown that the evolution is a multi-relaxation phenomenon.

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