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Asymmetric adsorption in an open electrolytic cell

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ABSTRACT

We investigate the effect of adsorption–desorption phenomenon of ions in an asymmetric electrolytic cell at open circuit conditions. Our approach is based on the Poisson–Nernst–Planck theory for electrolytes and the kinetic model of Langmuir for the description of adsorption–desorption phenomena on the electrodes. When the electrodes are immersed into the solution, selective ion adsorption takes place. It is shown, that the selective ion adsorption is responsible for generating an electrical potential difference between the electrodes of the cell. The analytical expressions for the potential difference and for the charge distribution are calculated. Finally, the time evolution of the system is investigated and the relaxation times of the problem are deduced numerically.

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1. Introduction

Specific adsorption of ions at interfaces is an omnipresent phenomenon in a large variety of systems such as biological systems, colloids, geological systems, electrolytic cells, liquid crystals, ionic liquids, gels, etc. [1–6]. Specific adsorption of ions (SAdI) starts when an electrode is immersed in a solution or comes into contact with another medium. The effect is determined by ion–electrode, ion–solvent, and solvent–electrode interactions. The SAdI may drive profound effects on both the electrode and the solution with implications for the system itself and for the detection of signals and therefore to all experimental methods that require the use of electrodes, such as Impedance Spectroscopy, Electrocardiogram, Electromyography [7], Impedance Tomography, Bio-Impedance [8] etc. In ordered systems such as liquid crystals, adsorption affects molecular orientation, stability of orientation via the surface electric field, anchoring energy, dc-switching of liquid crystal displays, electro-optical modulation, etc. [3,9].

The adsorption in a electrolytic cell has been mainly considered under an externally applied voltage for electro-optical effects [10–14] and for experimental methods that require the application of an electric field. Recently, the potential difference between an electrode and the bulk of an electrolytic solution has been discussed in absence of an external field [15]. We think that it is interesting to consider the potential difference between the electrodes of a cell due to SAdI because it is essential to know the charge distribution in the cell prior to the application of any electric field especially when transient effects are considered.

The goal of the present study is to investigate the establishment of a potential difference and of charge distribution between the electrodes of an electrolytic cell when a dielectric liquid is introduced in the cell, in the absence of any external voltage and for an open circuit. This potential difference should arrive when the two electrodes have different properties related to selective adsorption of ions, that is, the electrodes are asymmetric in what concerns SAdI. Our approach is developed in the frame of the Poisson–Nernst–Planck (PNP) theory, that is one of the most used theories describing ion effects in complex systems, and with many applications in physics, chemistry, and biology [1–3,16–25]. The PNP model is based on the coupled continuity equations of each ion type and the Poisson equation for the electric potential. However, the PNP theory has some well known drawbacks, such like the neglect of finite volume effects and the ion–ion interactions [26] which are considered in the frame of a mean field approach. Specific adsorption on the electrodes is taken into account by introducing the adequate boundary conditions for the coupled differential equations of the bulk. In our approach we use the Langmuir model [27,28] to describe the kinetics of adsorption–desorption at the electrodes. In order to respect the limitations of the model we assume adsorption is weak, low enough density of ions, and absence of ion generation–recombination effects [29].

The rest of the present paper is organised as follows. In section 2, we introduce the equations of the PNP model and the adequate BCs according the Langmuir kinetic for adsorption/desorption phenomena. In section 3, we linearise the bulk equations and decompose the charge distributions and the potential at a steady state and a transient component. In Section 4, we calcu-

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late analytically the charge distribution, the potential in the bulk, and the adsorbed charge at the electrodes. A numerical application is performed for the case of a liquid crystal cell with asymmetric electrodes. In Section 5, we treat the transient part of the problem and we show that the evolution towards equilibrium is a multi-relaxation process. The last section of the paper, is devoted to conclusions.

2. Fundamental equations

We consider an electrolytic cell composed by an isotropic dielectric liquid between two flat electrodes in parallel position, the left (L) electrode located at $z = -d/2$ and the right (R) electrode located at $z = +d/2$. The surface area of each electrode is $A_{e\ell}$. The electrolytic solution contains two types of ions denoted p, m, where p stands for cations and m for anions, with charge $\pm q$ respectively. In the present analysis, we assume that the density of ions in thermodynamical equilibrium, N, is very small with respect to the bulk density of the liquid molecules, so that association–dissociation effects can be neglected [29]. The ions are supposed point-like and the system as one-dimensional. In the presence of an electric field $E(z,t)$, the current number densities $j_a(z,t)$ are given by

$$j_a = -D_a \frac{\partial n_a}{\partial z} \pm \mu_a n_a E \tag{1}$$

where $n_a(z,t)$, with $a = p, m$, are the local densities of the ions. D_a are the diffusion coefficients of the ions which are related with their mobilities via the Einstein–Smoluchowski relations: $\mu_a/D_a = q/k_B T$ [27], where k_B is the Boltzmann constant and T the temperature.

The fundamental equations that describe the system under investigation are the bulk continuity and Poisson's equations

$$\frac{\partial n_a}{\partial t} = -\frac{\partial j_a}{\partial z} \tag{2}$$
$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(n_p - n_m)$$

where ε is the dielectric permittivity of the solvent, and $V(z,t)$ the electrical potential in the sample.

2.1. Boundary conditions

The boundary conditions of the problem are defined from the current at the electrodes

$$j_a(\pm d/2, t) = \pm \frac{\mathrm{d}\sigma_a(\pm d/2, t)}{\mathrm{d}t} \tag{3}$$

where σ_a are the surface densities of the adsorbed ions. The sign minus applies for the L-electrode at $-d/2$ and sign plus for the R-electrode at $+d/2$. According to Langmuir kinetic model [9,10,27], at the electrodes holds

$$\frac{\mathrm{d}\sigma_a}{\mathrm{d}t} = k_a n_a - \frac{1}{\tau_a}\sigma_a \tag{4}$$

where k_a and τ_a are the adsorption and desorption coefficients respectively. Langmuir approach holds under the following assumptions: (i) all adsorbing sites are equivalent, (ii) the surface is uniform, (iii) adsorption occurs only in a first layer, and (iv) the probability of a particle being adsorbed is independent of the surface density of particles already adsorbed. These assumptions are valid for low density of ions at thermodynamical equilibrium. Taking into account that $n_a \sim N$, whereas the surface density of adsorbed particles has to be $\sigma_a << \frac{1}{l_a^2}$, it follows that $k_a \tau_a << \frac{1}{N l_a^2}$, where l_a are the typical dimensions of ions [1]. In the present approach, we consider different adsorption and desorption coefficients for each type of ions and for each electrode. We indicate by k_a^i, τ_a^i the adsorption and desorption coefficients respectively at the electrodes, $i = L, R$.

Since we consider asymmetric electrodes the two Eqs. (4) split to four equations that, in compact form (see Appendix A), are written as

$$\frac{d\sigma_a^i}{dt} = k_a^i n_a^i - \frac{\sigma_a^i}{\tau_a^i} \tag{5}$$

Furthermore, the condition on the conservation of the number of ions implies the following equations

$$\sigma_p^R + \sigma_p^L + \int_{-\frac{d}{2}}^{\frac{d}{2}} n_p(z,t)\,\mathrm{d}z = Nd$$

$$\sigma_m^R + \sigma_m^L + \int_{-\frac{d}{2}}^{\frac{d}{2}} n_m(z,t)\,\mathrm{d}z = Nd \tag{6}$$

2.2. Linearisation

The presence of the electrodes in contact with the electrolyte, creates a small variation of the charge densities $\delta n_a << N$, that become $n_a = N + \delta n_a$. Henceforth, we introduce the following reduced quantities $\mathcal{P}(z,t) = \frac{\delta n_p}{N}$, $\mathcal{M}(z,t) = \frac{\delta n_m}{N}$, $\mathcal{U}(z,t) = \frac{V}{V_\theta}$ where $V_\theta = \frac{kT}{q}$ is the thermal voltage. After linearisation, the bulk Eqs. (2), are written as

$$\frac{\partial \mathcal{A}}{\partial t} = -D_a\left(\mathcal{A}'' \pm \mathcal{U}''\right) \tag{7}$$
$$\mathcal{U}'' = -\frac{\mathcal{P} - \mathcal{M}}{2\lambda^2} \tag{8}$$

where the prime means a derivation with respect to z, $\mathcal{A} = \mathcal{P}, \mathcal{M}$, and $\lambda = \sqrt{\frac{\epsilon k_B T}{2Nq^2}}$ is the Debye length. Note that when $\mathcal{A}$ stands for cations, $\mathcal{P}$, then a stands also for cations p. The bulk densities of currents are given from

$$j_a = -N D_a\left(\frac{\partial \mathcal{A}}{\partial z} \pm \frac{\partial \mathcal{U}}{\partial z}\right) \tag{9}$$

In terms of the new quantities, conditions (6) take the form

$$\mathcal{S}_p^R + \mathcal{S}_p^L + \int_{-\frac{d}{2}}^{\frac{d}{2}} \mathcal{P}dz = 0$$

$$\mathcal{S}_m^R + \mathcal{S}_m^L + \int_{-\frac{d}{2}}^{\frac{d}{2}} \mathcal{M}dz = 0 \tag{10}$$

where $\mathcal{S}_a(z,t) = \sigma_a/N$. Eqs. (5) that relate the surface charge density to the ions density at the electrodes, are rewritten as

$$\frac{d\mathcal{S}_a^i}{dt} = k_a^i(1 + \mathcal{A}^i) - \frac{\mathcal{S}_a^i}{\tau_a^i} \tag{11}$$

At this point we decompose the charge distributions and the potential in their steady state and transient components as follows

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