SIMULATION OF ELECTROKINETIC FLOWS THROUGH MEMBRANES USING THE LATTICE BOLTZMANN METHOD

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Abstract. *The transport of ions in a domain containing a membrane is studied using the theory of electrokinetic flows. The equations are solved by the lattice Boltzmann method. The physical characteristics of the phenomena are described, followed by the equations and the numerical solution. Results applied for a biological membrane show good agreement with analytical predictions.*

Keywords*: Eletrokinectic flow, lattice Boltzmann, membranes, Nernst-Planck equation, Poisson equation*

1. INTRODUCTION

Electrokinetic flows can be found in numerous applications such as material manufacturing by electroplating and electrowinning, separation processes, micro-flow devices, batteries, fuel cells, MEMS (micro electro-mechanical systems) and also as the driving force of many biological phenomena (He and Li, 2000). Besides its multi-component nature, it is also necessary to solve the electrostatic interaction and, in some applications, chemical reactions and energy transfer (Wang and Kang, 2010). It is common in this kind of flow the need to solve several spatial and temporal scales requiring the combination of several types of physical theories and multi-scale computational approaches (Capuani *et al*., 2004).

In this article, we are interested in understanding the underlying physics occurring in an electrokinetic flow when a membrane is introduced, separating two domains with different ion concentrations. The focus are the natural or artificial selective double layer membranes, constituted of a hydrophobic core and hydrophilic surfaces. This kind of membrane is found, mainly, in biological systems and synthetic biotechnology applications. There are a number of publications on the macroscopic behavior of the flow near this type of membranes (*e.g*.: Qian and Sejnowski, 1989 ; Lopreore *et al*., 2008; etc.). On the other hand, there is also a great effort in describing the structure of those membranes mainly using experimental techniques, such as x-ray crystallography (Doyle *et al*., 1998; Gouaux and MacKinnon, 2005; etc.); or simulations, as Molecular Dynamic methods (*e.g*. :Benz *et al*., 2005; etc.). Nonwithstand, we have found a lack of methods linking those kinds of approaches.

Here we solve the concentration of ions and electrical potential using the lattice Boltzmann method applied to a system composed of two sub-domains separated by a semi permeable membrane. The membrane properties control the flux of ions across it. This approach can be used in many problems, mainly in nanoscale biotechnology and chemical processes. We believe that by exploring the problem using a mesoscopic method, it may allow the understanding and characterization of new phenomena important for the design and analysis of the many applications.

2. PROBLEM DESCRIPTION

When the fluids near a membrane are aqueous, the ions are linked with the water molecules. As the surface of such membranes possesses hydrophilic surfaces, it maintains the ions near them but not allowing the diffusion through it. On the other hand, this membranes can transport ions by specific channels (in biological membranes, *e.g*., this channels are constituted of proteins spanning the lipid bilayer). These ion channels are specific for each ion and, combined with the isolation properties of the membranes, enables the controlled transport of ions.

The different concentration of ions existed in domains A and B creates an electrical potential across the membrane, V_m, which can be calculated as:

$$V_m = V^B - V^A \tag{1}$$

where V^A and V^B are, respectively, the electrical potential on the membrane surface with domains A and B.

The chemical potential, μ for any ion i can be calculated as:

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i FV \tag{2}$$

where μ_i^0 is the electrical potential of pure i, R is the gases universal constant, T is the system temperature, a_i is the ion activity, z_i is the ion valence and F is the Faraday constant.

For a very thin membrane that permits the passage of only one type of ion i (*i.e.* if there is only one kind of ion channel) the membrane potential, relative to V^A, is equal to the equilibrium potential, E_i, of that ion and is calculated by the Nernst equation:

$$V_m = E_i = \frac{RT}{z_i F} \ln\left(\frac{C_i^A}{C_i^B}\right) \tag{3}$$

where C_i^A and C_i^B are, respectively, the concentration of ion i on the membrane surface with domain A and B.

If the membrane is in rest and if there is other types of ion channels, the net flux through it will be zero and the potential across it is calculated by the Goldman equation:

$$V_m = V_R = \frac{RT}{F} \ln\left(\frac{\sum_i z_i P_i C_i^A}{\sum_i z_i P_i C_i^B}\right) \tag{4}$$

where V_R is called the resting potential and P_i is the velocity in which the ion i cross the membrane. This velocity P_i depends on the quantity and type of ion channels the membrane has.

Generally, biological cells need to have a negative membrane potential. The most common ions involved in the process of maintain such potential are the potassium and sodium, being the exterior of the cell (domain A) more concentrated in sodium, and the interior (domain B), in potassium. As the membrane has much more channels for the passage of potassium, the membrane potential is slightly more positive than it would be if there were no sodium channels. Imagine now a situation where this membrane would have its sodium channels closed. The system would be in a steady state and the membrane potential would be the reversal potential for the potassium. If, suddenly, the sodium channels were opened, that ion would enter the cell. The influx of sodium would happen because of the electric and chemistry driving forces. But, as the sodium enters the cell, the membrane potential will be less negative and so, potassium would be expulsed from it. This process continues until a steady state is achieved. Fig. 1 shows this phenomenon.

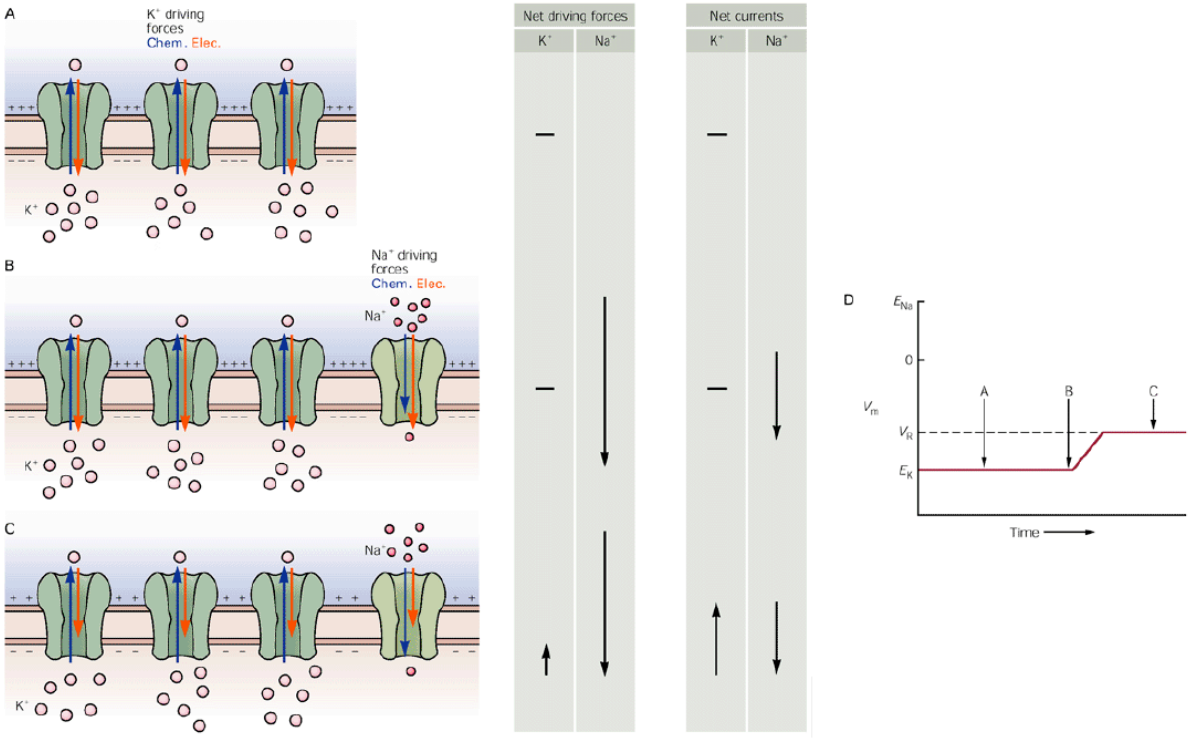

Figure 1. Resting potential establishment. (a) Membrane with only potassium channels. (b) Opening of sodium channels. (c) Steady state re-establishment. (d) Membrane potential *versus* time. Obtained from Kandel *et al.* (2000).

Equations (3) and (4) can only be used to calculate electrical potentials in stationary situations. For the calculation of V_m in dynamic systems we choose to use a capacitive model adapted from Qian and Sejnowski (1989).

$$V_m = V_R + \frac{Fd}{4C_m}\left[\sum_i z_i\left(C_i^B - C_{i,R}^B\right) - \sum_i z_i\left(C_i^A - C_{i,R}^A\right)\right] \tag{5}$$

where d is the cell diameter, C_m is the specific capacitance of the membrane and the subscribe R refers to resting values.

Qian and Sejnowski didn't take the concentration changes on domain A into account. Equation (5) is a modification of the original model to include the influence of those changes.

3. MACROSCOPIC EQUATIONS

We consider that the fluids of domains A and B are electrolytic aqueous dilute solutions of ions. The ion-ion, and ion-dipole interactions are neglected as also heat exchange and advection. Under these conditions, the electrokinetic equations are, respectively, the Nernst-Planck equation and the Poisson equation:

$$\frac{\partial C_i}{\partial t} + \left(\boldsymbol{u}\cdot\nabla\right)C_i = -\nabla\cdot\left[-D_{i,\mathrm{efe}}\nabla C_i - \frac{D_{i,\mathrm{efe}}C_i z_i F}{RT}\nabla V\right] \tag{6}$$

$$\nabla^2 V\left(\boldsymbol{r},t\right) = -\frac{\rho_r(\boldsymbol{r})}{\varepsilon_r\varepsilon_0} = -\frac{e_0 A_v}{\varepsilon_r\varepsilon_0}\sum_i C_i(\boldsymbol{r},t)z_i \tag{7}$$

where $D_{i,\mathrm{efe}}$ is the effective diffusive constant for ion i; V is the local electrical potential; $\boldsymbol{r}$ represents the position, ρ_r is the charge density; ε_r is the dimensionless fluid dielectric constant, ε_0 is the permittivity of the vacuum, e_0 is the charge of a proton and A_v is the Avogadro number.

And the motion equations for the mixture are:

$$\frac{\partial \rho}{\partial t} + \nabla\cdot\left(\rho\boldsymbol{u}\right) = 0 \tag{8}$$

$$\frac{\partial \rho\boldsymbol{u}}{\partial t} + \boldsymbol{u}\cdot\nabla\left(\rho\boldsymbol{u}\right) = -\nabla p + \nabla\cdot\left[\nu\nabla\left(\rho\boldsymbol{u}\right)\right] + \boldsymbol{F} \tag{9}$$

where ρ is the mixture density, $\boldsymbol{u}$ is the macroscopic velocity of the mixture, p is the pressure, ν is the viscosity and $\boldsymbol{F}$ is a source term

4. NUMERICAL SOLUTION

Equations (6) to (9) represent the macroscopic effect of an electrokinetic flow. However, in micro and nano scale problems (such as the neighboring of a cell membrane), that description can be insufficient. Because of that, recently, electrokinetic flows are solved using the lattice Boltzmann method (*e.g.*: He and Li, 2002; Melchionna and Succi, 2004; Capuani *et al*., 2004; Wang and Kang, 2010 among many others). The lattice Boltzmann method is based on evolution equations of particle distribution functions. The computation domain consists of a net, the lattice, composed by sites, in each of them; there are a finite number of particles and velocities that follows collision and propagation rules.

In this work, a two dimensional domain is divided into two sub-domains (the above mentioned domains A and B) separated by the membrane. The corresponding evolution equation for the Nernst-Planck equation can be found in He and Li (2000):

$$f_{i,k}^{+} = f_{i,k} + \frac{\left(f_{i,k}^{eq} - f_{i,k}\right)}{\tau_i} + \frac{z_i F\delta t_i}{RT} f_{i,k}^{eq}\left(\boldsymbol{\xi}_k - \boldsymbol{u}\right)\cdot\nabla V \tag{10}$$

where k represents each velocity direction, $f_{i,k} = f_{i,k}\left(\boldsymbol{r},t\right)$ is the evolution equation for the concentration of ion i in the velocity direction k in position $\boldsymbol{r}$ and time t; $f_{i,k}^{+} = f\left(\boldsymbol{r} + \boldsymbol{\xi}_k\delta_{t,i}, t + \delta_{t,i}\right)$ is the evolution equation for the concentration of ion i in the position $\boldsymbol{r} + \boldsymbol{\xi}\delta t_i$, and time $t + \delta t_i$, *i.e.*, after the propagation, δt_i is the time step for the ion i and $\boldsymbol{\xi}_k$ is the discrete velocity. The equilibrium distribution for a D2Q9 lattice is:

$$f_{i,k}^{eq} = \omega_k C_i\left[1 + 3\boldsymbol{\xi}_k\cdot\boldsymbol{u} + \frac{9}{2}\boldsymbol{\xi}_k\cdot\boldsymbol{u} - \frac{3}{2}\boldsymbol{u}^2\right] \tag{11}$$

where:

$$\omega_k = \begin{cases} 4/9 & \text{for } k = 0 \\ 1/9 & \text{for } k = 1,\ 2,\ 3,\ 4 \\ 1/36 & \text{for } k = 5,\ 6,\ 7,\ 8 \end{cases} \tag{12}$$

and,

$$\boldsymbol{\xi}_k = \begin{cases} 0 & \text{for } k = 0 \\ (\pi/2)\left[\cos(k-1), \sin(k-1)\right] & \text{for } k = 1,\ 2,\ 3,\ 4 \\ \sqrt{2}\left[(\pi/2)\cos(k-5) + \pi/4, (\pi/2)\sin(k-5) + \pi/4\right] & \text{for } k = 5,\ 6,\ 7,\ 8 \end{cases} \tag{13}$$

The relaxation time is related to the diffusivity such as:

$$\tau_i = \frac{3D_i}{2\delta_x} + 0.5 \tag{14}$$

where δ_x is the distance between two sites.

And the concentration is calculated as follows:

$$C_i = \sum_k f_{i,k} \tag{15}$$

For solving the Poisson equation the Chai and Shi (2008) model is used. The evolution equation is equal to:

$$f_{i,k}^{+} = f_{i,k} + \frac{\left(f_{i,k}^{eq} - f_{i,k}\right)}{\tau_V} - \delta t_V \bar{\omega}_k R D_V \tag{16}$$

where τ_V is the relaxation time, δt_V is the time step for the electrical potential, R is the right side term of the Poisson equation and D_V is a artificial diffusion calculated as:

$$D_V = \alpha \frac{\delta x^2}{\delta t_V}\left(\tau_V - \frac{1}{2}\right) \tag{17}$$

For a D2Q9 lattice we found:

$$f_{i,k}^{eq} = \omega_k V \tag{18}$$

$$\omega_k = \begin{cases} -8/9 & \text{for } k = 0 \\ 1/9 & \text{for } k \neq 0 \end{cases} \tag{19}$$

$$\bar{\omega}_k = \begin{cases} 0 & \text{for } k = 0 \\ 1/8 & \text{for } k \neq 0 \end{cases} \tag{20}$$

$$\alpha = 2/3 \tag{21}$$

And the electrical potential is:

$$V = \frac{9}{8}\sum_{k=1}^{8} f_{i,k} \tag{22}$$

The membrane is introduced as an internal boundary condition when the time steps are equal. A flux, J_i (normal to the membrane), is calculated for each ion:

$$J_i = J_i^{\text{chem.}} + J_i^{\text{elec.}} = -\frac{g_i E_i}{z_i F} + \frac{g_i V_m}{z_i F} = g_i \frac{(V_m - E_i)}{z_i F} \tag{23}$$

where g_i is the conductance of the membrane for ion i, related to P_i, and the superscripts "chem." and "elec." accounts, respectively, for the portions of the flux which are induced by chemical and electrical forces.

Based on Eq. (23) particles are added, or subtracted, in the nodes representing the surface of membrane with each side of the domain:

$$C_i^B = C_i^B - J_i \frac{\delta_t}{e} \qquad \text{and} \qquad C_i^A = C_i^A + J_i \frac{\delta_t}{e} \tag{24}$$

where e is the membrane thickness and δ_t is the biggest time step.

In this work, the above mentioned mechanisms are investigated. The advection is negligibly and, so, the Navier-Stokes equation is not solved, *i.e.*, $\boldsymbol{u}$ = 0. Besides, the electrical potential influence on the solution of the ions concentrations, *i.e.*, the source term in equation (10), is not introduced.

5. RESULTS AND DISCUSSION

The method was applied to a hypothetical membrane surrounded by aqueous solutions containing sodium, Na^+, and potassium, K^+. A slightly perturbation is introduced to observe how the steady state is achieved. This perturbation is applied as differences from the resting concentrations. A negative ion is included to maintain the macroscopic eletroneutrality.

Resting values for a typical neuron cell, used here as an example, are showed next on Table 1. A square domain was used with prescribed concentrations on top and bottom boundaries and periodic conditions on lateral boundaries. The particles were introduced in a linear profile with average vales equals to the initial ones. Two types of simulation were made. In the first one, only potassium channels exists, *i.e.*, g_{Na} = 0.0 S/m^2. In a second simulation, it is allowed for

the sodium to cross the membrane, with a condutante of g_{Na} = 0.12 S/m2. The resting potential for the first simulation is - 80.02 mV and, for the second simulation is – 62.68 mV. Other parameters used are: C_m = 0.01 F/m^2; d = 1 μm; e = 34 Å; P_K / P_{Na} = 25; g_K = 3 S/m^2; g_{Na} = 0.12 S/m^2; T = 298.2 K.

Table 1. Initial and resting values.

Species and domain	Resting values C_i (mM)	Initial values C_i (mM)	Species and domain	Resting values C_i (mM)	Initial values C_i (mM)
Potassium on A	6	1	Sodium on A	145	162
Potassium on B	135	140	Sodium on B	18	1
Anions on A	151	151	Anions on B	153	153

Obs: resting values for potassium and sodium were obtained from Zigmond (1999).

Figure 2 shows the potassium molar concentration and electrical potential profiles for the first scenario simulated (absence of sodium channels).

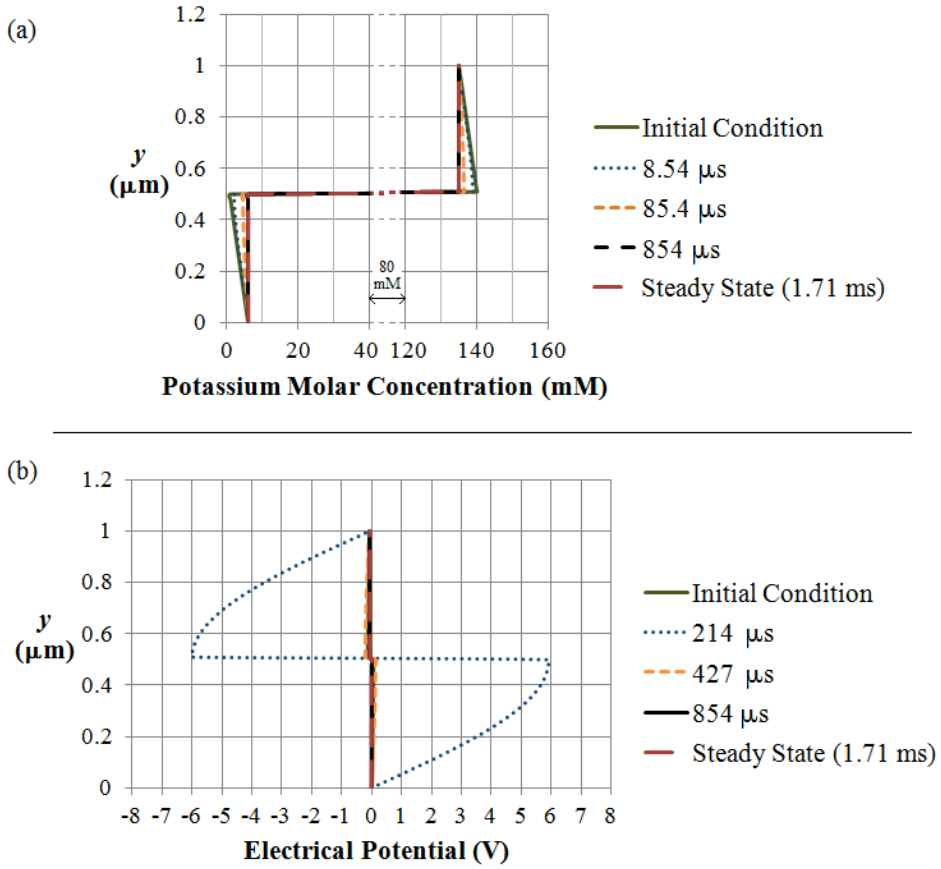

Figure 2. Results of simulation 1: profiles for different time steps until establishment of the steady state. (a) Potassium molar concentration profiles. (b) Electrical potential profiles.

Figure 3 shows the results for the second scenario where there are sodium channels.

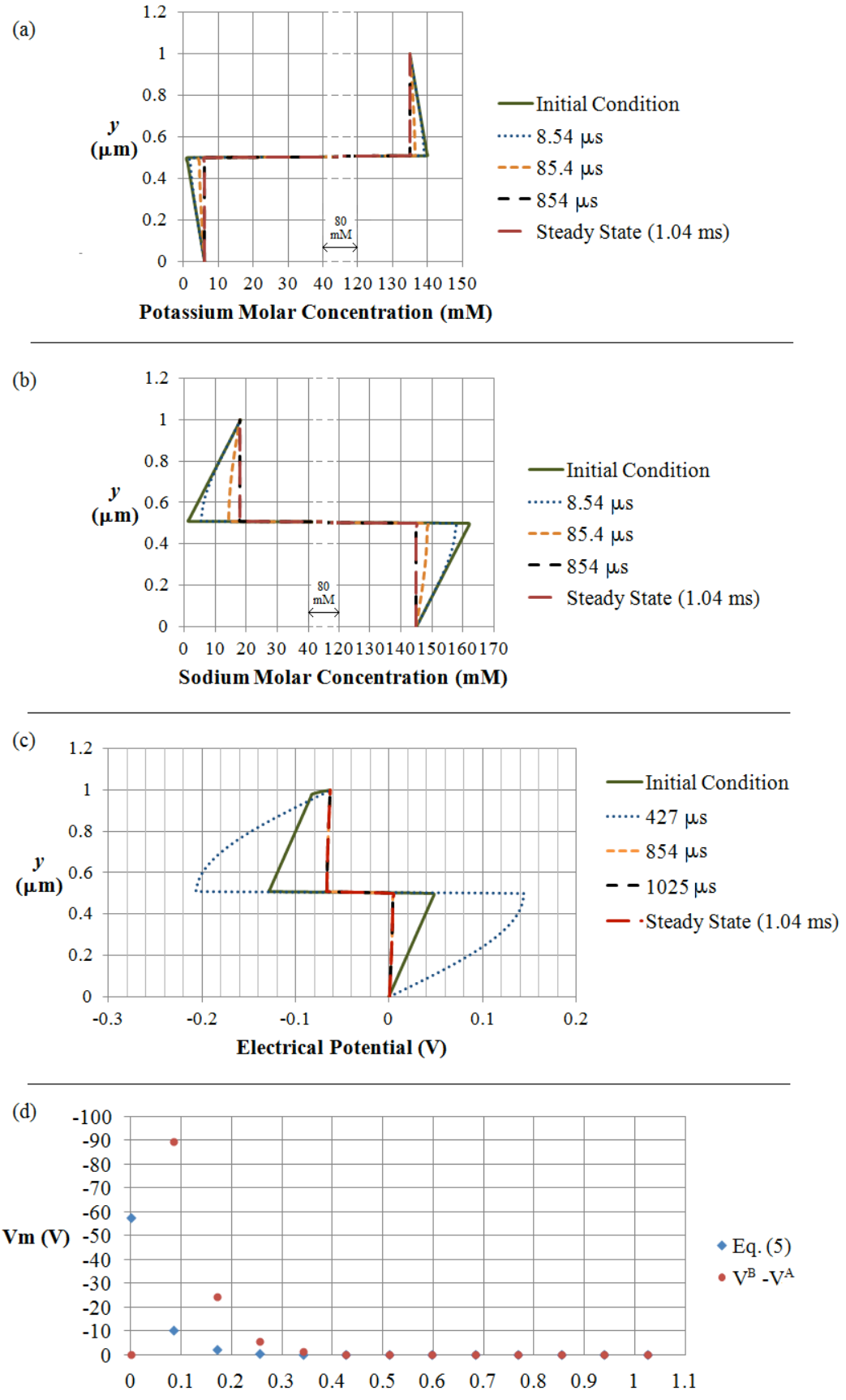

Figure 3. Results of simulation 2: profiles for different time steps until establishment of the steady state. (a) Potassium molar concentration profiles. (b) Sodium molar concentrations profiles. (c) Electrical potential profiles. (d) Evolution of membrane potential with time.

The fluxes of ions across the membrane are showed on Table 2.

Table 2. Fluxes across the membrane.

SIMULATION 1					
		Time = 8.54×10^{-6} s	Time = 8.54×10^{-5} s	Time = 8.54×10^{-4} s	Steady State = 1.71×10^{-3} s
Flux of Potassium (10^{-6} mM.m/s)	Chemical driving force	-3.41	-2.72	-2.49	-2.49
	Electrical driving force	1290	324	2.49	2.49
	Total flux	1290	321	0.000452	~ 0
SIMULATION 2					
		Time = 8.54×10^{-6} s	Time = 8.54×10^{-5} s	Time = 8.54×10^{-4} s	Steady State = 1.04×10^{-3} s
Flux of Potassium (10^{-6} mM.m/s)	Chemical driving force	-3.41	-2.72	-2.49	-2.49
	Electrical driving force	1290	321	2.00	2.00
	Total flux	1290	318	-0.489	-0.489
Flux of Sodium (10^{-6} mM.m/s)	Chemical driving force	0.108	0.0746	0.0667	0.0667
	Electrical driving force	51.6	12.8	0.08	0.0799
	Total flux	51.7	12.9	0.147	0.147

Obs.: positive fluxes are in the direction A to B, *i.e.*, from the exterior to the cell interior.

As it can be seen, the simulations converge to constant concentration and electrical potential profiles, as expected, because the fluxes are very small. Interesting to see is that for the first time steps, the electrical potential diverges. Probably, the concentration perturbations were too big causing those unrealistic values.

Another important result is showed on Fig. (3d). It shows the differences between the membrane potential calculated from Eq. (5) and (1). As the result from Eq. (1) is the real value of the membrane potential, we can infer that the Eq. (5) model is just suitable for membranes near the resting state.

6. CONCLUSION

The results found in table 2 agree with the behavior described by Fig. 1. However, it was expected that, for the steady state of simulation 2, the module of the total flux of potassium should be equal to the module of the total flux of sodium. This difference will be investigated deeply in the future, as so the influence of the electrical potential on the concentration profiles.

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