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Electrostatics of Photosynthetic Reaction Centers in Membranes

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Abstract—**Photosynthetic reaction centers are integral membrane complexes. They have potential application as molecular photovoltaic structures and have been used in diverse technological applications. A three-dimensional electrostatic model of the Photosystem I reaction center (PSI) embedded in a lipid membrane is presented. The potential is obtained by solving the Poisson-Boltzmann equation with the finite element method (FEM). Simulations showing the potential distribution in a vesicle containing PSI reaction centers under different conditions are presented. The results of the simulations are compared with previous findings and a possible application of PSI to provide light activation of voltage-gated ion channels is discussed.**

I. INTRODUCTION

PHOTOSYNTHETIC organisms capture and utilize sunlight by means of membrane protein complexes known as photosynthetic reaction centers. In addition to photosynthesis research, photosynthetic reaction centers have attracted attention from other scientific fields. They have been used as light-driven molecular devices in diverse technological applications [1]-[4]. One of the best known reaction centers, from both a structural and a functional point of view, is the Photosystem I (PSI) from green plants and cyanobacteria. Light activation of PSI causes a net charge separation across the cell membrane, consequently each reaction center can be considered as an electric dipole spanning the membrane with an associated electric potential [5]. Ultimately, our purpose is to efficiently activate denervated muscles, using PSI to provide activation nearby voltage dependent ion channels in the muscle membrane. This possibility was recently suggested in [4], as it was found that PSI triggers movement of calcium in mammalian cells.

Theoretical calculations of the charge separation potential across photosynthetic reaction centers embedded in lipid membranes have been used to interpret empirical observations. The simplest approach estimates the electric potential dividing the amount of light-separated charge by the average capacitance of the membrane [6]. This approximation gives just a rough estimation of the charge separation potential, because the membrane-reaction center system is considered to be uniform dielectric medium. On the other hand, a more sophisticated description of the process has been provided by using continuum electrostatics [7]. Although this approach provides a picture of the potential distribution in a plane perpendicular to the membrane, the light-separated charge is considered to be a uniform membrane surface charge and so, there is a lack of information about the spatial distribution of the electric potential around a single reaction center. This information is necessary, for instance, to evaluate the distance and number of PSI reaction centers surrounding a voltage-gated channel that are required to activate it. Therefore, the aim of this work is to present a more detailed description of the electric potential associated with charge separation when photosynthetic reaction centers are embedded in a lipid membrane.

In particular, a three dimensional electrostatic model of the PSI reaction center in a lipid membrane is presented. The potential is obtained with the Poisson-Boltzmann equation, a three-dimensional nonlinear partial differential equation which is solved with the finite element method (FEM). Simulations are presented, where distributions of the potential across the membrane and the reaction center are obtained for different conditions. Finally, it will be discussed if PSI could trigger the opening of a voltage-gated ion channel in excitable cells.

II. METHODOLOGY

A. The model

A 3-D finite element model capturing the geometric and electrical properties of a PS1 reaction center embedded in a membrane was realized. Using the known structural data of the reaction center, PSI was approximated as a cylinder of 5 nm of radius and 7 nm of height, composed by five stacked cylindrical layers (Fig. 1). Each layer represents a portion of the complex whose relative permittivity (ε_r) is known to be distinct [8]. The reaction center was embedded in a dielectric membrane of 5 nm thickness separating two aqueous compartments. To avoid the use of extremely large dimensions along the plane of the membrane, symmetric boundary conditions were enforced, which also allowed simulating different surface densities of PSI according to the lateral dimensions of the membrane domain.

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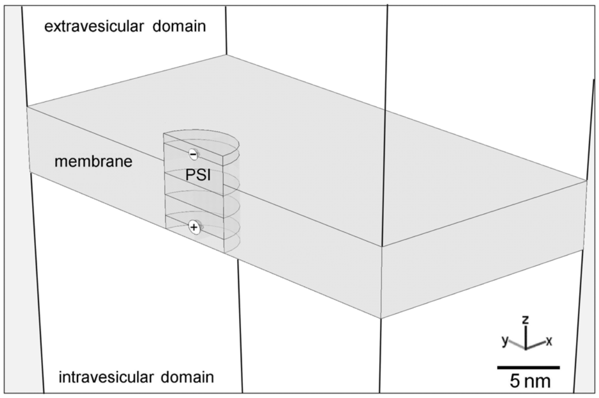

Fig. 1. The drawing shows half section of the model geometry. The extravesicular and intravesicular spaces are not shown entirely to allow displaying the reaction center and membrane geometry in more detail.

The aqueous compartments were modeled as finite size domains located above and below the membrane domain. Those three domains together represent a volumetric section of a spherical vesicle. This geometry allows simulating a special case, where the inner domain is charged.

It was assumed that PSI is illuminated with continuous saturating light and that there are no carriers of charge in the aqueous compartments. This means that PSI is biased in the active state with the absorption of light energy, resulting in a steady-state single charge separation between the charge donor site (also known as P700, a pair of chlorophyll molecules) and the charge acceptor site (also known as F_A/F_B, a pair of iron-sulfur molecules). This situation was modeled as a dipole of point charges, the positive charge was located in the central coordinate of P700 and the negative charge located in the central coordinate of F_A/F_B (Fig. 1).

B. *The Poisson-Boltzmann equation*

The system was considered to be in equilibrium. Therefore the problem reduces to one where only electrostatic interactions occur. To obtain estimates of the electrostatic potential in membrane-electrolyte systems, Poisson-Boltzmann theory has been previously used [9]. The solvent is assumed to be a dielectric medium containing an ionic charge density which is given by a Boltzmann distribution. For the case of a 1:1 electrolyte of monovalent ions, the full nonlinear Poisson-Boltzmann equation in rectangular coordinates is:

$$-\nabla.(\varepsilon\nabla u)+\varepsilon\kappa^2 \sinh u = 2e\rho / kT \quad (1)$$

where ε is the dielectric constant, e is the elementary unit of charge, and kT is Boltzmann's constant times the temperature. In the above equation, ρ is the fixed charge density and κ is the inverse of the Debye-Hückel length which satisfies,

$$\kappa^2 = 2Ie^2 / \varepsilon kT \quad (2)$$

where I is the ionic concentration. When the solvent is a non-ionic medium, $I=0$ and (1) reduces to the Poisson equation.

A dimensionless potential u has also been defined, which is related with the true electrostatic potential ϕ by

$$u = e\phi / kT \quad (3)$$

C. *The solver*

The Poisson-Boltzmann equation was solved with the finite element method (FEM), using a commercial FEM solver (Comsol Multiphysics, Comsol A/S). The electrostatics module was used, where the subdomain equations were adjusted to implement the full Poisson-Boltzmann equation. A non-linear solver in the weak form was used. Using arguments of rotational symmetry, it was possible to realize the model simulating only ¼ of the PSI. Even when the symmetry of the problem would allow reducing the geometry to a bi-dimensional space, the three-dimensional approach was preferred because it will be applicable to more complex geometries and the problem is solvable with relatively simple computer resources.

III. RESULTS

The distribution of electrical potential near a single PSI embedded in a spherical vesicle was calculated. The lateral dimension of the membrane was adjusted to 10 nm, so the surface density of reaction centers was $2.5\text{x}10^{11}$ cm^{-2}. The spatial distribution of the electric potential around the reaction center is shown in Fig. 2 and Fig. 3. The figures show color maps representing the distribution of potential in the y-z plane for x=0. The thick black lines represent equipotential curves traced at the voltage indicated near them. These curves have rotational symmetry around the z axis. Fig. 2 is a simulation using water as aqueous medium, while Fig. 3 shows the result for 0.01 M electrolyte.

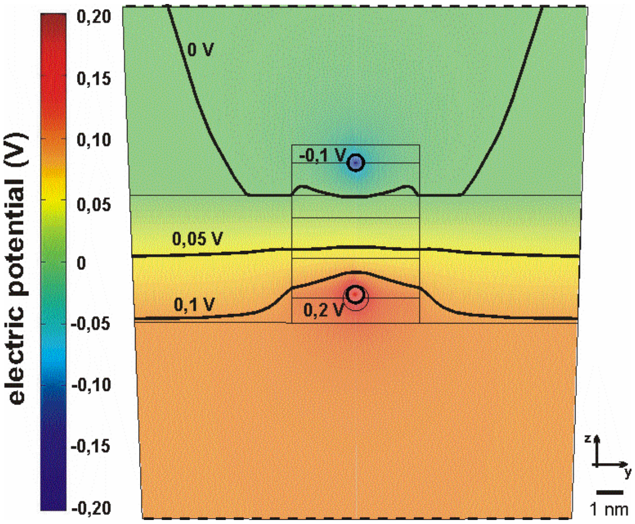

Fig. 2: Potential distribution close to a reaction center inserted in a membrane. Figure shows the y-z plane for x=0. The aqueous compartments were simulated containing water.

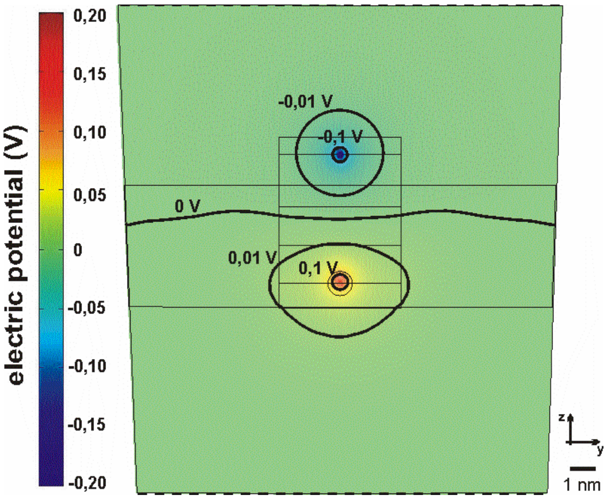

Fig. 3: Potential distribution close to a reaction center inserted in a membrane. Figure shows the y-z plane for x=0. The aqueous compartments were simulated containing an electrolyte of monovalent ions, 0.01 M.

Fig. 4 shows the dependence of electric potential on distance when the aqueous compartments contain a 0.01M electrolyte. Fig. 4a shows the potential through the center of rotational symmetry (x=y=0) where the transmembrane potential reaches the maximum values. Fig. 4b shows the potential through an axis positioned just in the middle of two reaction centers ($x^2+y^2=r^2$, r=10 nm) where the transmembrane potential reaches minimum values.

To study the dependence of the electric potential with the density of reaction centers in the membrane, three different concentrations of PSI were simulated: $1.1\text{x}10^{11}$ cm^{-2}, $1.6\text{x}10^{11}$ cm^{-2} and $2.5\text{x}10^{11}$ cm^{-2}. This was done by adjusting the lateral dimension of the membrane domain in the model to 15 nm, 12.5 nm and 10 nm respectively. It was found that there is a linear relationship between number of reaction centers and the surface potential measured across the membrane. The obtained ratios, per reaction center and for a membrane area of 1 cm^2, are $4.5\text{x}10^{-15}$ V in 0.01 M electrolyte and $2.7\text{x}10^{-13}$ V in water.

IV. DISCUSSION

An electrostatic model of a PSI reaction center inserted in a lipid membrane was presented. First, the spatial distribution of potential was calculated in water and in electrolyte. In both cases, it was found that there is a non-symmetric distribution of the equipotential surfaces across the membrane where the reaction center is inserted, because the charges are located in a non-homogeneous dielectric environment. The potential dissipates faster in the aqueous compartments since these are regions with high dielectric constant, which is consistent with previous observations [9]. In electrolyte, the potential difference is mostly confined to the reaction center, because the charges are screened by the cloud of mobile charges close to the membrane surface, the so called diffuse double layer [10]. This restricts the transmembrane potential to a surface phenomenon. The situation is different in water, where a transmembrane potential is produced. The potential measured between the bulk compartments and for the density of reaction centers presented is about 100 mV. Experimental measurements of potential in PSI proteoliposomes adsorbed in a lipid bilayer and bathed with a non-electrolyte medium provided a peak value of 20 mV [11]. The value is lower than the provided by the model because the density of reaction centers in that case was about 5 times lower.

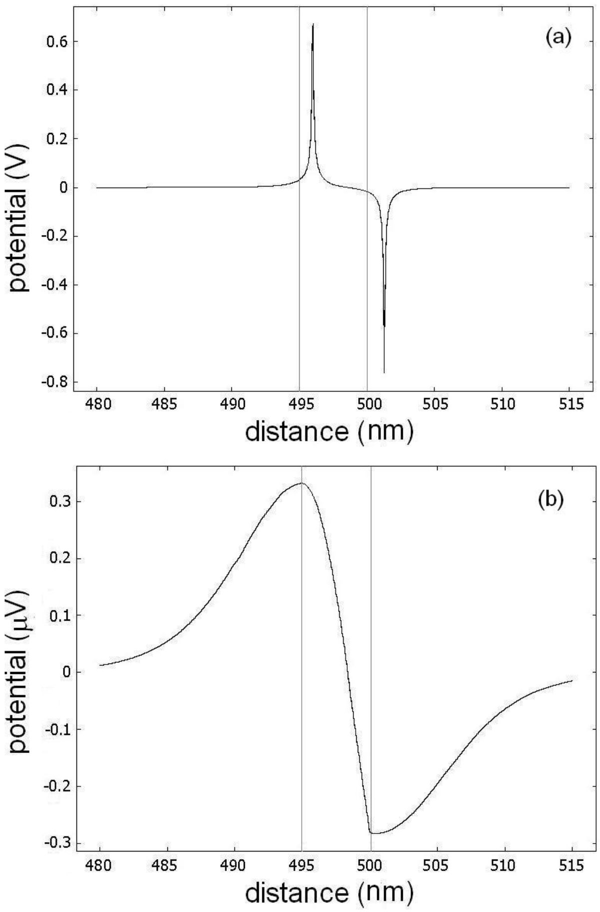

Fig. 4: Potential across a reaction center embedded in a membrane in 0.01 M electrolyte. (a) potential through the axis of rotational symmetry (x=y=0) and (b) potential through an axis located in the middle of two reaction centers ($x^2+y^2=r^2$, r=10 nm). The grey vertical lines in both figures represent the limits of the membrane.

Subsequently, the potential along two axis perpendicular to the membrane were analyzed for the electrolyte case. First, across the central symmetry axis (x=y=0), where the potential difference is maximum. As it is shown in Fig. 4a, the peak value resulted in approximately 1.4 V, close to the open circuit values that have been measured on isolated PSI with Kelvin force microscopy [12]. This potential decays very fast to zero with the distance z. Secondly, across the axis located in the middle of two reaction centers, it is shown in Fig. 4b that the potential difference is restricted mostly to the membrane surface and, for the density of reaction centers presented, is about 0.6 μV. It was also shown that the surface potential depends on the concentration of PSI in a linear fashion.

The above presented results can be used to describe the sequence of events occurring in the membrane when the reaction center is activated by a pulse of light. The results in water can be used to provide a picture of what is happening immediately after the charges have been separated by the reaction center. That is, there is an intense localized electric field across the reaction center due to charge separation between P700 and F_A/F_B. The potential across the charges is about 1.4 V and the transmembrane potential rises up to 100 mV. Then, the results in electrolyte provide a picture to what happens in steady state after the relaxation time of the ionic solution, which is about 5 ns for a 0.01 M concentration. That is, there is an ion redistribution, which energizes the aqueous phases at the boundary. This produces a small concentration jump of ions and a small surface potential in the order of 1 mV.

If we try to extrapolate the results to a situation where the reaction center is inserted in a cell membrane bathed with physiological concentration of ions, the conditions will be somehow similar to what was presented for the electrolyte environment. The activation of the reaction centers with light will produce a short-lasting localized perturbation of the membrane potential and a sustained but very low surface potential modification. It is very improbable that this situation could lead to the opening of voltage activated ion channels, which in turn require a sustained depolarization in the order of tens of mV to open. The cause by which the movement of calcium ions induced by PSI activation in retinoblastoma cells might not be an opening of voltage-activated ion channels but might be associated with secondary mechanisms as discussed in [4]. Another possibility is the existence of a surface potential gating mechanism, like the one described in [13] related to the early receptor potential produced by bacteriorhodopsin.

In conclusion, a model was presented which gives a detailed description of the electric potential associated with charge separation when photosynthetic reaction centers are embedded in a lipid membrane. Although further experimental studies need to be conducted in order to validate these approximations, the results will provide valuable help in setting the experimental design of applications involving photosynthetic reaction centers as photovoltaic devices.

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