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Distribution of the electric field in an axially symmetric pore

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Abstract

The membrane system with a non-cylindrical pore has been considered. The internal surface of a pore has been approximated by a hyperboloid of rotation. A simple analytical expression for the steady state electric potential distribution has been found. It has been shown that the obtained expression appeared to be exact for two limiting cases of cylindrical pores of a small radius and non-cylindrical pores of a large radius. This gives an opportunity to describe pore evolution when both its size and its shape are being changed. An example of pore evolution in a bilayer lipid membrane is considered, and the different variants of evolution are discussed.

1. Introduction

While studying ion transport through homogeneous biological and artificial membranes under the influence of an electric field, one usually suggests that the transport is carried out by defects existing in the membrane, because the membrane itself is a dielectric and can be considered as an insulator. If the membrane does not include any additional macromolecules, for example protein, electrical characteristics of a membrane are mainly defined by the number of pores, their size and their shape.

Analysing porous structures, one usually considers only the first two factors, while the shape is perceived to be given [1]. Comparatively narrow cylindrical pores, whose diameter is much less than their length, are usually studied. In this case the electrical field can be considered homogeneous over the entire volume of a pore, and errors connected with the change in the electric field near the ends of the cylinder can be neglected [1]. The other particular case is the case of wide, short pores. In the limit it becomes a problem on the passage of an electric current through a round hole in an unlimited non-conducting plane [2].

In ref. 3 pores of a somewhat more complicated shape were studied. It was suggested that a pore consists of three pieces: the middle portion is a normal cylindrical pore; the two others are transition pieces, where the electric field changes linearly from the volume value to a constant value inside the pore. Comparison of this rather simple theoretical model with the experimental data allows one to evaluate the size of each inlet piece. For pores in lipid membranes it varies from 15% to 33% of a membrane thickness. In addition, the electrical resistance appeared to be extremely sensitive to the shape of a pore: a change in the transition site size of 10% results in resistance change of more than one order of magnitude.

This means that the pore shape plays a decisive role, but not a minor role, as was suggested earlier. In addition, the assumption that there are inlet sites of a relatively small size is not correct, because those sites occupy up to 2/3 of the membrane thickness. That is why it is to be supposed that all the inner surface of a pore makes up just one curvilinear surface, narrowing as the centre of a membrane is approached.

The most obvious approximation for a pore of such a shape is a toroidal surface. One assumed that the inner surface of a pore is part of a torus ("inner" part), which merges with the plane surfaces of a membrane. Calculation of the elastic energy for the toroidal surface is rather simple [4]. At the same time, the calculation of the electric properties for a toroidal geometry is much more complicated. For calculation of the resistance in ref. 4 it was assumed that equipotential sur-

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faces inside the pore are planes, parallel to the membrane surface. The current flow near the pore wall is parallel to its surface, which is why in this system the current is not perpendicular to the equipotential surfaces (at least near the wall). This problem was overcome in ref. 5 where equipotential surfaces were chosen as a set of spherical fragments, perpendicular to the pore surface. This gave more accurate expressions for the resistance of the whole pore and for the tension of the electric field near walls. They also give the first approach to the problem of studying the pores of different shapes. They take into account that the pore can be constructed from a cylindrical part in the middle, combined with the toroidal surfaces and the latter are merged with the plane surface of the membrane. At the same time the main model difficulty is still here. Both Nanavati *et al.* [4] and Pastushenko and Petrov [5] took some basic set of simple equipotential surfaces, while the consequent approach requires finding the potential distribution (and equipotential surfaces) from the solution of the Laplace equation with appropriate boundary conditions. Moreover, it can be easily shown that a set of spheres cannot be equipotential surfaces in a system with toroidal boundaries.

In the present paper the distribution of the electric potential, and the strength and energy of the electric field for pores of more complicated shapes than cylindrical are found by direct solution of the Laplace equation. It is shown that both the narrow cylindrical pore and the wide pore are particular cases of this shape and the obtained solution is exact in these two asymptotic cases.

2. Problem statement

Let us consider the membrane $2h$ in thickness, inside which there is an axially symmetrical pore. A three-dimensional sketch of the inner surface of the pore is shown in Fig. 1. The pore is axially symmetric, i.e. horizontal sections are circles of different radii. The section of minimal size (the middle section) is a circle of radius r_0. All the axial sections of the pore are the same and are shown in Fig. 2. Let us approximate the inner surface of the pore by a hyperboloid of rotation:

$$\frac{r^2}{r_0^2} - \frac{z^2}{b^2} = 1 \qquad (1)$$

where r and z are cylindrical coordinates with the origin in the centre of the above-described section and b is the parameter defining the shape of the pore. The value of c, the radius of the maximal curvature in the vicinity of the minimal section, describes the curvature

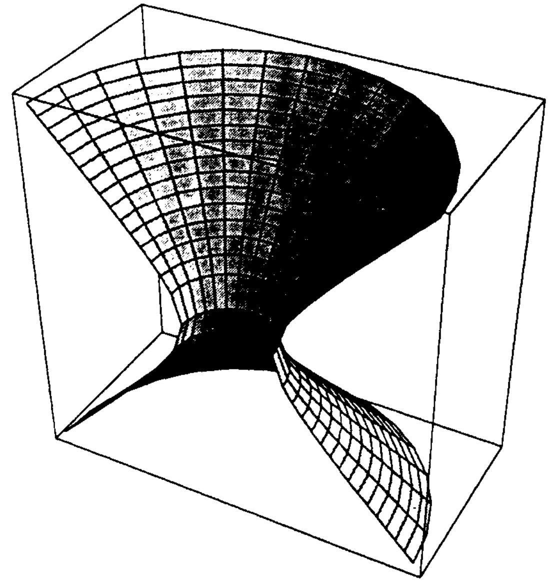

Fig. 1. Three-dimensional sketch of the inner surface of the pore. The external surface membrane is not shown for simplicity.

of the hyperboloid surface in a most logical way. In this case $b^2 = r_0 c$.

The problem of the electric field in such a system can be most conveniently solved in the oblate ellipsoidal coordinate system (σ, τ). The transition from cylindrical (r, z) to ellipsoidal system is carried out by the formulae [6]

$$\frac{r^2}{a^2(1+\sigma^2)} + \frac{z^2}{a^2 b^2} = h^2 \qquad (2)$$

$$\frac{r^2}{a^2(1-\tau^2)} - \frac{z^2}{a^2 \tau^2} = h^2 \qquad (3)$$

Here $a = (r_0^2 + r_0 c)^{1/2}/h$ is the dimensionless focal distance: each fixed σ defines cofocal ellipsoids $(\sigma \geq 0)$; each τ defines cofocal hyperboloids $(0 \leq \tau \leq 1)$. The condition $|\tau| > \tau_0$ corresponds to the interior of the pore, where

$$\tau_0 = (1 + r_0/c)^{-1/2} = \text{constant} \qquad (4)$$

corresponds to the inner surface of the pore in the ellipsoidal coordinate system.

Coordinates of the minimal section points are defined by the conditions $\sigma > 0$, $\tau \geq \tau_0$. Coordinates of the borderline points, in which the hyperboloid is conjugate with the external plane surface of the membrane, are defined by conditions $r = R$, $|z| = h$ in the cylindrical coordinate system, and by the conditions $\sigma = \sigma_0$, $\tau = \tau_0$ in ellipsoidal coordinates, where

$$\sigma_0 = 1/a\tau_0,$$

$$R = ha\left(1 - \tau_0^2\right)^{1/2}\left(1 + \sigma_0^2\right)^{1/2} \qquad (5)$$

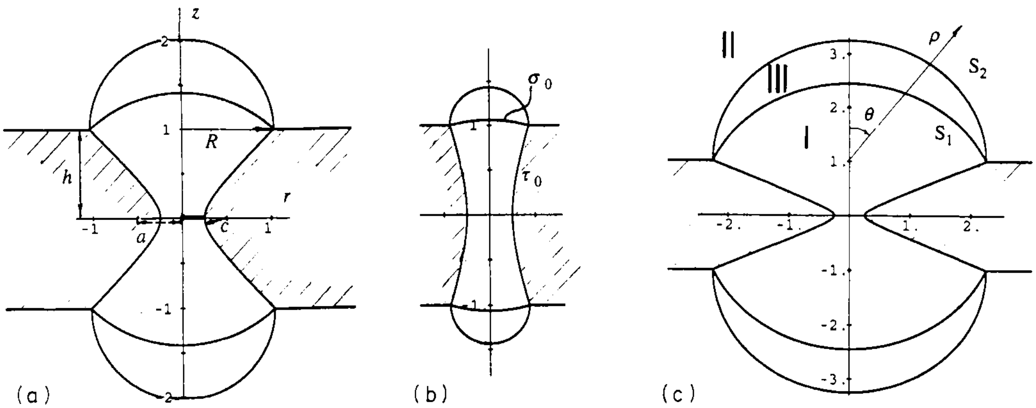

Fig. 2. Axial sections of a pore: (a) typical pore; (b) narrow pore; (c) wide pore.

We should notice that the condition $\sigma = \sigma_0$, $|\tau| \geq \tau_0$ refers not to the plane circle being an extension of the membrane surface, but to the ellipsoid overhanging the plane $z = h$ (see Fig. 2).

Assume that the electric current value is not high and that it is possible to neglect concentration changes. We also neglect specific adsorption of ions on the surfaces. Under such assumptions in order to define the electrical current distribution in the system, one has to solve the Laplace equation for the potential Φ:

$$\Delta\phi = 0 \tag{6}$$

with the boundary conditions being specified by zero flux of the current through the boundary between solution and dielectric

$$\left(\frac{\partial\Phi}{\partial \boldsymbol{n}}\right)_s = 0 \tag{7}$$

and the conditions

$$\Phi \to \Phi_0 \text{ at } z^2 + r^2 \to \infty,\ z > h$$

$$\Phi \to -\Phi_0 \text{ at } z^2 + r^2 \to \infty,\ z > -h \tag{8}$$

at infinity.

It can be easily shown that because of symmetry of the system, $\Phi(z, r) = -\Phi(-z, r)$, the second of the conditions (8) can be replaced by $\Phi = 0$ at $z = 0$ and it is enough to consider the upper part of the space, $z \geq 0$, only.

3. Solution

Let us divide the entire upper semispace into three areas (see Fig. 2(b)):

(I) $0 \leq \sigma \leq \sigma_0$, $\tau_0 \leq \tau \leq 1$, the inner part of the pore;

(II) the space area located over the plane $z = h$ and the semisphere

$$(z-h)^2 + r^2 = R^2 \tag{9}$$

(III) the small area between planes I and II, restricted by the ellipsoidal boundary $\sigma = \sigma_0$ and the spherical boundary (9).

The potential distribution in areas I and II will be found separately in what follows. It will be also shown that the contribution of area III can usually be neglected.

In the first area the Laplace equation (6) and the boundary conditions (7) and (8) can be written as [6]:

$$\frac{\partial}{\partial\sigma}\left[(1+\sigma^2)\frac{\partial\Phi}{\partial\sigma}\right] + \frac{\partial}{\partial\tau}\left[(1-\tau^2)\frac{\partial\Phi}{\partial\tau}\right] = 0$$

$$\left(\frac{\partial\Phi}{\partial\tau}\right)_{\tau=\tau_0} = 0,\ (\Phi)_{\sigma=0} = 0,\ (\Phi)_{\sigma=\sigma_0} = \Phi_1 \tag{10}$$

where Φ_1 is the potential drop inside the pore. The potential distribution, satisfying eqn. (10), is described by a simple relation:

$$\Phi = \Phi_1\frac{\arctan\sigma}{\arctan\sigma_0} \tag{11}$$

In the second area (outside the pore) it is convenient to introduce the spherical coordinate system (ρ, θ), "raised" to the height $z = h$ about the origin:

$$z = r\cos\theta + h,\ \rho = r\sin\theta \tag{12}$$

Then the relations (6)–(8) can be rewritten as

$$\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial\Phi}{\partial\rho}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\rho}\right) = 0$$

$$\left(\frac{\partial\Phi}{\partial\theta}\right)_{\pi/2} = 0,\ (\Phi)_{\rho=R} = \Phi_1,\ (\Phi)_{\rho\to\infty} = \Phi_0 \tag{13}$$

From relations (13) it is easy to find the potential distribution in this area:

$$\Phi = \Phi_0 + (\Phi_1 - \Phi_0)R/\rho \tag{14}$$

The expression for the electric field strength E can be found from eqns. (11) and (14):

$$E = \frac{\Phi_1}{ah} \frac{1}{(1+\sigma^2)^{1/2}(\tau^2+\sigma^2)^{1/2}} \frac{1}{\arctan \sigma_0}$$
in area I (15)
$$E = (\Phi_1 - \Phi_0) R/\rho^2$$
in area II

The constant Φ_1 can be found from the condition of charge absence inside area III, which is equivalent to the total flux through its two surfaces S_1 and S_2 (see Fig. 2(c)) being equal to zero:

$$\int_{S_1} \mathrm{d}s\, E(\sigma=\sigma_0) + \int_{S_2} \mathrm{d}s\, E(\rho=R) = 0 \qquad (16)$$

Writing down the expression (16) we took into account that the corresponding surfaces $\sigma=\sigma_0$ and $\rho=R$ are equipotential surfaces, i.e. that the strength vector is always perpendicular to the surface at the point of integrate. Integrating eqn. (16) in the curvilinear coordinates (4), we can find the expression for Φ_1:

$$\Phi_1 = \frac{\Phi_0}{1 + ha(1-\tau_0)/R \arctan \sigma_0} \qquad (17)$$

Substituting eqn. (17) into relations (11) and (15) we find the final expressions for the electric field potential and strength distributions inside the pore.

The total current I through the pore is given by the relation

$$I = 2\pi\kappa R(\Phi_0 - \Phi_1) \qquad (18)$$

where κ is the specific electroconductivity of the solution.

Expressions (15) and (17), (11) and (14), and (18) describe the distributions of the electric field, the potential and the current in the axially symmetrical pore in an explicit form. These expressions can be used in different areas of the electrochemistry of porous bodies.

4. Evolution of a pore in a bilayer lipid membrane

As an example of such an application we will consider the evolution of pores in a model membrane under the influence of the electric field. The theory for cylindrical pores has been developed in refs. 1 and 7–10]. The problems of pores evolution are discussed in a number of recent works (see ref. 11 for more detail).

There are two forces that affect the evolution: surface tension on the boundary of a membrane and solution, tending to reduce the membrane surface, and the electric field pressure, tending to make pores wider. As the electric conductivity vector inside the liquid is parallel to the border of the phases, the electric field energy is calculated as an integral over the entire volume V:

$$W_e = \tfrac{1}{2}\int_V \mathrm{d}V\, \epsilon |E|^2 \qquad (19)$$

where ϵ is the dielectric permeability of the liquid.

One can show that in the case of a constant electric field energy this approach coincides with the more strict approach, where the electric field work is calcu-

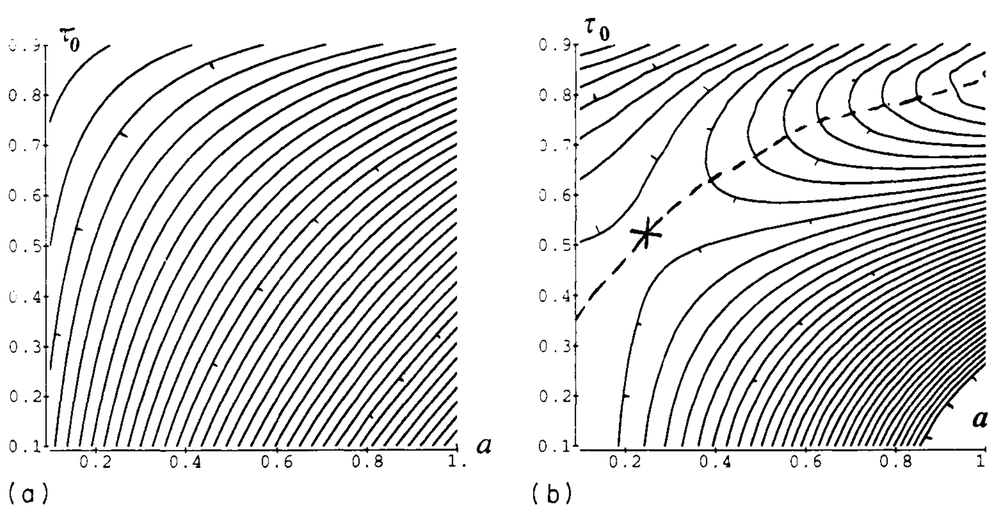

Fig. 3. Contour plot of surfaces of potential energy as a function of the size a and shape τ_0: (a) the energy W_e of the electric field; (b) the energy W_s of the surface tension. ⟍, direction of gradients; ×, pass point.

lated from the Maxwell tensor of densities [8]. Evaluating the integral (19) with relations (15), one obtains

$$W_e = 2\pi a h \epsilon(\Phi_1)^2 \sigma_0(1-\tau_0)/\arctan\sigma_0 + 2\pi R\epsilon(\Phi_0-\Phi_1)^2 \qquad (20)$$

The contour plot ("map") of W_e as a function of two variables τ_0 and a is presented in Fig. 3(a). The surface tension energy W_s is proportional with the coefficient α to the change in the membrane surface area due to the occurrence of a pore:

$$W_s = 2\pi\alpha h^2 a^2(1-\tau_0^2)^{1/2}\left(\sigma_0(\tau_0^2+\sigma_0^2)^{1/2} + \tau_0^2 \ln\left\{\frac{\sigma_0}{\tau_0} + \left[1+\left(\frac{\sigma_0}{\tau_0}\right)^2\right]^{1/2}\right\}\right) - 2\pi\alpha R^2 \qquad (21)$$

which is shown in Fig. 3(b). The total energy of the system is

$$W = W_e + W_s \qquad (22)$$

On the surface of the two parameters τ_0 and a any pore is described by a point. Parameter $\tau_0 \to 1$ refers to a cylindrical pore, while $\tau_0 \to 0$ refers to a round hole in a thin plane; $a \to 0$ indicates a "narrow" pore, while $a \to \infty$ indicates a wide pore.

The shape of the surface $W(a, \tau_0)$ depends on dimensional parameters involved in eqns. (20) and (21): membrane thickness h, dielectric constant ϵ, coefficient of surface tension and applied potential difference Φ_0. Luckily, all these parameters are combined in the only dimensionless parameter $\psi = (\epsilon/h\alpha)^{1/2}\Phi_0$ which can be considered as a dimensionless potential for a given membrane. For small potential difference $\psi \ll 1$ we have $W_e \ll W_s$ and the shape of $W(a, \tau_0)$ corresponds to Fig. 3(b). In the opposite case ($\psi \gg 1$) the shape of $W(a, \tau_0)$ corresponds to Fig. 3(a). In the intermediate cases some kind of combination of Figs. 3(a) and 3(b) appears.

Let us assume that at a certain moment a pore characterized by the parameters a and τ_0 has arisen. It then starts moving along the direction of the gradient of potential energy W. As far as the acceleration in each state is proportional to the gradient of W, it is possible to describe the changing dynamics of the pore as well.

It is easy to see from Fig. 3(b) that in the case of $\Psi \ll 1$ there are two different ways of evolution, depending on the location with respect to the broken line (which can be considered as a backbone): either decreasing radius $a \to 0$ (and at the same time the pore becomes more and more cylindrical) or unlimited increasing radius $a \to \infty$ and decreasing τ_0 (the pore looks like a hole in the infinite plane). This is a well-known fact for cylindrical pores. In the opposite case of a high voltage difference, $\Psi \gg 1$, only unlimited pore expansion is possible, because W_e decreases without limit in the directions $a \to \infty$ and $\tau_0 \to 1$.

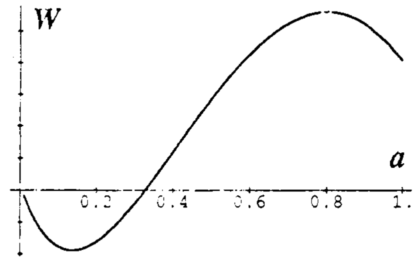

Fig. 4. Dependence of the total energy W on the pore size for approximately cylindrical pores ($\tau_0 = 0.99$) and dimensionless potential difference $\psi = 3.6$.

At some intermediate values of ψ a new possibility appears: the electric and elastic forces compensate each other and pores with some specific size and shape can exist permanently. In Fig. 4 the section of the surface $W(a, \tau_0)$ corresponding to an approximately cylindrical pore is given. The minimum corresponding to a stationary position was originally found by Pastushenko and Chizmadzev [7].

One can assume that a stationary position can exist also on the boundary between two slopes (broken line in Fig. 3(b)). Of course, it is not a stable equilibrium, but the system can spend sufficient time in a such position for several experimental measurements which give us a possibility to describe the pore as quasi-stable. The necessary condition of quasi-stability is an absence of the gradient, i.e. the point must be a "top" or "pass". It is easy to show that cylindrical pores cannot be quasi-stable because, at the point where the function $W(a, \tau_0 = 1)$ has a maximum, i.e. $\partial W(a, \tau_0 = 1)/\partial a = 0$, a change in the shape, i.e. τ_0, must occur: $\partial W(a, \tau_0 = 1)/\partial a \neq 0$. Formally not more than one quasi-stable point labelled by $\times$ in fig. 3(b) exists in the system. However, in reality this point is placed in the middle of a "pass plateau", where $W \approx$ constant. The system situated on the "plateau" will move down from it very slowly and also may be described by the term "quasi-stable pore".

For example, the "pass plateau" included a segment $a \ll 1$, $0.1 < \tau_0 < 0.4$, which corresponds to an "invisible" pore. It is obvious, that the current flowing through the pore that is characterized by the finite value τ_0 and unlimitedly small value of the radius a will be comparatively low, but electric forces cannot be neglected because the narrowest section of the pore also has a certain length, and that is why the strength and the pressure of the electric field can be significant.

One has to notice that all the above given speculations are strictly valid only when the external potential is supposed to be constant in time. However, in the case of a step-like external potential, formulae (20)–(22) can also be considered valid. For example, under a certain potential value after the evolution, let an "invisible" pore with certain a and τ_0 appear. After a change in the potential value the state of this pore will cease to be stable and evolution will continue. It is obvious that, depending on the value of ψ, one of the above-described cases is possible.

It is important to stress that in any case of pore evolution with reasonably chosen initial parameters the system never does "climb" to the area $a \gg 1$, $\tau_0 \approx 1$ (indicating a wide pore of cylindrical shape) when the potential drop in area III of the pore (Fig. 2) cannot be neglected (we neglected it in all our calculations).

5. Conclusion

A simple analytical expression for the electric potential within a non-cylindrical axially symmetric pore has been obtained. The main restriction on the applicability of the results is that the shape of the pore has to make the potential drop in an intermediate region negligible. In the first approximation we can describe any errors by the ratio $\eta = V_{\mathrm{III}}/V_{\mathrm{I}}$ of volumes of regions I and III.

For the cylindrical pore with small radius $r_0 \ll h$ the error of calculations is given by $\eta \approx 2r_0/3h \ll 1$ (see also ref. 8). For the other limiting case when the pore radius is much larger than the membrane thickness, and the pore edge is rounded ($\tau_0 \ll 1$), areas II and III are removed to infinity and $\eta \approx \tau_0$.

Therefore, the proposed model of an axially symmetric pore bridges the previously developed models and thus can be used for describing complicated porous structures.

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