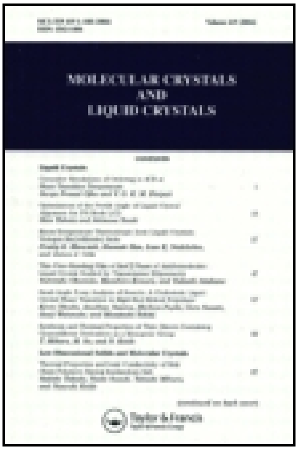

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Influence of the Electric Double Layers of the Membrane on the Value of Its Flexoelectric Coefficient

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The potential jump due to the electric double layers across a spherically deformed charged membrane is calculated. The equations of Langmuir adsorption are used to estimate the change in the surface density of the membrane. The flexoelectric coefficient due to the electric double layers of the membrane is obtained for the cases of blocked and free flip-flop.

I. INTRODUCTION

Flexoelectricity in membranes is manifested in the generation of an electric potential difference across the membrane as a result of its deformation. The first theoretical investigations on membrane flexoelectricity were carried out by Petrov.[1] In his paper the flexoelectric coefficient of a membrane was defined as the ratio between the electric polarization of the bilayer and its curvature in analogy to the liquid crystal flexoelectricity, suggested by Robert Meyer.[2] Later on the existence of the effect was proved and it was studied experimentally. Recently Derzhanski[3,4] on the base of a new approach to the flexoeffect,[5,6] expressed the flexocoefficient f through the charge distribution throughout the membrane. According to the definition given in References 4 and 6 in the case of spherical deformation f is expressed by the experimentally measured potential difference $\Delta\Phi$ across the membrane and the curvature of the membrane c as

$$\Delta\Phi = \frac{f}{\varepsilon_0} 2c, \tag{1}$$

where ε_0 is the dielectric constant of vacuum. Actually $\Delta\Phi$ is a more complex function of c, $\Delta\Phi = \Delta\Phi(c)$. If this function is known the flexocoefficient can be defined through:

$$f = \varepsilon_0 \frac{d(\Delta\Phi)}{d(2c)}.$$

This expression can be generalized in the case of non-spherical deformation but it will not be needed in our work.

2. THE MODEL

When we refer to a membrane we understand the medium inside two parallel surfaces, outside which there are no nonhomogeneties. We consider a simplified, but realistic model, according to which the membrane consists of a dielectric part constructed by the hydrophobic tails of the lipids and the part of the heads, where the electrolyte cannot penetrate, and of two electric double layers comprising the hydrophilic heads with the adsorbed ions and the adjacent to them counterions from the electrolyte.

In this work we calculate only the contribution of the electric double layers to the flexocoefficient of the membrane. Without restriction of generality in what follows we consider the spherically symmetric case (Figure 1), and we neglect the effects of the edges of the membrane.

Let the electrolyte contain two types of ions with charges $-ze$ and ze, where e is the electron charge. Their concentrations n^+ and n^- are expressed through the

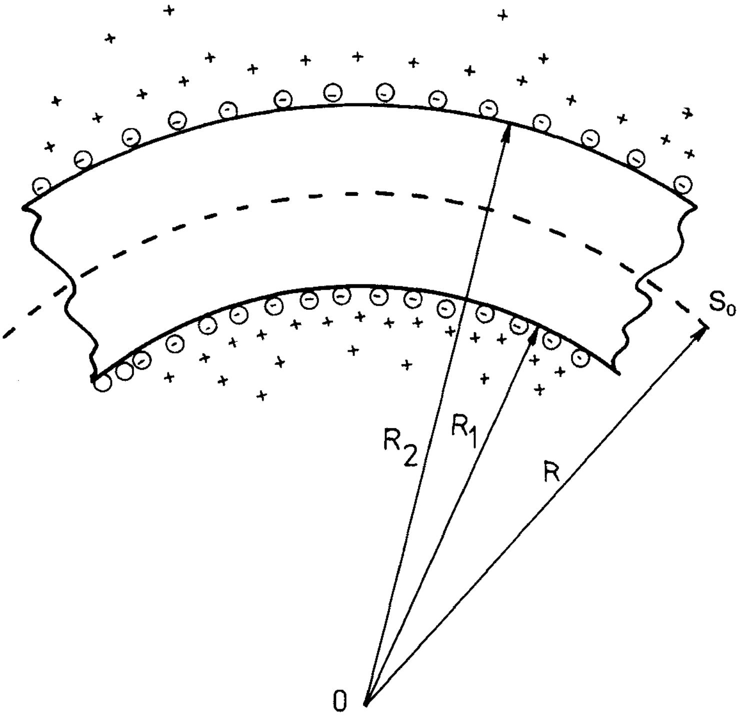

FIGURE 1 Schematic representation of a spherically deformed membrane. S_0 is the neutral surface. Due to the negative charges on the dielectric part of the bilayer a diffuse layer of positive counterions is formed. R_1, R_2 and R are the radii of the inner, outer and neutral surface respectively.

potential Φ, generated by the charges of the membrane. The charge density in the electrolyte is $\rho = ze(n^+ - n^-)$. Here we will consider only monovalent electrolytes ($z = 1$).

As a result of the Debye-Huckel approximation, often applied in membrane theory when the ion concentration is high enough, the Poisson equation $\nabla^2\Phi = -\rho/\varepsilon\varepsilon_0$ acquires for the inner and the outer electrolyte media the form:

$$\nabla^2\Phi = \kappa^2\Phi$$

$$\kappa^2 = \frac{2n_0e^2}{\varepsilon\varepsilon_0 kT}, \tag{2}$$

where ∇^2 is the Laplacian, κ is the reciprocal value of the Debye length, n_0 is the concentration of one type of the ions in the electrolyte far from the membrane surface, k is the Boltzman constant, T is the absolute temperature, ε is the dielectric constant of the solution.

We assume that each of the monolayers building up the bilayer is electrically neutral. In the case of blocked flip-flop there is no exchange of lipids between the two layers upon deformation of the membrane at all. In the case of free flip-flop, an exchange of uncharged lipids between the two monolayers is assumed to be performed (i.e., through the torus). This means that the two regions, separated by the surface S_0 dividing the monolayers (Figure 1) are electrically neutral. Since we consider only symmetric bilayers this surface is assumed to coincide with the neutral surface (the surface that does not change locally its area upon deformation). The potential distribution across the membrane due to the electric double layers is given by the following expression:

$$\Phi(r) = \begin{cases} \dfrac{\sigma_1 R_1^2}{\varepsilon\varepsilon_0 \mathrm{ch}(\kappa R_1)(\kappa R_1 - 1)}\dfrac{\mathrm{sh}(\kappa r)}{r} + \dfrac{\sigma_2 R_2}{\varepsilon\varepsilon_0(\kappa R_2 + 1)} - \dfrac{\sigma_1 R_1 \mathrm{th}(\kappa R_1)}{\varepsilon\varepsilon_0(\kappa R_1 - 1)} & r < R_1 \\ \dfrac{\sigma_2 R_2}{\varepsilon\varepsilon_0(\kappa R_2 + 1)} & R_1 < r < R_2 \\ \dfrac{\sigma_2 R_2^2}{\varepsilon\varepsilon_0(\kappa R_2 + 1)}\dfrac{e^{-\kappa(r - R_2)}}{r} & r > R_2 \end{cases} \tag{3}$$

where R_1 and R_2 are the radii of the inner and the outer bilayer surfaces (Figure 1), r is the current coordinate, σ_1 and σ_2 are the surface charge densities of the inner and outer surfaces of the dielectric part of the membrane. This expression assures the potential to be 0 at $r = \infty$ and to have a finite value at $r = 0$.

The potential jump, created by the deformed membrane, is:

$$\Delta\Phi = \Phi(r = \infty) - \Phi(r = 0)$$

$$\Delta\Phi = -2\frac{\sigma_1 \kappa R_1^2}{\varepsilon\varepsilon_0 \mathrm{ch}(\kappa R_1)(\kappa R_1 - 1)} - \frac{\sigma_2 R_2}{\varepsilon\varepsilon_0(\kappa R_2 + 1)} + \frac{\sigma_1 R_1 \mathrm{th}(\kappa R_1)}{\varepsilon\varepsilon_0(\kappa R_1 - 1)} \tag{4}$$

We use the model of Langmuir adsorption to determine the values of σ_1 and σ_2. We consider the case when in the aqueous solution each lipid molecule loses one of its protons (ionizable lipids). In case there were no adsorption/desorption processes the surface charge density in the undeformed state σ^0 would be equal to e/A_0, where A_0 is the area of the lipid head in the flat membrane. Some of the ions from the diffuse layer of the counterions (assumed to be monovalent) can be adsorbed on the heads. As a result of this some of the lipids become electrically neutral and the surface charge density decreases. We consider the case when the concentration of the electrolyte ions is that high, so the adsorption of the protons on the heads can be neglected.

We will use the following symbols: σ_1^0, the maximal surface charge density of the inner bilayer surface; σ_2^0, the maximal surface charge density of the outer bilayer surface; n_1^+ and n_2^+, the concentration of the counterions in the diffusive layer close to the charged surface of the lipid heads of the inner and the outer monolayer; b, the adsorption constant.

Then from the equation of Langmuir adsorption we get:

$$\begin{aligned} \sigma_1 n_1^+ &= b(\sigma_1^0 - \sigma_1) \\ \sigma_2 n_2^+ &= b(\sigma_2^0 - \sigma_2) \end{aligned} \tag{5}$$

where σ_1 and σ_2 are defined above. The case $b = \infty$ corresponds to the maximal surface charge, whereas $b = 0$—to uncharged monolayers.

n_1^+ and n_2^+ can be expressed through the potential Φ by the following equations:

$$\begin{aligned} n_1^+ &= n_0 e^{-e(\Phi(R_1)-\Phi(0))/(kT)} \\ n_2^+ &= n_0 e^{-e\Phi(R_2)/(kT)} \end{aligned} \tag{6}$$

3. DETERMINATION OF THE FLEXOCOEFFICIENT DUE TO THE DOUBLE LAYERS

A. Blocked Flip-Flop

Upon bending a stretching/compression occurs in the outer/inner monolayer of the membrane. This leads to changes in the respective areas of the molecules, i.e., to a change in the charge density. The neutral surface coincides with the surface, separating the two monolayers. The areas per a lipid head in the inner and the outer monolayer A_1 and A_2 can be expressed through the membrane curvature $c = 1/R$ and the membrane thickness d^7:

$$\begin{aligned} A_1 &= A_0(1 - cd) \\ A_2 &= A_0(1 + cd) \end{aligned} \tag{7}$$

Then

$$\begin{aligned} \sigma_1^0 &= \sigma^0(1 + cd) \\ \sigma_2^0 &= \sigma^0(1 - cd) \end{aligned} \tag{8}$$

From Equations (4), (5) and (8) using the Debye-Huckel approximation the following result for the potential jump across the membrane is obtained:

$$\Delta\Phi = \frac{2b\sigma^0}{\varepsilon\varepsilon_0\kappa\sqrt{(n_0+b)^2+4\frac{e}{kT}\frac{n_0b\sigma^0}{\varepsilon\varepsilon_0\kappa}}}c(d+1/\kappa)+O(c^2) \tag{9}$$

If we assume that b depends on the curvature as $b = b_0 + O(c)$, where b_0 is the equilibrium constant in the case of a flat membrane, formula (9) will not change.

The respective value of the flexocoefficient in the case of blocked flip-flop f_B is obtained from Equations (9) and (1):

$$f^B = \frac{b\sigma^0}{\varepsilon\kappa\sqrt{(n_0+b)^2+4\frac{e}{kT}\frac{n_0b\sigma^0}{\varepsilon\varepsilon_0\kappa}}}(d+1/\kappa) \tag{10}$$

If there are no adsorption /desorption processes ($b = \infty$), which corresponds to fully ionized molecules the first order approximation of the potential with respect to the curvature is:

$$\Delta\Phi = \frac{2\sigma^0c(d+1/\kappa)}{\varepsilon\varepsilon_0\kappa} \tag{11}$$

and

$$f^B = \frac{\sigma^0(d+1/\kappa)}{\varepsilon\kappa} \tag{12}$$

B. Free Flip-Flop

In this case the number of the molecules n_1 and n_2 in the two monolayers per a unit area of the neutral surface after the bending depends on the elastic constants and can be expressed by the flip-flop coefficient α[8]:

$$n_1 = n_0(1-\alpha c)$$

$$n_2 = n_0(1+\alpha c) \tag{13}$$

For a given α the areas per a lipid head in the two monolayers are:

$$A_1 = A_0(1-c(d-\alpha))$$

$$A_2 = A_0(1+c(d-\alpha)) \tag{14}$$

and

$$\sigma_1^0 = \sigma^0(1+c(d-\alpha))$$

$$\sigma_2^0 = \sigma^0(1 - c(d - \alpha)) \tag{15}$$

The potential jump is:

$$\Delta\Phi = -\frac{2b\sigma^0}{\varepsilon\varepsilon_0\kappa\sqrt{(n_0 + b)^2 + 4\frac{e}{kT}\frac{n_0 b\sigma^0}{\varepsilon\varepsilon_0\kappa}}}c(d + 1/\kappa - \alpha) \tag{16}$$

The flexoelectric coefficient in the case of free flip-flop f^F (see (1)) is:

$$f^F = \frac{b\sigma^0}{\varepsilon\kappa\sqrt{(n_0 + b)^2 + 4\frac{e}{kT}\frac{n_0 b\sigma^0}{\varepsilon\varepsilon_0\kappa}}}(d + 1/\kappa - \alpha) \tag{17}$$

If ($b = \infty$):

$$\Delta\Phi = \frac{2\sigma^0 c(d + 1/\kappa - \alpha)}{\varepsilon\varepsilon_0\kappa} \tag{18}$$

$$f^F = \frac{\sigma^0(d + 1/\kappa - \alpha)}{\varepsilon\kappa} \tag{19}$$

We can make some estimations of the values of the obtained quantities for $\sigma^0 \approx 0.25\ C/m^2$, $d \approx 4.10^{-9}\ m$, $\kappa = 10^9\ m^{-1}$, $0 < \alpha < d$, $b \propto n_0$. They yield $f \propto 10^{-19} - 10^{-20}\ C$). We would like to note again, that this is the contribution to the flexocoefficient due to the existence of the surface charge of the membrane.

4. DISCUSSION

The potential difference ΔU across the membrane depends on the frequency of the deformation of the membrane as well. The proposed model is valid for a definite frequency interval $\nu_1 << \nu << \nu_2$. $\nu_1 \propto 1\ s^{-1}$ is the reciprocal value of the characteristic time for ion diffusion through the membrane and $\nu_2 > 10^6\ s^{-1}$ (for physiological solution)—the one for the rearrangement of the ions in the boundaries of the double layers of the membrane. All the experimental investigations of the effect up to now are performed in this frequency interval.[9–11] There is another characteristic frequency ν_f, defined by the flip-flop characteristic time. It can depend on the experimental conditions. In a definite frequency interval around ν_f there exists a transition process, related to the kynetics of the flip-flop. This phenomenon can not be explained by the electrostatic considerations, presented here. Our results are valid far from the transition frequency ν_f, i.e., in the cases of "pure" free and blocked flip-flop. This shows, that a nontrivial analysis should be carried out in order to obtain the value of the flexocoefficient on the basis of any experimental data.

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