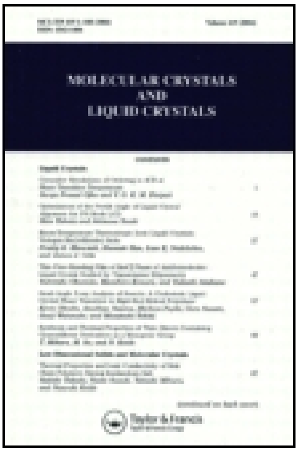

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Frequency Dependence of the Membrane Flexoelectric Voltage Response. Adsorption of Multivalent Counterions on the Surface of Curved Lipid Bilayer

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FREQUENCY DEPENDENCE OF THE MEMBRANE FLEXOELECTRIC VOLTAGE RESPONSE. ADSORPTION OF MULTIVALENT COUNTERIONS ON THE SURFACE OF CURVED LIPID BILAYER.

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ABSTRACT

The flexoelectric response of the oscillating membrane for different frequencies is studied. The influence of the adsorption of ions of different valencies on the membrane flexoeffect is considered. Different adsorption mechanisms corresponding to different binding of the electrolyte counterions to the lipid molecules are proposed.

Keywords: flexoelectricity, ion layers, membranes, frequency dependese, ion adsorption

1. INTRODUCTION

A number of papers dealing with flexoelectricity in membranes exists in the literature [1–7]. The problems of the phenomenology and the molecular mechanisms of this effect are studied there. There are also experiments proving its existence [8–13]. However, the processing of experimental data, associated with this effect is not trivial. The results to a great extent depend on the composition and the properties of the electrolyte, in which the membrane is embedded (valency, concentation, specific adsorption). This work is aimed to solve these problems.

2. PHEMENOLOGICAL THEORY OF THE FLEXOELECTRIC RESPONSE OF AN OSCILLATING MEMBRANE.

We consider only symmetric membranes under spherical deformation, which is the case in the experiments, performed up to now. Conditionally we call one of the monolayers first and the other- second. The curvature c is positive if the center of curvature is from the side of the first monolayer, otherwise it is negative. Let Φ_1 and Φ_2 be the potentials of two points in the electrolyte far from the membrane from the side of the first and the second monolayer, respectively. We denote $\Delta\Phi = \Phi_2 - \Phi_1$.

We use the definition of flexocoefficient, given in [5] and expanded in [14]. When there is no charge exchange through the membrane the potential difference $\Delta\Phi$ across it under spherical deformation with radius R and a fixed curvature $c = 1/R$ is:

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

where f is the flexoelectric coefficient for free or blocked flip- flop of the membrane, depending on the experimental conditions and 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:

$$f = \varepsilon_0 \left(\frac{d(\Delta\Phi)}{d(2c)} \right)_{c=0}.$$

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

When we refer to a membrane we understand the medium inside two parallel surfaces, outside which there are no unhomogeneties. We consider a 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 [4]. The potential jump across the membrane can be represented as a sum of the potential differences across the dielectric part and the double layers:

$$\Delta\Phi = \Delta\Phi_{diel} + \Delta\Phi_{dl}$$

and respectively

$$f = f_{diel} + f_{dl} \tag{2}$$

The value of f depends on the lipid exchange between the monolayers, constituting the membrane. Let n_1 and n_2 be the number of molecules of the outer and inner monolayer per unit mid-surface (the surface dividing the thickness of the dielectric layer). As defined by Helfrich [15] $\alpha = (n_2 - n_1)/(n_2 + n_1)$ is the flip-flop coefficient. α is assumed to be the same for all the points of the membrane in a given moment.

Let the membrane curvature oscillate as $c = c_0 \cos(\omega t)$, where c_0 is the maximal curvature of the oscillations. It is clear that $\alpha = \alpha(t)$. When the value of the curvature is fixed there exists a certain equilibrium value

$$\alpha(c) = \alpha_0 c \tag{3}$$

If the curvature is a function of time because of membrane viscosity equation (3) is not true any more. In this case we suppose that the rate of change of α is proportional to its deviation from the equilibrium value:

$$\frac{d\alpha}{dt} = m(\alpha_0 c_0 \cos(\omega t) - \alpha) \tag{4}$$

where m is a coefficient, associated with the rheological properties of the membrane. The stationary solution of this equation is:

$$\alpha = \frac{m^2 \alpha_0 c_0}{\omega^2 + m^2} \cos(\omega t) + \frac{m\omega\alpha_0 c_0}{\omega^2 + m^2} \sin(\omega t) = \frac{m\alpha_0 c_0}{\sqrt{\omega^2 + m^2}} \cos(\omega t + \phi) \tag{5}$$

where

$$\tan\phi = -\frac{\omega}{m}$$

We consider frequencies, for which the charge exchange due to the membrane intrinsic conductivity can be neglected (for egg yolk lecithine membrane this condition is fulfilled for frequencies $\omega > \omega_{thr} = 2\pi\nu_{thr}$ with $\nu_{thr=}10Hz$). The upper frequency limit $10^5 Hz$ for the proposed theory is defined by the charactestic time for the rearrangement of the ions in the boundaries of the double layers of the membrane.

Let f^F be the flexocoefficient of free flip-flop and f^B – of blocked flip-flop. Then assuming linear responses of the system with respect to α and c we can express the flexoelectric potential difference in the form:

$$\Delta\Phi(t) = \frac{1}{\varepsilon_0}\left(f^B c(t) + \frac{f^F - f^B}{\alpha_0}\alpha(t)\right) \tag{6}$$

where $\alpha(t)$ is the solution of (4). Substituting (4) in (6) we have:

$$\Delta\Phi(t) = \frac{1}{\varepsilon_0}\left(f^B + (f^F - f^B)\frac{m^2}{(\omega^2 + m^2)}\right) c_0 \cos(\omega t) \tag{7}$$

$$+\frac{1}{\varepsilon_0}(f^F - f^B)\frac{m\omega}{(\omega^2 + m^2)} c_0 \sin(\omega t)$$

$$= \sqrt{(f^B)^2\left(\frac{\omega^2}{\omega^2 + m^2}\right) + (f^F)^2\left(\frac{m^2}{\omega^2 + m^2}\right)}\frac{c_0}{\varepsilon_0}\cos(\omega t + \varphi), \tag{8}$$

where

$$\tan\varphi = \frac{(f^B - f^F)m\omega}{f^F m^2 + f^B\omega^2}$$

We note that the flexoelectric response of the membrane depends on three parameters - f^B, f^F and m. For the usual case $f^F > f^B$ the phase of the signal is positive, i.e. the membrane has the behaviour of a capacitance. To our knowledge this is the first prediction of this kind.

At high deformation frequences the dielectric response is:

$$\Delta\Phi(t) = \frac{f^B}{\varepsilon_0} c_0 \cos(\omega t)$$

At high enough values of m for frequences greater, but of the order of ω_{th_r} the flexoelectric response tends to:

$$\Delta\Phi(t) = \frac{f^F}{\varepsilon_0} c_0 \cos(\omega t),$$

These two limiting cases are considered in [10].

3. MICROSCOPIC THEORY OF DOUBLE LAYER FLEXOELECTRICITY

The flexoelectric response, given by (8) is determined by the sum $f_{diel} + f_{dl}$. An interesting question is what changes the flexoelectric response undergoes upon changes of the parameters of the medium, in which the membrane is embedded. It is natural to assume that the medium influences most f_{dl}. That is why here we consider this problem. We note, that experiments of exactly this type are been carried out [13].

To proceed later on we will introduce the following symbols:

b – the adsorption constant of Langmuir adsorption. (see the equations of Langmuir adsorption (10)). If $b = \infty$ the adsorption is zero;

σ_1^0 – the surface charge density of the dielectric border of the first monolayer of the deformed bilayer if there is no adsorption (for details see [14]);

σ_2^0 – the same for the dielectric border of the second monolayer;

n_1^+ and n_2^+ – the concentration of the counterions in the diffuse layer close to the dielectric borders of the two monolayers.

As it follows from the results in [14] $\Delta\Phi_{dl}$ is expressed through the surface charge densities σ_1 and σ_2 on the two dielectric borders.

$$\Delta\Phi_{dl}(c) = \frac{1}{\varepsilon\varepsilon_0\kappa}(\sigma_1(c) - \sigma_2(c)) + \frac{(\sigma_1(c=0) + \sigma_2(c=0))}{\varepsilon\varepsilon_0\kappa}\frac{c}{\kappa} \qquad (9)$$

Later on we assume that for the case when each molecule of the membrane is exactly one site of adsorption σ_1 and σ_2 are solutions of Langmuir adsorption equations:

$$\begin{aligned}\sigma_1 n_1^+ &= b(\sigma_1^0 - \sigma_1)\\ \sigma_2 n_2^+ &= b(\sigma_2^0 - \sigma_2).\end{aligned} \tag{10}$$

Here we consider several different cases. For all of them we assume the validity of Debye - Huckel approximation.

3.1. ADSORPTION OF MONOVALENT IONS

This case is considered recently in details elsewhere [14]. The result is:

$$f_{dl} = \frac{b\sigma^0}{\varepsilon\kappa\sqrt{(n_0+b)^2 + 4\frac{e}{kT}\frac{n_0 b\sigma^0}{\varepsilon\varepsilon_0\kappa}}}(d + 1/\kappa - \alpha') \tag{11}$$

where 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, e is the elementary electric charge, ε is the dielectric constant of the solution, $\sigma^0 = -e/A_0$, where A_0 is the area per molecule in the flat membrane, d is the thickness of the dielectric layer. For the case of free flip-flop $\alpha' = \alpha_0$ and for blocked flip-flop $\alpha' = 0$.

The constant b can be determined by independent experiments [16].

3.2. ADSORPTION OF MULTIVALENT IONS

At least two types of adsorption of divalent ions are described in the literature. In the fist one the additive divalent ion is supposed to be adsorbed on one lipid molecule (1:1), while in the second the divalent ion is adsorbed on a couple of charged neighbors (1:2). Here we confine ourselves to the case when the adsorption of the electrolyte monovalent ions can be neglected.

For the (1:1) model of adsorption of z-valent ions, following an algorithm in analogy to the one, described in [14] for the flexocoefficient f_{dl} we get:

$$f_{dl} = \frac{\sigma^0}{\varepsilon\varepsilon_0\kappa}\left(\frac{z\left(\theta_0(n_0 z + n_0) - \frac{n_0 kT\varepsilon\varepsilon_0\kappa}{ze\sigma^0} - 2n_0\right)}{\sqrt{\left(n_0 z + n_0 + (n_0+b)\frac{kT\varepsilon\varepsilon_0\kappa}{ze\sigma^0}\right)^2 - 4n_0^2 z\left(\frac{kT\varepsilon\varepsilon_0\kappa}{ze\sigma^0} + 1\right)}} - 1\right)(d - \alpha' + 1/\kappa) \tag{12}$$

where

$$\theta_0 = \frac{n_0 z + n_0 + (n_0+b)\frac{kT\varepsilon\varepsilon_0\kappa}{ze\sigma^0} + \sqrt{(n_0 z + n_0 + (n_0+b)\frac{kT\varepsilon\varepsilon_0\kappa}{ze\sigma^0})^2 - 4n_0^2 z\left(\frac{kT\varepsilon\varepsilon_0\kappa}{ze\sigma^0} + 1\right.}}{2n_0 z}$$

Equation (11) can be obtained from this general case for $z = 1$. For divalent ions $z = 2$.

Change in the sign of the flexocoefficient, that could be explained by this model is experimentally observed [13].

For the (1:2) case we suppose that all the lipid heads have lost one of their protons. A divalent ion sticks to a lipid couple, thus making it neutral.

We consider analytically two limiting cases of adsorption – when the number of the adsorbed cations is less than the total number of the lipid molecules and when this number is close to the maximal one.

We use the following symbols:

M_1^{++} - the number of possible charged couples of lipid neighbors for the first monolayer;

M_2^{++} - the same for the second monolayer;

M_1^{00} - the number of neutralized due to the adsorption couples of lipid neighbors for the first monolayer;

M_2^{00} - the same quantity for the second monolayer;

N - the lipid concentration in the flat membrane;

N_1^-, N_2^- and N^- - the numbers of charged lipids per unit area in the first and second deformed monolayer and in the flat membrane;

p - the number of the nearest neighbors of the lipid molecule.

In this case the Langmuir adsorption equations must be:

$$\begin{aligned} M_1^{++} n_1^+ &= b M_1^{00} \\ M_2^{++} n_2^+ &= b M_2^{00} \end{aligned} \tag{13}$$

For small concentrations of the adsorbed divalent cations:

$$M_{1,2}^{++} = \frac{N(1-p) + N_{1,2}^-(2p-1)}{2}$$

$$M_{1,2}^{00} = \frac{N - N_{1,2}^-}{2}$$

Under these assumptions

$$f_{dl} = \frac{\sigma^0}{\varepsilon\varepsilon_0\kappa} \frac{(b + n_0(p-1))\left(d - \alpha' + \frac{1}{\kappa}\right)}{\sqrt{\left(b + n_0(2p-1) + \frac{2e^2}{kT}\frac{n_0 N}{\varepsilon\varepsilon_0\kappa}(1-p)\right)^2 + \frac{8e^2}{kT}\frac{n_0 N}{\varepsilon\varepsilon_0\kappa}(2p-1)(n_0(p-1)+b)}} \tag{14}$$

For the case of high divalent ion adsorption we suppose that there exists a certain minimal concentration N_{min}^- of the charged lipids that cannot be further decreased because each charged molecule is surrounded by neutralized ones and the adsorption of divalent cations cannot be performed. Assuming the validity of the mean field approximation and using the symbols, defined above, for $N^- > N^-_{min}$ we get:

$$f_{dl} = \frac{\sigma^0}{\varepsilon\varepsilon_0\kappa} \frac{\left(b\frac{N-N^-_{min}}{N^-_{min}p} + n_0\frac{N^-_{min}}{N} + \frac{2e^2}{kT}\frac{n_0}{\varepsilon\varepsilon_0\kappa}\frac{(N^-)(N^-_{min})}{N}\right)\left(d - \alpha' + \frac{1}{\kappa}\right)}{\sqrt{A^2 + \frac{4e^2}{kT}\frac{n_0}{\varepsilon\varepsilon_0\kappa}\left(bN\frac{N-N^-_{min}p}{N^-_{min}p} + 2n_0N^-_{min}\right)}} \tag{15}$$

where N^- is given by:

$$N^- = \frac{-A + \sqrt{A^2 + \frac{4e^2}{kT}\frac{n_0}{\varepsilon\varepsilon_0\kappa}\left(bN\frac{N-N^-_{min}}{N^-_{min}p} + 2n_0N^-_{min}\right)}}{\frac{4e^2}{kT}\frac{n_0}{\varepsilon\varepsilon_0\kappa}}$$

and

$$A = \frac{b}{2}\frac{(N - N^-_{min})}{N^-_{min}p} + n_0 - \frac{2e^2}{kT}\frac{n_0N^-_{min}}{\varepsilon\varepsilon_0\kappa}$$

4. DISCUSSION

In the present work on the basis of realistic assumptions we obtain the amplitude and the phase of the flexoelectric response of the oscillating membrane for a wide frequency range. For the first time the interval around the characteristic frequency of the flip-flop is considered. The results comprise the explicit dependence of the rheological properties of the membranes. They can be used for the determination of the flexocoefficients of free and blocked flip - flop and of the rate of exchange of molecules between the monolayers of the membrane. There exist experimental data on flexoelectricity of oscillating membrane of egg yolk lecithine [13]. The frequency dependence of the amplitude of the voltage response is in good agreement with formulae (8).

The experiments, concerning the influence of the additive divalent ions on the flexoelectric response can elucidate the mechanism of adsorption. This can give an answer whether some of the considered adsorption models is relevant or further theoretical investigations are needed. In reality both monovalent and divalent ion adsorption take place. It is possible that for the over - all explanation of the observed effects the simultaneous action of the two mechanisms has to be studied.

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