A NEW MODEL FOR FLEXOELECTRIC POLARIZATION OF BILAYER LIPID MEMBRANES AT BLOCKED "FLIP-FLOP"

A. Petrov, Y. Pavloff

To cite this version:

A. Petrov, Y. Pavloff. A NEW MODEL FOR FLEXOELECTRIC POLARIZATION OF BILAYER LIPID MEMBRANES AT BLOCKED "FLIP-FLOP". Journal de Physique Colloques, 1979, 40 (C3), pp.C3-455-C3-457. <10.1051/jphyscol:1979391>. <jpa-00218787>

HAL Id: jpa-00218787
https://hal.archives-ouvertes.fr/jpa-00218787
Submitted on 1 Jan 1979

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
A NEW MODEL FOR FLEXOELECTRIC POLARIZATION
OF BILAYER LIPID MEMBRANES AT BLOCKED «FLIP-FLOP»

A. G. PETROV and Y. V. PAVLOFF

Liquid Crystal Group, Institute of Solid State Physics, Bulgarian Academy of Sciences,
72, bd Lenin, Sofia 1113, Bulgaria

Résumé. — La polarisation flexoélectrique d'une membrane courbée avec libre flip-flop a été
calculée par l'un des auteurs quelques années auparavant. Si le flip-flop est bloqué, le nombre de
molécules lipidiques dans chaque monocouche de la membrane ne change pas. Dans ce cas le chan-
gement de leurs densités d'empaquetage a comme résultat le changement de la composante normale
des dipôles lipidiques. On obtient une formule pour le calcul du coefficient flexoélectrique et on
utilise les données expérimentales des monocouches pour calculer les coefficients flexoélectriques
de différentes substances. Les résultats sont du même ordre qu'avec libre flip-flop mais ce mécanisme
doit agir beaucoup plus vite.

Abstract. — The flexoelectric polarization of a curved membrane at free flip-flop was calculated
by us earlier. At blocked flip-flop the number of lipid dipoles in each monolayer remains unchanged.
In this case the change of their packing densities results in change of the normal component of the
lipid dipole. A formula for the flexoelectric coefficient is derived and monolayer data are used in
order to calculate the flexoelectric coefficient for different substances. The order of magnitude is the same
as with free flip-flop. But this mechanism should be faster.

1. Introduction. — A phenomenological expression
for the flexoelectric polarization per unit area of a
curved membrane was proposed by one of the authors
as early as 1974 [1] (see Fig. 1): 

\[ P = e(1/R_1 + 1/R_2) \]  

where \( e \) is the flexoelectric coefficient (dimension of
charge) and \( R_1, R_2 \), the radii of curvature of the
membrane.

A molecular model of this phenomenon at the
conditions of free flip-flop was developed later on.
At such a condition transitions of dipolar lipid
molecules from the compressed inner monolayer of
the curved membrane to the expanded outer-one
have to take place until the lipid densities become
equal. In this case [2] :

\[ e = (1/2) \bar{\mu} \bar{v} d(2 k_h + k_c)/(k_h + k_c) \]  

where :

\( \mu \) is the normal component of the lipid dipole,
\( \bar{v} \) is the mean lipid density,
\( d \) is the membrane thickness,
k_h, k_c is the elastic moduli per head, resp. chains.

2. The model. — In the case of blocked flip-flop
lipid transitions are impossible. The change of lipid
packing (more compact in the inner monolayer and
more loose in the outer-one in comparison with the
non-deformed state) results in some changes in the
polar head's conformation and in the water structured
around each head. Consequently, the resultant normal
component of the dipole moment per lipid molecule
in the outer expanded monolayer and in the inner
compressed monolayer will change in an opposite
manner. So, a dipole debalance in respect to the mid-
plane (non-stretched) will arise and the curved
membrane will be polarized (see Fig. 2). For the
calculation of the flexoelectric coefficient, expressing
the proportionality between curvature and polariza-
A. G. PETROV AND Y. V. PAVLOFF

FIG. 2. Transverse section of the curved bilayer — the dipoles of the expanded monolayer increase, while these of the compressed decrease. As a result the bilayer will be polarized. The flexoelectric coefficient should be negative.

Fig. 2. — Transverse section of the curved bilayer — the dipoles of the expanded monolayer increase, while these of the compressed decrease. As a result the bilayer will be polarized. The flexoelectric coefficient should be negative.

The polarization $P$ in this case is merely similar to the polarization under bending of a bimorph plate, composed by two halves with opposite directions of the polar axes. Considering dipolar densities as spreaded over the whole membrane thickness one can reach an equivalent description in terms of quadrupolar densities [3]. A quadrupolar model was recently applied to layered smectic systems [4].

3. Monolayer data. — Experimental data for surface potential measurements are used here in order to calculate flexoelectric coefficients for different substances. The surface potential $\Delta V$ due to the presence of dipolar lipid molecules spread at an interface can be measured experimentally. It is determined by the following expression [5] (see Fig. 3):

$$\Delta V = 4 \pi \mu / A$$

where:

$$\mu = \mu_{\text{head}} + \mu_{\text{H}_2\text{O}} + \mu_{\text{end}}$$

$\mu_{\text{head}}$ is the dipole moment of the lipid head,
$\mu_{\text{H}_2\text{O}}$ is the total moment of the water structured around each head,
$\mu_{\text{end}}$ is the dipole moment at the end group of each chain.

The flexoelectric coefficient can be calculated from the experimentally established dependence $\Delta V(A)$ by means of the following expression:

$$e = \left(1/4 \pi\right) (\Delta V + Ad \Delta V' dA) d \quad (8)$$

4. Results. —

A. Dipalmitoyl lecithin, air-water interface [6]:

$$\mu (60 \text{\AA}^2) = 0.72 \text{ D} \quad \mu (44 \text{\AA}^2) = 0.64 \text{ D}$$

$$d\mu / dA \approx \Delta \mu / \Delta A = 5 \times 10^{-5} \text{ statcoul., so :}$$

$$e = 5 \times 10^{-11} \text{ statcoul. at } 52 \text{ \AA}^2 \quad (9)$$

B. Dipalmitoyl lecithin, air-water interface [7] (see Fig. 4). From the slope of the curve $\mu(A)$ at 25°C below 45 \AA$^2$ (condensed state of the monolayer) we obtain:

$$e = 8.3 \times 10^{-11} \text{ statcoul. at } 44 \text{ \AA}^2 \text{ and } 25 \text{ °C}. \quad (10)$$

Fig. 3. — Schema of the surface potential measurements: lipid dipoles and oriented water dipoles contribute to $\Delta V$.

Fig. 4. — Surface potential ($\Delta V$), area ($A$) and surface dipole moment per molecule ($\mu$), area ($A$) curves for L-$\alpha$-dipalmitoyl lecithin at air/water interface (after Vilallonga, ref. [7], Fig. 1). The flexoelectric coefficient is determined from the slope of the curve $\mu(I)$ at 25°C in the region below 45 \AA$^2$. 
C. Dimiristoyl ethanolamine, oil-water interface [8]. In this case, the maximal value of the flexocoefficient corresponds to the area at which no dependence of $\Delta V$ on $A$ is observed, so that in expression (8) one can put $d \Delta V/dA = 0$ (see Fig. 5). The results are:

$$e = 8.7 \times 10^{-11} \text{ statcoul. at } 59 \text{ Å}^2 \text{ and } 20 \text{ °C} \quad (11)$$
$$e = 7.4 \times 10^{-11} \text{ statcoul. at } 73 \text{ Å}^2 \text{ and } 6 \text{ °C} \quad (12)$$

5. Conclusion. — The arising of a polarization in our new model is, as we pointed out, merely similar to the polarization under bending of a bimorph plate, composed by two halves of piezoelectric material with opposite directions of the polar axes. The order of magnitude is the same as with free flip-flop [9]. But this mechanism should be faster, because no redistribution of the lipid material after bending is necessary. In fact, the two mechanisms appear as two limiting cases — when the first is operating, the second is not active (no change of the area per head) and vice versa.

It was found very recently that in a mixed system (dipalmitoyl lecithin + sphingomyelin) the variation $d\rho/dA$ is more pronounced [10]. These findings increase the importance of our new mechanism for native membranes, which are complicated mixtures of different lipids.

riad potential-surface density curves for 1,2-dimyristoyl ethanolamine at the n-heptane/water interface (after Pethica et al., ref. [8], Fig. 5). The flexocoefficients are calculated from the plateau regions of both curves.

Note added in proof. — All flexocoefficients calculated here, are negative. Recently it was found that according to curve 6 °C on figure 5 a reversal of sign of flexocoefficient from negative to positive took place above $v = 1.9 \times 10^{14} \text{ mol./cm}^2$, $\epsilon$ quickly approaching its absolute negative value at higher densities (Petrov, A. G., Studia Biophysica, in press).

References