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Elastic properties of strongly curved monolayers. Effect of electric surface charges

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Abstract. — The structural and elastic properties of strongly curved cylindrical interface are characterised by spontaneous curvature, spontaneous area per molecule and three elastic moduli corresponding respectively to area extension, bending and mixed deformation of spontaneous state [6, 7]. All characteristics are influenced by the electrical charge of interface. We have calculated in terms of a general approach [16] the change of spontaneous geometrical characteristics and of the full set of elastic moduli of a cylindrical interface due to the electrical charge. The analysis is performed for an arbitrary dividing surface. The theoretical results are applied to the analysis of recently obtained experimental data [11]. The qualitative agreement between experimental data and theoretical predictions prove the validity of the developed approach. The quantitative comparison of results obtained with experimental data allows us to estimate the effective surface charge density of cylindrical DOPE/DOPS (3/1) monolayer in the hexagonal HII phase. This value is equal approximately to \(3 \times 10^{-3}[Q/m^2]\).

Introduction and statement of the problem.

In recent years the concept of elasticity has been widely used to describe the behaviour of interfaces formed by a dense monolayer of surfactant [1]. In the case of small deformations the change of free energy of a cylindrical interface may be described by three elastic moduli. Two of them, the area extension modulus \(E_{AA}\) [2, 3] and the bending modulus \(E_{JJ}\) [4, 5] are widely known. Recently [6, 7] we pointed out that a third elasticity modulus \(E_{AJ}\), corresponding to mixed deformation, is important, especially for highly curved interfaces.

Measurements of elastic moduli of soft interfaces are very complicated to perform. However, those for area extension modulus \(E_{AA}\) are now improved and almost standardized [2, 3]. Concerning the modulus of bending \(E_{JJ}\), different values for the same material have been reported [4, 5]. Nevertheless, enough data is now available to ask the basic

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question of what causes the values of elasticity: whether the hydrocarbon chains are responsible or whether the polar headgroup dominates.

The influence of electrostatic surface charges on the elasticity moduli has been theoretically investigated in various papers. Some years ago, Israelachvili et al. [8] proposed a condenser model to account for bending energy of fluid membranes. It assumes surface charges and electrolytic countercharges of each monolayer to form a condenser of fixed spacing which is held together by the interfacial tension of the water/oil boundary.

More recently, Lerche et al. [9] investigated the question about the influence on the spontaneous curvature of a bilayer membrane with an asymmetric charge distribution.

Other papers deal with the electrostatic contribution to Helfrich's elastic moduli [10] based on the Debye-Hückel approximation. Later, these theories were enlarged to allow high charge densities and to account for coupling between both bilayer interfaces. This theory allows spontaneous vesiculation, however a crucial parameter is that of the neutral surface.

Recently the first measurement was performed of the influence of electrical charge on the mechanical characteristics of a strongly curved interface [11].

The experiments have been performed on phospholipid membranes in the inverted H_{12}-phase. The monolayer has the electrical charge due to the presence of acidic phospholipid PS (phosphatidylserine). The experimental procedure was the same as that in previous works [12, 14] which investigated the deformation of lipid cylinders under the action of an osmotic pressure difference. The theoretical analysis [6, 7] of such experiments allows the determination of the values of the three elastic parameters of the lipid monolayer corresponding to the dividing surface situated between lipid and water and to find the position of the neutral surface.

In the present paper, we first calculate theoretically the effect of surface charge on the entire set of elastic moduli of cylindrical monolayer concerning E_{AA}, E_{AJ}, E_{JJ} and on the spontaneous geometrical characteristics of the monolayer concerning the spontaneous curvature and the spontaneous area per molecule. In the appendix of the paper we analyse the experimental results obtained in reference [11]. The analysis concerns first the calculation of spontaneous geometrical characteristics and of the set of elastic moduli of a charged monolayer by means of a recently elaborated method [6, 7]. Secondly, we compare the obtained results with the corresponding characteristics of a neutral monolayer and prove the validity of theoretical approach. From this comparison, we estimate also the effective electrical surface charge of the cylindrical monolayer investigated experimentally in reference [11].

Main equations.

DESCRIPTION OF THE SYSTEM. — Let us consider a lipid monolayer of cylindrical shape. A part of lipid polar heads has the electrical charge. The internal volume of the cylinder is occupied by the electrolyte solution with concentration c_e.

To describe the mechanical properties of the monolayer we have to choose the dividing surface (Fig. 1). The internal dividing surface Σ_i is situated in the region of polar heads and is characterised by zero Gibbs excess of water [6]. The electrical charge is assumed to be uniformly distributed on the plane of the internal dividing surface Σ_i with the surface charge density σ. We will describe the monolayer in terms of an arbitrary dividing surface Σ. The distance between Σ_i and Σ is equal to z (Fig. 1).

Let us consider an element of monolayer corresponding to the element of dividing surface dΣ. The number of lipid molecules corresponding to dΣ is assumed to be constant during the deformations. Therefore we will characterize the element of dividing surface by the area per
lipid molecule \( A \) and the curvature \( J \). We will assume that the free energy of the monolayer element consists of mechanical \( F^m \) and electrical \( F^{el} \) parts
\[
F = F^m + F^{el} \quad (1)
\]
The mechanical part \( F^m \) comprises all effects except electrostatic ones. If the electrical charge is compensated, \( \sigma = 0 \), the free energy consists only of mechanical part \( F^m \).

**SPONTANEOUS STATE AND SPONTANEOUS GEOMETRICAL CHARACTERISTICS.** — The change of the free energy \( F \) due to the deformation is equal to [15]
\[
dF = \gamma \, dA + C_1 \, A \, dJ \quad (2)
\]
where the surface tension \( \gamma \) and bending moment \( C_1 \) depend on the choice of the dividing surface and are referred to as interface surface factors. Both surface factors are defined as derivatives of the free energy and consist of mechanical and electrical parts
\[
\gamma = \gamma^m + \gamma^{el}; \quad \gamma^m = \left( \frac{\partial F^m}{\partial A} \right) \bigg|_{J = \text{const.}}; \quad \gamma^{el} = \left( \frac{\partial F^{el}}{\partial A} \right) \bigg|_{J = \text{const.}} \quad (3)
\]
\[
C_1 = C_1^m + C_1^{el}; \quad C_1^m = \frac{1}{A} \left( \frac{\partial F^m}{\partial J} \right) \bigg|_{A = \text{const.}}; \quad C_1^{el} = \frac{1}{A} \left( \frac{\partial F^{el}}{\partial J} \right) \bigg|_{A = \text{const.}} \quad (4)
\]
The surface tension \( \gamma \) and bending moment \( C_1 \) depend on the deformation \( \gamma = \gamma(A, J) \); \( C_1 = C_1(A, J) \). In the spontaneous state the surface tension and bending moments are equal zero [16]
\[
\gamma(A_s, J_s) = 0 \quad (5)
\]
\[
C_1(A_s, J_s) = 0 \quad (6)
\]
In the spontaneous state the element of dividing surface is characterised by the spontaneous geometrical characteristics: spontaneous area per molecule \( A_s \) and spontaneous curvature \( J_s \), which satisfy equations (5) and (6). Spontaneous geometrical characteristics can be expressed in the following form
\[
A_s = A_s^m + \Delta A_s^{el} \quad (7)
\]
\[
J_s = J_s^m + \Delta J_s^{el} \quad (8)
\]
where $A^p_s$ and $J^m_s$ are the spontaneous area and the spontaneous curvature in the state with compensated charge, $\sigma = 0$; $\Delta A^p_s$ and $\Delta J^m_s$ are the changes of spontaneous geometrical characteristics due to the electrical charge.

**THE ELASTIC MODULI.** — The elastic moduli come into play as the second derivative of the monolayer free energy with respect to the deformation from the spontaneous state and consist also of mechanical and electrical parts. The modulus of extension is equal to

$$E_{AA} = E_{AA}^m + E_{AA}^{el}, \quad E_{AA}^m = A_s \left( \frac{\partial^2 F^m}{\partial A^2} \right)_{J_s}, \quad E_{AA}^{el} = A_s \left( \frac{\partial^2 F^{el}}{\partial A^2} \right)_{J_s}$$

(9)

The bending modulus is equal to

$$E_{JJ} = E_{JJ}^m + E_{JJ}^{el}, \quad E_{JJ}^m = \frac{1}{A_s} \left( \frac{\partial^2 F^m}{\partial J^2} \right)_{A_s}, \quad E_{JJ}^{el} = \frac{1}{A_s} \left( \frac{\partial^2 F^{el}}{\partial J^2} \right)_{A_s}$$

(10)

The modulus of mixed deformation is equal to

$$E_{AJ} = E_{AJ}^m + E_{AJ}^{el}, \quad E_{AJ}^m = \left( \frac{\partial^2 F^m}{\partial A \partial J} \right)_{A_s}, \quad E_{AJ}^{el} = \left( \frac{\partial^2 F^{el}}{\partial A \partial J} \right)_{A_s}$$

(11)

In the state with compensated electrical charge the elastic moduli comprise only mechanical parts. The derivatives of the electrical part of the free energy in expressions (3), (4), (9)-(11) have to be calculated under the condition of constant electrical charge per molecule.

**ELECTRICAL PARTS OF SPONTANEOUS GEOMETRICAL CHARACTERISTICS.** — The definition of the spontaneous state (5), (6) and of the elastic moduli (9)-(11) allow us to express the electrical parts of spontaneous geometrical characteristics.

Let us begin from the state with compensated electrical charge, $\sigma = 0$. In spontaneous state the mechanical parts of the force factors are zero, $\gamma^m = 0$, $C^m_1 = 0$ and the corresponding geometrical characteristics consist of mechanical parts, $A^m_s$ and $J^m_s$. The deformation of the interface with zero surface charge $\sigma = 0$ with respect to the spontaneous state leads to the surface tension $\gamma^m$ and bending moment $C^m_1$ which can be expressed in terms of deformations $A - A^m_s$ and $J - J^m_s$ by means of mechanical parts of the elastic moduli (9)-(11) in the following form [6]:

$$\gamma^m = E_{AA}^m \left( \frac{A - A^m_s}{A^m_s} \right) + E_{AJ}^m (J - J^m_s)$$

(12)

$$C^m_1 = E_{AJ}^m \left( \frac{A - A^m_s}{A^m_s} \right) + E_{JJ}^m (J - J^m_s)$$

(13)

Let us now consider the effect of electrical charge. The electrical repulsion of polar heads leads to a deformation of the interface with respect to the initial neutral spontaneous state with $\gamma^m = 0$, $C^m_1 = 0$ and to a transition to a new spontaneous state with $\gamma = \gamma^m + \gamma^{el} = 0$ and $C_1 = C^m_1 + C^{el}_1 = 0$. We will assume that the deformation of the initial neutral interface due to the electrical charge is small and the mechanical parts of force factors are given by (12) and (13). The equation for the new spontaneous state taking into account (5)-(8) and (12), (13) have the following form:

$$E_{AA}^m \left( \frac{\Delta A^p_s}{A^m_s} \right) + E_{AJ}^m \Delta J^{el} = -\gamma^{el}$$

(14)

$$E_{AJ}^m \left( \frac{\Delta A^{el}_s}{A^m_s} \right) + E_{JJ}^m \Delta J^{el} = -C^{el}_1$$

(15)
The solution of equation (14), (15) allows us to express the electrical part of the spontaneous geometrical characteristics through the elastic moduli and spontaneous geometry of the state with zero charge

$$\Delta A_{s}^{el} = A_{s}^{m} \left( \frac{E_{AA}^{m} C_{1}^{el} - E_{JJ}^{m} \gamma^{el}}{D_{m}^{m}} \right)$$

(16)

$$\Delta J_{s}^{el} = \frac{E_{AA}^{m}}{D_{m}^{m}} \gamma^{el} - \frac{E_{JJ}^{m}}{D_{m}^{m}} C_{1}^{el}$$

(17)

where $D_{m}^{m} = E_{AA}^{m} E_{JJ}^{m} - (E_{AA}^{m})^{2}$ is the determinant of the matrix of elastic moduli in neutral state.

**Theoretical results.**

The expressions (16), (17) and (9)-(11) allow us to determine the change of spontaneous area per molecule, spontaneous curvature and elastic moduli of the interface due to the electrical charge. All values are expressed through the partial derivatives of the electrical part of the free energy with respect to deformation of extension and bending.

Let us obtain the final expressions for structural and elastic characteristics of charged monolayer through the surface charge density $\sigma$ and electrolyte concentration $c_{e}$. The electrical charge is assumed to be distributed on the internal dividing surface $\Sigma_i$. Therefore we will use in the following expressions the geometrical characteristics of the internal dividing surface $\Sigma_i$. The area per molecule and the curvature corresponding to the internal dividing surface will be indicated below by the subscript $i$. These quantities are related to geometrical characteristics of the dividing surface $\Sigma$ by the following simple expressions:

$$A_i = A (1 - zJ), \quad J_i = J/(1 - zJ).$$

We will assume that the surface potential of the monolayer is small ($\approx 25 \text{ mV}$). Moreover we will assume that the electrical energy consists only of Debye layer energy. The possible effects of changes in polar heads (hydration, etc.) are not considered. In this case the electrical part of the free energy per molecule can be readily expressed in the following form [10]

$$F_{el} = \frac{1}{2} \frac{\sigma^2}{\varepsilon_{w} \varepsilon_{0} \chi} A_{i} \frac{I_{0}(\chi/J_{i})}{I_{1}(\chi/J_{i})}$$

(18)

where $I_{0}$ and $I_{1}$ are the modified Bessel functions, $\varepsilon_{w}$ and $\varepsilon_{0}$ are respectively the dielectric permeability of electrolyte solution and of vacuum, $\chi = \left\{ \frac{(2 \varepsilon_{e} e_{0}^{2})^{1/2}}{(\varepsilon_{w} \varepsilon_{0} kT)} \right\}^{1/2}$ is the inverse Debye length in 1 : 1 electrolyte and $e_{0}$ is the elementary charge. The quotient of the Bessel functions will be referred to as $B_{i} = \frac{I_{0}(\chi/J_{i})}{I_{1}(\chi/J_{i})}$

**SPONTANEOUS GEOMETRICAL CHARACTERISTICS.** — In accordance with equations (3) and (4) the electrical part of surface tension and bending moment are expressed through (18) in the following form

$$\gamma^{el} = - \frac{1}{2} \frac{\sigma^2}{\varepsilon_{w} \varepsilon_{0} \chi} (1 - zJ^{m}) B_{i}^{m}$$

(19)
and
\[ C_i^{el} = -\frac{1}{2} \frac{\sigma^2}{\varepsilon_w \varepsilon_0 X} \left( \frac{1}{J_i^m} B_i^m + \frac{X}{J_i^m J_m} \left( 1 - (B_i^m)^2 \right) \right) \tag{20} \]
where
\[ B_i^m = \frac{I_0(X/J_i^m)}{I_1(X/J_i^m)} \]

The substitution of expressions (19)-(20) in (16)-(17) gives the final equations for the electrical part of spontaneous geometrical characteristics of monolayer.

If the radius of curvature of internal dividing surface is greater than the Debye length these expressions have the approximate form
\[ \Delta A_s^{el} = \frac{1}{2} \frac{\sigma^2}{\varepsilon_w \varepsilon_0 X} \frac{A_s^m}{E_{AA}^m} \left( 1 + \frac{J_s^m}{2 X} - zJ_s^m \right) \tag{21} \]
\[ \Delta J_s^{el} = \frac{1}{2} \frac{\sigma^2}{\varepsilon_w \varepsilon_0 X^2} \frac{1}{E_{JJ}^m} \left( -\frac{1}{2} - \frac{3J_s^m}{4 X} - zX - J_s^m z \right) . \tag{22} \]

The expressions obtained allow the direct calculation of monolayer extension and of change of spontaneous curvature of monolayer due to the electrical charge. Figures 2a, b illustrate the dependence of spontaneous area per molecule and spontaneous curvature on the surface charge density. The figure is dealing with internal dividing surface \((z = 0)\) which will be important for the analysis of experimental data.

![Fig. 2. — Dependency of spontaneous geometrical characteristics of the internal dividing surface on surface charge density. a) Plot of the spontaneous curvature vs. surface charge density. b) Plot of spontaneous area per molecule vs. surface charge density.](image)

**Elastic moduli.** — The calculation of second partial derivatives of electrical free energy in the spontaneous state give the expressions for electrical parts of elastic moduli. Such expressions have the following form
\[ E_{AA}^{el} = \frac{\sigma^2}{\varepsilon_w \varepsilon_0 X} (1 - zJ_s^m) B_i^m \]
\[ E_{AJ}^{el} = \frac{1}{2} \frac{\sigma^2}{\varepsilon_w \varepsilon_0 X} \left( \frac{1}{J_i^m} B_i^m + \frac{X}{J_i^m J_m} \left( 1 - (B_i^m)^2 \right) \right) \]
\[ E_{jj}^{el} = \frac{1}{2} \frac{\sigma^2}{\varepsilon_w \varepsilon_0 X} \frac{1}{(J_s^m)^2} \left[ 2 \left( \frac{J_s^m}{J_i^m} \right) B_i^m \left( \frac{4X}{J_i^m} \right) + \left( \frac{2X^2}{J_i^m J_s^m} \right) \left( 1 - (B_i^m)^2 \right) \right] \]

\[ \frac{\Delta A_s^{el}}{A_s} = \frac{\Delta A_s^{el}}{A_s} = \frac{\Delta A_s^{el}}{A_s} \frac{\Delta J_s^{el}}{J_s} = \frac{\Delta J_s^{el}}{J_s} \frac{\Delta J_s^{el}}{J_s} = \frac{\Delta J_s^{el}}{J_s} \frac{\Delta J_s^{el}}{J_s} \]

\[ \Delta J_s^{el} = \frac{1}{2} \frac{\sigma^2}{\varepsilon_w \varepsilon_0 X} \frac{1}{E_{JJ}^m} \left( -\frac{1}{2} - \frac{3J_s^m}{4 X} - zX - J_s^m z \right) . \]
where

\[ B_{m}^{s} = \frac{I_{0}(\chi \mu_{s}^{m})}{I_{1}(\chi \mu_{s}^{m})} \]

The expressions (23)-(25) allow us to compute the change of electrical parts of elastic moduli as a function of the charge density \( \sigma \), the spontaneous curvature in neutral state \( J_{s}^{m} \), the Debye length \( \chi \) and the position of dividing surface with respect to the internal surface \( z \).

If the radius of curvature of the internal dividing surface is greater than the Debye length, \( \chi \mu_{s}^{m} \gg 1 \), the expressions (23)-(25) can be presented in approximate form

\[ E_{AA}^{el} = \frac{\sigma^2}{\varepsilon_{w} \varepsilon_{0} \chi} \]

(26)

\[ E_{AJ}^{el} = -\frac{1}{2} \frac{\sigma^2}{\varepsilon_{w} \varepsilon_{0} \chi} \left( z + \frac{1}{2} \chi \right) \]

(27)

\[ E_{JJ}^{el} = \frac{1}{2} \frac{\sigma^2}{\varepsilon_{w} \varepsilon_{0} \chi} \left( \frac{z^2 + \frac{z}{\chi} + \frac{3}{8} \chi^2}{\chi^2} \right) \]

(28)

In the appendix we will apply the obtained results to analyse the experimental data for the internal dividing surface \( z = 0 \) of cylindrical monolayer.

**Appendix**

**Analysis of experimental results.**

The parameters measured in experiments. — Let us analyse the experimental results obtained in reference [11] for a cylindrical monolayer in the H\(_{II}\) phase consisting of the 3/1 mixture of the neutral lipid DOPE and charged lipid DOPS. In experiments one measured the dependence of repeat distance of the system on the osmotical pressure difference between the outer electrolyte solution and the internal volume of the cylinder. The concentration of 1 : 1 electrolyte in these experiments was equal \( c_{e} = 2 \) mM. Such data allow [12-14] the calculation of the change of internal radius of cylinder \( R \), and the area per molecule on the internal dividing surface \( A_{r} \). Furthermore the theoretical treatment of this kind of data allow [7] to determine the values of elastic parameters of the internal dividing surface of the monolayer. These parameters are equal to the quotients of elastic moduli and the determinant of the matrix of elastic moduli : \( E_{AA}^{el}, E_{AJ}^{el}, E_{JJ}^{el} \)

\[ \frac{E_{AA}}{D}, \frac{E_{AJ}}{D}, \frac{E_{JJ}}{D} \]

Below we will give the analysis of these experimental data in terms of electrical effects considered in the main part of the paper. However, we would like to point out that such analysis can have only a qualitative character. There are at least two reasons for the changes of monolayer elastic properties under the action of the electrical charge. The first one is the electrostatic interaction considered above. The second one is hydration of the monolayer surface. The hydration energy gives a considerable contribution to the total free energy of the monolayer and consequently influences the effective values of elastic moduli [17]. On the other hand the hydration of the surface of lipid monolayer is strongly affected by the surface charge density and ionic strength of the bathing electrolyte [18]. The effects of the change of head group hydrations were not taken into account in the present consideration and can cause the effectively small value of the determined charge density.
The theoretical expressions for the elastic parameters can be readily obtained from (9)-(11) and (23)-(25) and are quite complicated. We will assume that the electrical parts of the elastic moduli are smaller than the mechanical ones. In this case the elastic parameters of the charged monolayer can be expressed through the corresponding parameters of neutral monolayer and the electrical part of elastic moduli (23)-(25) in the following form

\[
\frac{E_{AA}}{D} = \frac{E_{AA}^m}{D^m} \left( 1 - E_{AA}^{el} \frac{E_{AA}^m}{D^m} + 2 E_{AA}^{el} \frac{E_{AJ}^m}{D^m} \right) - E_{AA}^{el} \left( \frac{E_{AJ}^m}{D^m} \right)^2 \quad (A1)
\]

\[
\frac{E_{JJ}}{D} = \frac{E_{JJ}^m}{D^m} \left( 1 - E_{AA}^{el} \frac{E_{JJ}^m}{D^m} + 2 E_{AJ}^{el} \frac{E_{AJ}^m}{D^m} \right) - E_{JJ}^{el} \left( \frac{E_{AJ}^m}{D^m} \right)^2 \quad (A2)
\]

\[
\frac{E_{AJ}}{D} = \frac{E_{AJ}^m}{D^m} \left( 1 - E_{AA}^{el} \frac{E_{JJ}^m}{D^m} - E_{JJ}^{el} \frac{E_{AA}^m}{D^m} + E_{AJ}^{el} \frac{E_{AJ}^m}{D^m} \right) + E_{AJ}^{el} \left( \frac{E_{AA}^m}{D^m} \right) \left( \frac{E_{JJ}^m}{D^m} \right) \quad (A3)
\]

The dependence of elastic parameters on the surface charge density taking into account the expressions (23)-(25) is presented in Figure A1. All parameters decrease with surface charge.

![Figure A1](image-url)

**Fig. A1.** — Dependency of elastic parameters of the internal dividing surface on surface charge density. a) Plot of the elastic parameter of extension-compression $\frac{E_{AA}}{D}$ vs. surface charge density. b) Plot of the elastic parameter of bending $\frac{E_{JJ}}{D}$ vs. surface charge density. c) Plot of the elastic parameter of mixed deformation $\frac{E_{AJ}}{D}$ vs. surface charge density.
VALUES OF SPONTANEOUS GEOMETRICAL CHARACTERISTICS AND ELASTIC MODULI OF CHARGED MONOLAYER. — By means of theoretical treatment [7] of the experimental data of reference [11], we can determine the elastic parameters and spontaneous geometrical characteristics corresponding to the internal dividing surface of the monolayer from the mixture DOPE/DOPS (3/1). Such analysis gives the following values: the spontaneous curvature is equal to

\[ J_{si} = 2.8 \times 10^8 \, [m^{-1}] \]  

(A4)

which corresponds to the spontaneous radius of curvature \( R_{si} = 35.4 \times 10^{-10} \, [m] \). The spontaneous area per molecule is equal

\[ A_{si} = 76.7 \times 10^{-20} \, [m^2] . \]  

(A5)

The values of elastic parameters corresponding to the internal dividing surface of the monolayer under consideration are equal to

\[ \frac{E_{AA}}{D} = 6 \times 10^{19} \, [J^{-1}] , \quad \frac{E_{AJ}}{D} = 4 \times 10^{10} \, [N^{-1}] , \quad \frac{E_{II}}{D} = 110 \, [m/N] . \]  

(A6)

COMPARISON WITH THE CHARACTERISTICS OF A NEUTRAL MONOLAYER. — The values of elastic parameters and spontaneous geometrical characteristics of a charged monolayer determined above comprise mechanical and electrical contributions. To prove the developed theoretical approach we have to compare these results with the corresponding characteristics of a neutral monolayer. To make the correct comparison one needs the experimental data dealing with mixed DOPE/DOPS (3/1) monolayer with compensated electrical charge, \( \sigma = 0 \). Such a monolayer can be investigated only in a bathing solution with extremely low pH. At this time, we do not have such experimental data. However it is known [19] that neutralised DOPS in water forms a lamellar mesophase. Another lipid forming a lamellar mesophase in water is DOPC. Therefore we will assume that the properties of neutralized DOPE/DOPS monolayer are similar to the properties of a monolayer formed from 3/1 mixture of DOPE and the other neutral lipid DOPC. Such a monolayer has been experimentally investigated in a series of works [12-14]. The theoretical analysis of elastic properties of the internal dividing surface of this monolayer performed by us recently [7] gave the following values: the spontaneous curvature is equal to

\[ J_{si}^m = 3.3 \times 10^8 \, [m^{-1}] \]  

(A7)

the spontaneous area per molecule has the value

\[ A_{si}^m = 69 \times 10^{-20} \, [m^2] \]  

(A8)

the values of the elastic parameters are equal to

\[ \frac{E_{AA}}{D^m} = 6.4 \times 10^{19} \, [J^{-1}] , \quad \frac{E_{AJ}}{D^m} = 4.8 \times 10^{10} \, [N^{-1}] , \quad \frac{E_{II}}{D^m} = 120 \, [m/N] . \]  

(A9)

The comparison of values (A7)-(A9) with characteristics of a charged monolayer (A4)-(A6) shows that the spontaneous curvature and all elastic parameters decrease with surface charge, the spontaneous area per molecule increases with \( \sigma \). These results are in qualitative agreement with the theoretical predictions illustrated in figure 2 and A1. Such accordance supports the validity of the developed approach.
The comparison of characteristics of charged monolayer (A4)-(A6) with those of neutral monolayer (A7)-(A9) allows us to estimate the effective surface charge density $\sigma_{\text{eff}}$ of DOPE/DOPS monolayer. We have five independent equations (21)-(25) to determine $\sigma_{\text{eff}}$ by means of values (A4)-(A6) and (A7)-(A9). The solution of these equations gives the average value

$$\sigma_{\text{eff}} = 3 \times 10^{-3} \text{[Q/m}^2\text{]}. \quad \text{(A10)}$$

The deviation of $\sigma_{\text{eff}}$ obtained from different equations and from average value (A10) does not exceed 30%.

The effective value of surface charge density (A10) corresponds to small relative quantity of charged lipid head group equal approximately to 1.2%. In the same time 23.4% of monolayers consist of acidic phospholipid PS which theoretically has to be completely charged at the actual value of pH. Our estimate shows that only about 5% of DOPS molecules are dissociated. This effect can be due to different reasons.

First of all, the low charge density may be related to the value of apparent pK of lipid head groups which is different from the usual pK of the same groups on small molecules in dilute solution [20, 21]. In the detailed review of such effects [20] it is shown that the value of pK governing the dissociation of lipid polar groups depends strongly on the salt concentration of the electrolyte solution. In the experiments analysed in the present paper the salt concentration was extremely low and the value pK has to differ considerably from the usual one.

The other reason of the small values of charge density obtained can be related to the effects of monolayer hydration [13].

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References