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Interfacial tension of bilayer lipid membrane formed from phosphatidylethanolamine

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Abstract

The dependence of the interfacial tension of a lipid membrane on the pH of the aqueous solution has been studied. Interfacial tension measurements of phosphatidylethanolamine (PE) were carried out. A theoretical equation is derived to describe this dependence in the whole pH range. A maximum corresponding to the isoelectric point appears both in the theoretical equation and in the experimental data.

Keywords: Interfacial tension; Bilayer lipid membrane; Phosphatidylethanolamine

1. Introduction

The cell is the smallest structural element of all living organisms. Its functional state is characterized by a constant inner intercellular medium composition and by continuous exchange of substances with this medium and the environment. It is possible to meet these requirements owing to existence and function of a plasmatic membrane surrounding the cell. The plasmatic membrane is an integral part of each living cell [1–3].

A cell membrane is a very complex system; it contains various elements influencing its interfacial tension. Therefore, it is easier to study the effect of various factors; for example, pH of the medium, using artificial membranes called model membranes. The properties of the artificial membrane should be well known and similar to the properties of those occurring in living cells. Lipid monolayers, lipid bilayers, collodion, cellophane, milipore, ion exchanger, or other membranes are used as artificial membranes [2], but the interfacial tension of a cell membrane is best measured by means of a bilayer lipid model membrane.

Nowadays, it is doubtless that function and properties of a membrane are closely related to its structure. It has been demonstrated by suitable experimental techniques that all biological membranes have the same morphological structure: a phospholipid bilayer in which specialized proteins are incorporated and are connected with carbohydrates. An important property of a cell membrane is its interfacial tension [4,5]. Its importance is great as it endows the membrane with stiffness and stability. The interfacial tension of a bilayer lipid membrane depends on many factors like pH of the medium, the presence of cholesterol, of ionophores, or of pore-forming substances [6–8].

This paper is a continuation of studies of the effect of pH on interfacial tension of lipid bilayers. In this work, membranes have been formed from phosphatidylethanolamine (PE). The PE molecule is involved in acid–base equilibria with the medium.

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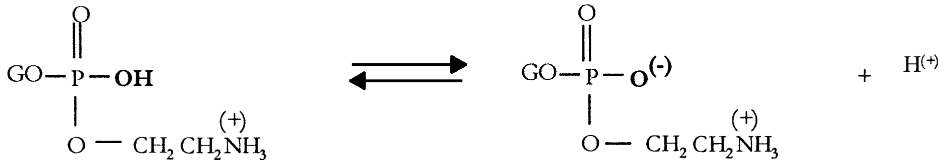
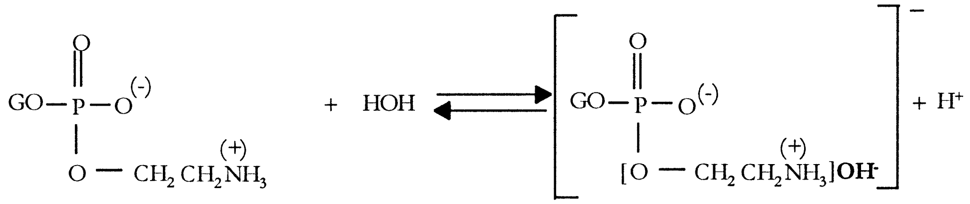
The equilibria can be written in the form:



$$GO-\overset{\overset{O}{\|}}{\underset{\underset{O-CH_2CH_2\overset{(+)}{NH_3}}{|}}{P}}-\mathbf{OH} \rightleftharpoons GO-\overset{\overset{O}{\|}}{\underset{\underset{O-CH_2CH_2\overset{(+)}{NH_3}}{|}}{P}}-\mathbf{O}^{(-)} + H^{(+)} \tag{1.1}$$



$$GO-\overset{\overset{O}{\|}}{\underset{\underset{O-CH_2CH_2\overset{(+)}{NH_3}}{|}}{P}}-O^{(-)} + HOH \rightleftharpoons \left[GO-\overset{\overset{O}{\|}}{\underset{\underset{[O-CH_2CH_2\overset{(+)}{NH_3}]\mathbf{OH^-}}{|}}{P}}-O^{(-)}\right]^- + H^+ \tag{1.2}$$

In the above equilibria, G is doubly acylated by the glycerol group [9,10].

2. Theory

2.1. Description I

The dependence of interfacial tension of a lipid membrane on pH of electrolyte solution can be described in terms of acid–base equilibria. The phospholipid molecule is in acid–base equilibria with the medium.

They can be written in the form:

$$AH \Leftrightarrow A^- + H^+ \tag{1.3}$$

$$B^+ + OH^- \Leftrightarrow BOH \tag{1.4}$$

$$HOH \Leftrightarrow H^+ + OH^- \tag{1.5}$$

Eqs. (1.4) and (1.5) yield

$$B^+ + HOH \Leftrightarrow BOH + H^+ \tag{1.6}$$

The dissociation constants of lipid membrane are presented as an equation,

$$K_a = \frac{a_{A^-} a_{H^+}}{a_{AH}} \tag{1.7}$$

$$K_b = \frac{a_{BOH} a_{H^+}}{a_{B^+}} \tag{1.8}$$

The H^+ and OH^- ions were assumed to be adsorbed at the phospholipid surface.

In such a case, the adsorption equilibria are presented by the following equations:

$$A^- + H^+ \Leftrightarrow AH \tag{1.9}$$

$$B^+ + OH^- \Leftrightarrow BOH \tag{1.10}$$

The lipid is present in the surface only. For this reason, its amount related to the membrane area yields the surface concentration of the lipid. This concentration and hydrogen and hydroxyl ion molarities in solution yield acid–base constants according to the following equations:

$$K_A = \frac{a_{AH}}{a_{A^-} a_{H^+}} \tag{1.11}$$

$$K_B = \frac{a_{BOH}}{a_{B^+} a_{OH^-}} \tag{1.12}$$

Concentrations of the dissociated and associated lipid forms in the above equations appear at the same (first) power.

The Gibbs equation can be written as:

$$d\gamma = -\Sigma \Gamma_i d\mu_i \tag{1.13}$$

Denoting the surface concentration of the lipid by s and considering an acid–base equilibrium form of Eq. (1.3) or (1.6), the following equations can be written:

$$a_{AH} + a_{A^-} = s \tag{1.14}$$

$$a_{BOH} + a_{B^+} = s \tag{1.15}$$

Eqs. (1.14) and (1.15) can be considered to be independent because they are interrelated by water self-ionization, which was not explicitly considered in deriving the equation system.

The dependence on pH of electrolyte solution of interfacial tension of lipid membrane formed from PE could be derived using the reasoning presented in a previous paper [7].

The equation obtained there has the form:

$$\gamma = -sRT\ln\left[\left(\frac{K_a}{a_{H^+}} + 1\right)\left(\frac{a_{H^+}}{K_b} + 1\right)\right] + \text{constant.} \tag{1.16}$$

Eq. (1.16) shows that interfacial tension maximum is imposed by the relationship:

$$a_{\mathrm{H}^+} = \sqrt{K_{\mathrm{a}}K_{\mathrm{b}}} \tag{1.17}$$

Substitution of Eq. (1.17) to (1.16) yields the dependence of interfacial tension of lipid membrane on pH of electrolyte solution.

$$\begin{aligned}\gamma = {} & \gamma_{\max} + 2sRT\ln\left(\sqrt{\frac{K_{\mathrm{a}}}{K_{\mathrm{b}}}}+1\right) \\ & - sRT\ln\left[\left(\frac{K_{\mathrm{a}}}{a_{\mathrm{H}^+}}+1\right)\left(\frac{a_{\mathrm{H}^+}}{K_{\mathrm{b}}}+1\right)\right]\end{aligned} \tag{1.18}$$

where: K_{a} and K_{b}—acid and base equilibrium constant, respectively; s [mol/m^2]—surface concentration of PE; R [J/(mol K)]—gas constant; T [K]—environment temperature; $\gamma_{\max}$ [mN/m]—maximum interfacial tension value of lipid membrane.

2.2. Description II

In Section 2.1, the surface excess of the H$^+$ and OH$^-$ ions has been assumed to be equal to their surface concentration. Although such an assumption has been frequent in adsorption phenomena analysis [11,12], it is correct only in the case of strong adsorption and low adsorbed ion concentration. In the case studied here, the surface excess definition used in derivation of Gibbs equation [13] should be strictly respected.

Equations describing surface excess values of H$^+$ and OH$^-$ ions are presented below:

$$\Gamma_{\mathrm{OH}^-} = a_{\mathrm{BOH}} - V_{\mathrm{H}^+}a_{\mathrm{AH}}a_{\mathrm{OH}^-} - V_{\mathrm{OH}^-}a_{\mathrm{BOH}}a_{\mathrm{OH}^-} \tag{2.1}$$

$$\Gamma_{\mathrm{H}^+} = a_{\mathrm{AH}} - V_{\mathrm{H}^+}a_{\mathrm{AH}}a_{\mathrm{H}^+} - V_{\mathrm{OH}^-}a_{\mathrm{BOH}}a_{\mathrm{H}^+} \tag{2.2}$$

where: V_{H^+} [m^3]—volume of the H$^+$ ions in the adsorption layer; V_{OH^-} [m^3]—volume of the OH$^-$ ions in the adsorption layer OH$^-$.

Substitution of Eqs. (2.1) and (2.2) to the Gibbs equation yielded:

$$\begin{aligned}\mathrm{d}\gamma = {} & -RTa_{\mathrm{BOH}}\frac{\mathrm{d}a_{\mathrm{OH}^-}}{a_{\mathrm{OH}^-}} + RTV_{\mathrm{H}^+}a_{\mathrm{AH}}\mathrm{d}a_{\mathrm{OH}^-} \\ & + RTV_{\mathrm{OH}^-}a_{\mathrm{BOH}}\mathrm{d}a_{\mathrm{OH}^-} - RTa_{\mathrm{AH}}\frac{\mathrm{d}a_{\mathrm{H}^+}}{a_{\mathrm{H}^+}} \\ & + RTV_{\mathrm{H}^+}a_{\mathrm{AH}}\mathrm{d}a_{\mathrm{H}^+} + RTV_{\mathrm{OH}^-}a_{\mathrm{BOH}}\mathrm{d}a_{\mathrm{H}^+}\end{aligned} \tag{2.3}$$

Thereafter, (Eqs. (1.11) and (1.12) and (1.14) and (1.15) from Section 2.1 were used to determine a_{AH} and a_{BOH}:

$$a_{\mathrm{AH}} = \frac{K_{\mathrm{A}}sa_{\mathrm{H}^+}}{1+K_{\mathrm{A}}a_{\mathrm{H}^+}} \tag{2.4}$$

$$a_{\mathrm{BOH}} = \frac{K_{\mathrm{B}}sa_{\mathrm{OH}^-}}{1+K_{\mathrm{B}}a_{\mathrm{OH}^-}} \tag{2.5}$$

Substitution of Eqs. (2.4) and (2.5) to Eq. (2.3), followed by elimination of a_{AH} and a_{BOH}, resulted in:

$$\begin{aligned}\mathrm{d}\gamma = {} & -sRT\frac{K_{\mathrm{B}}\mathrm{d}a_{\mathrm{OH}^-}}{1+K_{\mathrm{B}}a_{\mathrm{OH}^-}} + sRTV_{\mathrm{H}^+}\frac{K_{\mathrm{A}}a_{\mathrm{H}^+}\mathrm{d}a_{\mathrm{OH}^-}}{1+K_{\mathrm{A}}a_{\mathrm{H}^+}} \\ & + sRTV_{\mathrm{OH}^-}\frac{K_{\mathrm{B}}a_{\mathrm{OH}^-}\mathrm{d}a_{\mathrm{OH}^-}}{1+K_{\mathrm{B}}a_{\mathrm{OH}^-}} - sRT\frac{K_{\mathrm{A}}\mathrm{d}a_{\mathrm{H}^+}}{1+K_{\mathrm{A}}a_{\mathrm{H}^+}} \\ & + sRTV_{\mathrm{H}^+}\frac{K_{\mathrm{A}}a_{\mathrm{H}^+}\mathrm{d}a_{\mathrm{H}^+}}{1+K_{\mathrm{A}}a_{\mathrm{H}^+}} + sRTV_{\mathrm{OH}^-}\frac{K_{\mathrm{B}}a_{\mathrm{OH}^-}\mathrm{d}a_{\mathrm{H}^+}}{1+K_{\mathrm{B}}a_{\mathrm{OH}^-}}\end{aligned} \tag{2.6}$$

Integration of Eq. (2.6) for the conditions $\gamma = \gamma_{\max}$, $a_{\mathrm{H}^+} = a_{\mathrm{H}^+}^{\max}$ and $a_{\mathrm{OH}^-} = a_{\mathrm{OH}^-}^{\max}$ resulted in the expression:

$$\begin{aligned}\gamma = {} & \gamma_{\max} - sRT\left(1+\frac{V_{\mathrm{H}^+}}{K_{\mathrm{A}}} - V_{\mathrm{H}^+}K_{\mathrm{W}}K_{\mathrm{A}}\right)\ln\frac{1+K_{\mathrm{A}}a_{\mathrm{H}^+}}{1+K_{\mathrm{A}}a_{\mathrm{H}^+}^{\max}} \\ & - sRTV_{\mathrm{H}^+}K_{\mathrm{W}}K_{\mathrm{A}}\ln\frac{a_{\mathrm{H}^+}}{a_{\mathrm{H}^+}^{\max}} + sRTV_{\mathrm{H}^+}(a_{\mathrm{H}^+} - a_{\mathrm{H}^+}^{\max}) \\ & - sRT\left(1+\frac{V_{\mathrm{OH}^-}}{K_{\mathrm{B}}} - V_{\mathrm{OH}^-}K_{\mathrm{W}}K_{\mathrm{B}}\right)\ln\frac{1+K_{\mathrm{B}}a_{\mathrm{OH}^-}}{1+K_{\mathrm{B}}a_{\mathrm{OH}^-}^{\max}} \\ & - sRTV_{\mathrm{OH}^-}K_{\mathrm{B}}\ln\frac{a_{\mathrm{OH}^-}}{a_{\mathrm{OH}^-}^{\max}} + sRTV_{\mathrm{OH}^-}(a_{\mathrm{OH}^-} - a_{\mathrm{OH}^-}^{\max})\end{aligned} \tag{2.7}$$

2.3. Description III

The phospholipid layer observed from the aqueous solution side has uniformly distributed $-\mathrm{PO}^{(-)}$ and $-\mathrm{N}^{(+)}\mathrm{H}_3$ groups because it is built of the molecules each having one $-\mathrm{PO}^{(-)}$ group and one $-\mathrm{N}^{(+)}\mathrm{H}_3$ group. Therefore, two descriptions of the PE surface can be adopted. In Description I, the membrane surface is continuous with uniformly distributed functional groups being the active centres of adsorption of the H$^+$ and OH$^-$ ions. In Description II, the PE surface is composed of nonbonded molecules and of the molecules with bonded H$^+$ and OH$^-$ ions. A model is presented in Fig. 1.

Uniformly distributed active centres at which the H$^+$ and OH$^-$ ions can be adsorbed are present at the aqueous solution side.

They are schematically described with Eqs. (3.1) and (3.2):

$$-\mathrm{PO}^{(-)} + \mathrm{H}^{(+)}_{(\mathrm{A}^-)} \Leftrightarrow -\mathrm{PO}^{(-)} - \mathrm{H}^{(+)}_{(\mathrm{AH})} \tag{3.1}$$

$$-\overset{(+)}{\mathrm{N}}\mathrm{H}_3 + \mathrm{OH}^{(-)}_{(\mathrm{B}^+)} \Leftrightarrow -\overset{(+)}{\mathrm{N}}\mathrm{H}_3 - \mathrm{OH}^{(-)}_{(\mathrm{BOH})} \tag{3.2}$$

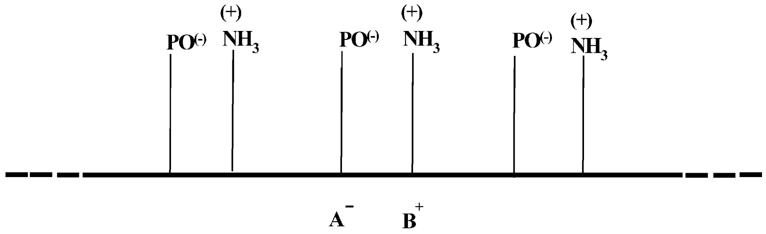


Fig. 1. The model of the PE surface, which presents the equilibria between the H^+ and OH^- ions from solution and the functional groups distributed on its surface.

Thus, four groups, namely, A^-, AH, B^+, and BOH are present at the layer surface.

The dependence of interfacial tension of lipid membranes on the pH solution can be described in terms of acid–base equilibrium. This dependence is presented in a previous paper [8].

$$\gamma = \gamma^0_{A^-}\left(\frac{1}{1+K_A a_{H^+}}\right) + \gamma^0_{AH}\left(\frac{K_A a_{H^+}}{1+K_A a_{H^+}}\right) + \gamma^0_{B^+}\left(\frac{1}{1+K_B a_{OH^-}}\right) + \gamma^0_{BOH}\left(\frac{K_B a_{OH^-}}{1+K_B a_{OH^-}}\right) \tag{3.3}$$

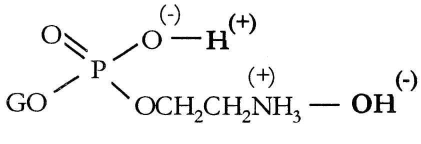
where: γ [N/m]—interfacial tension of the lipid membrane; $\gamma^0_{A^-}$, γ^0_{AH}, $\gamma^0_{B^+}$, γ^0_{BOH} [N/m]—specific interfacial tension of the membrane component, respectively.

Eq. (3.3) presents the dependence of the interfacial tension of the lipid membrane on pH of electrolyte solution.

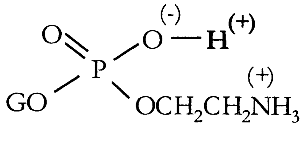
2.4. Description IV

The adsorption of the H^+ and OH^- ions at the lipid layer surface formed from PC or PS can result as presented in a previous paper [8].

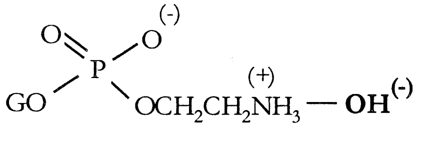
The adsorption of the H^+ and OH^- ions at the PE layer surface can result in the presence of the forms:



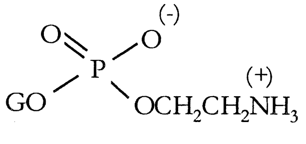
(EHOH)



(EH^+)



(EOH^-)



(E)

Thus, four groups, namely, EHOH, EH^+, EOH^-, and E are present at the layer surface.

Eq. (3.1) presents the dependence of the interfacial tension of the lipid membrane on pH of electrolyte solution.

$$\gamma = \gamma^0_{LHOH}\left(\frac{K_A a_{H^+}}{1+K_A a_{H^+}}\right)\left(\frac{K_B a_{OH^-}}{1+K_B a_{OH^-}}\right) + \gamma^0_{LH^+}\left(\frac{K_A a_{H^+}}{1+K_A a_{H^+}}\right)\left(\frac{1}{1+K_B a_{OH^-}}\right) + \gamma^0_{LOH^-}\left(\frac{1}{1+K_A a_{H^+}}\right)\left(\frac{K_B a_{OH^-}}{1+K_B a_{OH^-}}\right) + \gamma^0_{L}\left(\frac{1}{1+K_A a_{H^+}}\right)\left(\frac{1}{1+K_B a_{OH^-}}\right) \tag{4.1}$$

where: γ [N/m]—interfacial tension of the lipid membrane; γ^0_{LHOH}, $\gamma^0_{LH^+}$, $\gamma^0_{LOH^-}$, γ^0_{L} [N/m]—specific interfacial tension of the membrane component, respectively.

3. Experimental

3.1. Methods

The interfacial tension, γ, of the lipid bilayer was determined by measuring the curvature radius, R, of the convex surface formed by applying a pressure difference, Δp, on its sides. The method used was based on Young's and Laplace's equation [14].

$$2\gamma = R\Delta p.$$

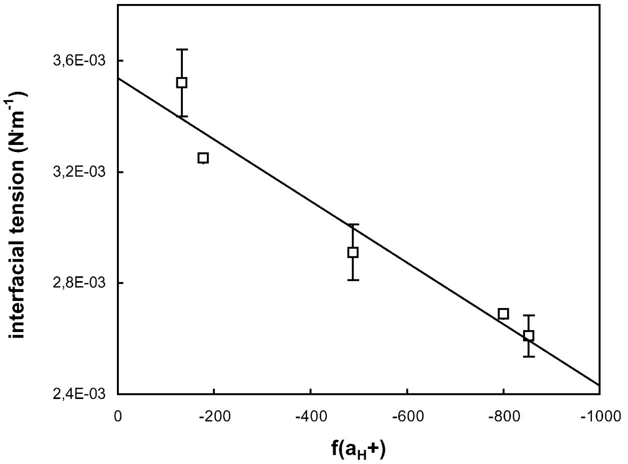


Fig. 2. The dependence of the interfacial tension of a lipid membrane formed from PE on the pH of the electrolyte solution.

3.2. Measurements

The apparatus and the measurement method were described in previous papers [6,7].

The lipid membranes were formed by the Mueller–Rudin method [15]. They were formed in a Teflon diaphragm of 1.5 mm outer diameter containing an orifice along its axis. An electrolyte solution was present on both sides of the orifice. The convexity of the spherical cap was measured by means of a microscope with an objective equipped with a scale with 0.1 mm interval scale marks. Therefore, the instrument readings of the lipid spherical cap were made with 0.05 mm precision. The convexity of the lipid membrane of the spherical cap, together with the Teflon element diameter corresponding to the lipid spherical cap diameter, yielded the radius of curvature. The measurement of the spherical cap was difficult, as the spherical cap is hardly visible. While using yellow light, its visibility gets better.

The interfacial tension was measured on freshly created lipid bilayer membrane 12–15 times for each pH electrolyte solution. For each membrane, about 10 instrument readings of the lipid spherical cap diameter, formed by pressure difference applied on both sides, were made. These measurements were made in the whole range, from the very low values of the lipid spherical cap diameter to those almost equal to the Teflon element radius. From all of instrument readings (100–150), the arithmetic mean and standard deviation were enumerated. Measurements with preparation of the electrolyte solution were made two to three times to test the repeatability of these determinations.

The solution used to form the model membrane contained 20 mg/ml of PE in solution (*n*-decan, chloroform).

In the measurements, the bilayer lipid membranes were also used in the form of liposomes. These could be formed owing to the fact that most phospholipids undergo spontaneously in water or in aqueous electrolyte solutions if shaken or subjected to ultrasounds. Bubbles of spherical or cylindrical shape sized, from less than 0.1 μm to a fraction of a millimetre, are then formed [16,17]. They were formed as follows [18]: 10 mg of PE (99%, Fluka) was dissolved in 1–2 ml of chloroform and the solvent was evaporated in the atmosphere of argon until 25–50 μm^3 of lipid film remained in the beaker. Fifteen cubic centimetres of 0.9% NaCl was then added and the beaker was placed in a water bath (at about 280.15 K). The head of an UD-20 ultrasound generator was then immersed in the solution and the solution was subject to ultrasounds five times for 1.5 min each time. The liposomes of 10–20 nm were obtained [19].

3.3. Materials

PE (99%) from Fluka was used in the experiment.

Buffers of 2–12 pH ranges were prepared according to Britton and Robinson [20] and used as the electrolyte. They were prepared by adding 0.2 M sodium hydroxide to 100 ml of solution having the following composition: 0.04 M acetic acid (80%, POCh), 0.04M phosphoric acid (POCh), and 0.04 M boric acid (POCh). A suitable pH of the buffer was established depending on the amount of added sodium hydroxide. Initial pH of the prepared buffer is 1.81. It changes to, for example, 3.29 after 20 cm^3 of NaOH is added or to 6.80 if 50 cm^3 is added.

4. Results and discussions

The effect of pH of the medium on interfacial tension of lipid membrane formed from PE was studied at room temperature in the 2–12 pH range.

The membranes formed by the Mueller–Rudin method were used to determine the dependence of the interfacial tension of the PE membrane on H$^+$ ion concentration in the electrolyte solution. The liposomes were used to determine the isoelectric point of the PE membrane.

The dependence of the interfacial tension of the lipid membrane on H$^+$ ion concentrations in the electrolyte so-

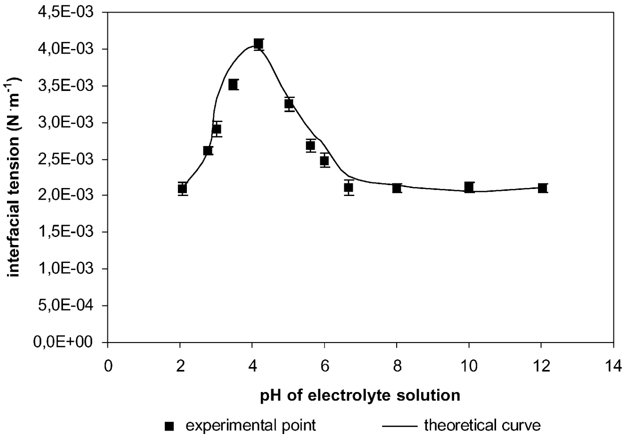


Fig. 3. A plot illustrating Eq. (1.18) in the pH range 2.8–5.6.

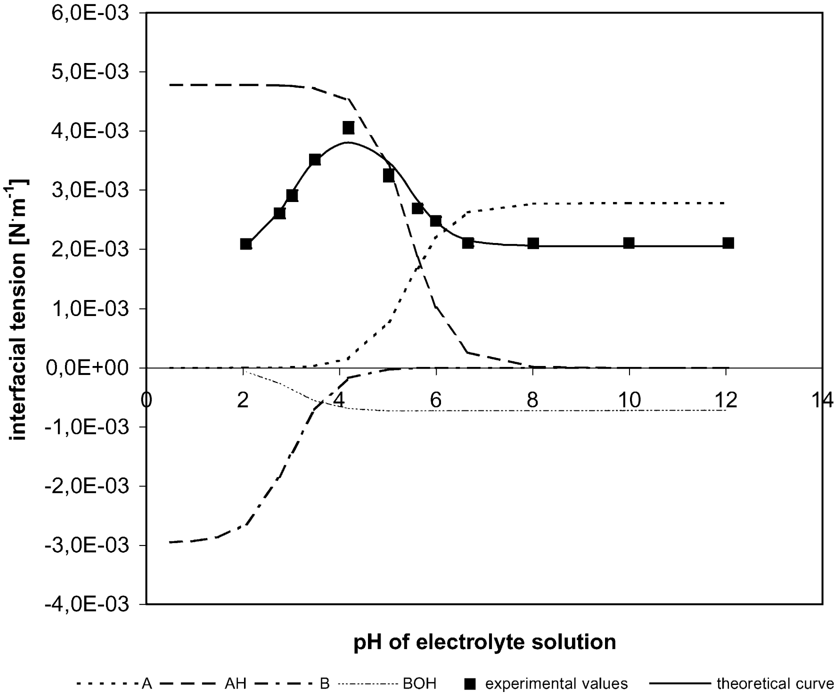


Fig. 4. The participation of A and B groups, calculated for Description III, in dissociated and associated forms in the interfacial tension of the bilayer formed from PE, as a function of pH of electrolyte solution.

lution is presented by Eq. (1.18). In this equation, the surface concentration and surface excess are identified. However, the theoretical interfacial tensions obtained from Eq. (1.18) coincide with the experimental ones of the PE membrane in proximity of its isoelectric point.

Variation in pH solution provokes changes in electric charge of the membrane by modifying acid–base equilibria of functional groups present in the membrane. In the isoelectric point, the number of positive and negative groups is equal and the net electric charge is zero. It is worth checking if the interfacial tension maximum of the membrane coincides with its isoelectric point.

Acid–base equilibria constants must be determined to calculate the isoelectric point. However, their determination is hampered by poor stability of PE in water. For this reason, liposomes were used like in a previous work [7]. In this way, uniform distribution of acidic and basic groups of PE molecules in the bulk solution was assured in spite of poor

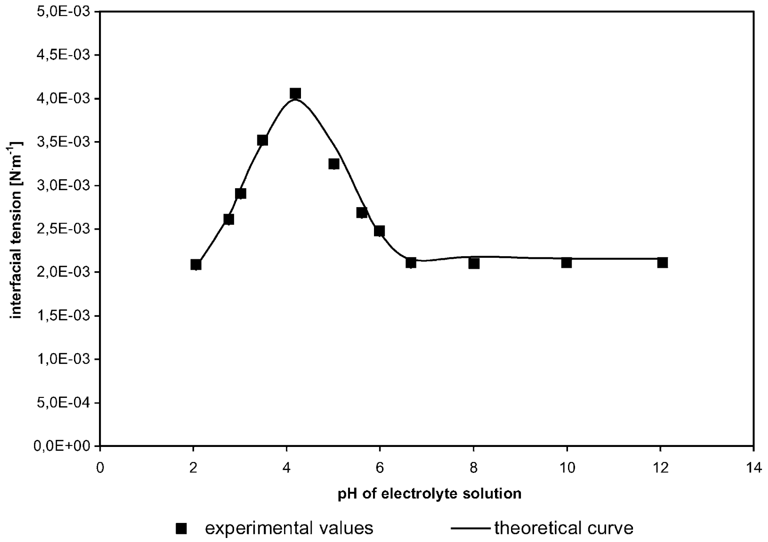


Fig. 5. The dependence of the interfacial tension of a lipid membrane formed from PE on the pH of the electrolyte solution calculated for Description IV.

solubility. It was assumed in calculations that only the outer-surface PE molecules present in calculations were half of the value introduced into solution.

Acid–base equilibria were determined by titrating the liposome system with hydrochloric acid and with sodium hydroxide. The acid–base equilibrium constants were found to be $pK_a = 2.42$ and $pK_b = 5.98$, respectively.

The dissociation constant data of the membrane permitted to calculate its isoelectric point; its position is at pH = 4.2.

The dependence of interfacial tension of PE membrane on solution pH is given by Eq. (1.18). It permits to determine maximum interfacial tension value, $\gamma_{\max}$, at pH = 4.18 and surface concentration of PE, S.

The dependence given by Eq. (1.18) is plotted in Fig. 2 in the coordinate system in which the plot should be rectilinear. The plot has been made in a narrow pH range in which theoretical interfacial tension points of PE membrane agree with the experiment. The slope of the line yielded S, surface concentration of PE, amounting to 2.225×10^{-6} mol/m^2. Intersection of the line with abscissa yielded the $\gamma_{\max}$ value equal to 4.07 mN/m. The values were determined by the least squares method. The surface area occupied by a PE molecule, 74.6 Å^2, could be determined from surface concentration.

Interfacial tension values of membrane formed from PE vs. pH are plotted in Fig. 3; the experimental values are presented as a point and the dependence resulting from Eq. 2.7 as a continuous line. As can be seen, theoretical interfacial tension values agree well with the experimental results.

Interfacial tension of the membrane formed from PE vs. pH of the electrolyte solution is plotted in Fig. 4. Points present the experimental values, the total values calculated from Eq. (3.3) are presented by a continuous line and the interfacial tension values of PE membrane components are marked with broken lines. Fig. 4 refers to the above-presented Description III, where the distribution of the $-PO^{(-)}$ and $-N^{(+)}H_3$ groups on the aqueous solution side of the lipid layer has been assumed to be uniform.

As can be seen in Eq. (3.3), the total interfacial tension value of the PE membrane is a sum of interfacial tension values of it components, namely, A^-, AH, B^+ and BOH.

Specific interfacial tension values of individual components of the PE membrane were determined. The results were obtained by linear regression using Excel 97. The $\gamma^0_{A^-}$, γ^0_{AH}, $\gamma^0_{B^+}$, γ^0_{BOH} values determined in this way are equal to 2.78×10^{-3}, 4.78×10^{-3}, -2.96×10^{-3}, and -7.3×10^{-4} mN/m, respectively.

Interfacial tension of the membrane formed from PE vs. pH of electrolyte solution is also plotted in Fig. 5. Points present the experimental values, the total values calculated from Eq. (3.1), which have been derived according to Description IV, are presented by a continuous line, and the interfacial tension values of PE membrane components are marked with broken lines.

The results of pH on interfacial tension of bilayer lipid membrane formed from phosphatidylcholine (PC), lecithin, and phosphatidylserine (PS) described in the papers [7,8] and of PE (this work) have permitted the determination of the effect of hydrophilic head of lipids on interfacial tension value of bilayer lipid membranes. Hydrophilic heads have been demonstrated to affect the interfacial tension values and, consequently, cell membrane properties. Unlike other phospholipids, for example, lecithin or PS, small hydrophilic head characterizes PE molecule. Regularity has been found: larger hydrophilic head of a lipid brings about lower interfacial tension.

Calculated interfacial tension values are $\gamma = 4.06 \pm 0.12$ mN/m for PE, $\gamma = 3.53 \pm 0.12$ mN/m for lecithin (large hydrophilic head), and $\gamma = 2.93 \pm 0.10$ mN/m for PS.

In addition, a relationship has been found between the size of hydrophilic head of the lipid and the isoelectric point pH value. With larger hydrophilic head, the isoelectric point appears at lower pH. The isoelectric point of PE was found to be at pH = 4.20, while those of lecithin and phosphatidylserine appear at pH = 4.15 and 3.80, respectively.

Interestingly, the interfacial tension value of the isoelectric point increases with decreasing hydrophilic head diameter of lipid. Surface energy of the isoelectric points for PC, PS and PE related to 1 mol of the substance are similar and amount to 1800, 1824 and 1854 J/mol, respectively.

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