



Physicochemical modelling of the surface-active phospholipid bilayer relative to acid-base equilibria



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ARTICLE INFO

Article history:

Received 2 September 2016

Received in revised form 20 October 2016

Accepted 21 October 2016

Available online 24 October 2016

Keywords:

Electrochemical impedance spectroscopy

Chronopotentiometry

pH

Bilayer membrane

Phosphatidylcholine

Lysophosphatidylcholine

ABSTRACT

The objective of this research was to evaluate interactions of hydrogen and hydroxide ions with bilayer membranes formed from phosphatidylcholine and lysophosphatidylcholine. Theoretical deliberations were successfully verified by experimental research studies that were conducted using electrochemical impedance spectroscopy and chronopotentiometry methods. Electrical capacitance and electrical resistance measurements were made on the membranes in various pH electrolyte solutions. The theoretical calculations were based on previously derived two theoretical models. In both models the contributions of the individual lipid molecule forms to the membrane electrical parameters were assumed to be additive.

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1. Introduction

The structural diversity of cell membranes makes it extremely difficult to study their properties. Therefore, scientific experiments are usually conducted on simplified models consist of one or more compounds. The most popular cell membrane models are planar bilayer lipid membranes (BLMs) dividing two aqueous solutions. This permits on location of electrodes in both aqueous solutions being in contact with the membrane and allows the exquisite studies of electrical properties by means of number of electroanalytical techniques [1–4].

The basic lipids for the preparation of bilayers are phospholipids (PLs) which are important constituents of biological cell membranes and are found in many animal tissues and organs [5]. The distribution of the different PLs between the outer and inner halves of the bilayer varies greatly in plasma membranes from different cells [6]. For example, the neutral choline-containing phospholipids, like phosphatidylcholine and sphingomyelin, reside in the outer leaflet of the red blood cell membrane while the charged amino-containing phospholipids, like phosphatidylserine, phosphatidylinositol and phosphatidylethanolamine, reside in the inner leaflet of the membrane [7].

The cell membrane is characterized by an equilibrium that is established within it, and at its surface with the external environment. In the literature, the equilibria existing between the cell membrane and the environment surrounding it is largely uncharacterized. One of the factors directly relevant to the establishment of this equilibrium is pH. The studies on acid-base equilibria between the bilayer lipid

membranes and solutions around membranes are of great importance in understanding the phenomena which take place in living organisms.

It is well known that the ionic transport properties in an electrochemical system can be obtained by analyzing the response of the system to externally applied electrical perturbations. The analysis in the time domain of the response of the system to controlled potential or current perturbations, or the analysis in the frequency domain of the steady state response to sinusoidal perturbations, are experimental techniques commonly used in electrochemistry [8]. The characterization of electrochemical systems by electrical response measurements requires the development of mathematical models for which the response can be determined theoretically and which serve as a basis for the interpretation of experimental data. The network simulation method has been used to numerically study the full electrochemical impedance of different kinds of non-ideal ion-exchange membrane systems, in which the ionic transport processes are described by the Nernst-Planck and Poisson equations [9–11]. The influence of the degree of inhomogeneity of the membrane fixed-charge distribution [9], the direct component of the electric current [10], and the asymmetry degree of the bathing ionic concentrations [11] on the electrochemical impedance and the linearity of the current–voltage relationship of an ion-exchange membrane system, has been analyzed and discussed in detail.

It has been shown, by means of electrochemical impedance spectroscopy [12], chronopotentiometry [13], chronoamperometry [14,15] and cyclic voltammetry [15], that membrane capacitance and membrane resistance change in response to changes in environment pH. In the paper [15] the effect of pH on the electrical parameters of membranes formed from chosen choline-containing phospholipids (CCPLs), phosphatidylcholine (PC) and lysophosphatidylcholine (LPC), were

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reported. The present work is a continuation of these studies - PC bilayers containing LPC were also tested in the electrolyte solution with different pH values but two other measurement methods were used: electrochemical impedance spectroscopy and chronopotentiometry. pH range was changed from 3.7 to 6.0 embracing the isoelectric CCPLs point (around pH 4.1). For the present work, PC was chosen because it is the most abundant phospholipid in mammalian cell membranes and it constitutes 40–50% of the total cell phospholipid content [16]; it is also described in detailed by biomembranes researchers. The choice of LPC is dictated by the fact, that the exact mechanism of action of this lipid is uncertain [17] and widely known is that it is extremely important to determine the properties of all kinds of membrane phospholipid in order to provide a proper understanding of processes taking place in biological membranes. LPC is a minor phospholipid in the blood plasma (8–12%) and in the cellular membranes ($\leq 3\%$) [18]. It results from partial hydrolysis of phosphatidylcholines, which removes one of the fatty acid groups. Among other properties, it activates endothelial cells during early atherosclerosis [19] and stimulates phagocyte recruitment when released by apoptotic cells [20]. Moreover, LPC can be used in the lab to cause demyelination of brain slices, to mimic the effects of demyelinating diseases such as multiple sclerosis. Further, it is known to stimulate phagocytosis of the myelin sheath and can change the surface properties of erythrocytes [18].

In the present paper, the quantitative characteristic of the equilibria between membranes composed from the CCPLs and H^+ and OH^- ions is shown. Two mathematical models, reported earlier by us [13,14], are adapted to describe these equilibria. In both models, the relative contributions of individual lipid molecule forms to electrical parameters of the bilayer are assumed to be additive and dependent on pH. Both models are validated by comparison between results from experimental studies and theoretical data.

2. Theory

2.1. pH effects on capacitance and conductance of the bilayer formed from choline-containing phospholipids

CCPLs as amphiphilic phospholipids can participate in equilibrium reactions with both H^+ and OH^- ions. The CCPLs layer observed from the aqueous solution side has uniformly distributed $-PO^{(-)}$ and $-N^{(+)}(CH_3)_3$ groups because it is built of molecules each having one $-PO^{(-)}$ group and one $-N^{(+)}(CH_3)_3$ group. Therefore, two models of the membrane surface can be assumed. Both models are based on the additivity of the electrical capacitance and the electrical conductance of the individual phospholipid molecule forms. In one model, the surface is continuous with uniformly distributed functional groups constituting the centers of H^+ and OH^- ions adsorption, while in the other the surface is built of CCPLs molecules, free or with attached H^+ and OH^- ions.

2.1.1. Model I

In the full model presented in [13,14], uniformly distributed active centers at which the hydrogen and hydroxide ions can be absorbed are present at the aqueous solution side. The adsorption equilibria can be given by:



where:

A^- presents $-PO^{(-)}$ group, B^+ is $-N^{(+)}(CH_3)_3$ group.

This means that the four groups: A^- , AH , B^+ and BOH can exist on the layer surface.

The lipid is present in the membrane only. Therefore, the surface concentration of the lipid is equal to its amount related to the

membrane surface area. The surface concentrations of the active center ions (C_{A^-} , C_{AH} , C_{B^+} , C_{BOH}) and the volume concentrations of the ions (C_{H^+} , C_{OH^-}) determine the acid-base constants according to the relationships:

$$K_A = \frac{C_{AH}}{C_{A^-} C_{H^+}} \quad (3)$$

$$K_B = \frac{C_{BOH}}{C_{B^+} C_{OH^-}} \quad (4)$$

Assuming that contributions of the individual forms of the CCPL molecule to the electrical parameters are additive, the dependencies of the membrane capacitance and membrane conductance on the pH of the electrolyte solution could be expressed as [13,14]:

$$C_m = C_{oA^-} \left(\frac{1}{1 + K_A C_{H^+}} \right) + C_{oAH} \left(\frac{K_A C_{H^+}}{1 + K_A C_{H^+}} \right) + C_{oB^+} \left(\frac{1}{1 + K_B C_{OH^-}} \right) + C_{oBOH} \left(\frac{K_B C_{OH^-}}{1 + K_B C_{OH^-}} \right) \quad (5)$$

$$R_m^{-1} = R_{oA^-}^{-1} \left(\frac{1}{1 + K_A C_{H^+}} \right) + R_{oAH}^{-1} \left(\frac{K_A C_{H^+}}{1 + K_A C_{H^+}} \right) + R_{oB^+}^{-1} \left(\frac{1}{1 + K_B C_{OH^-}} \right) + R_{oBOH}^{-1} \left(\frac{K_B C_{OH^-}}{1 + K_B C_{OH^-}} \right) \quad (6)$$

where:

C_m [$F m^{-2}$] – the electrical capacitance of membrane;

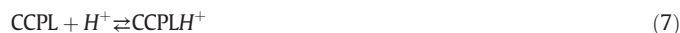
R_m^{-1} [$\Omega^{-1} m^{-2}$] – the electrical conductance of membrane;

C_{oA^-} , C_{oAH} , C_{oB^+} , C_{oBOH} [$F m^{-2}$] – the specific capacitances of the membrane components;

$R_{oA^-}^{-1}$, R_{oAH}^{-1} , $R_{oB^+}^{-1}$, R_{oBOH}^{-1} [$\Omega^{-1} m^{-2}$] – the specific conductances of the membrane components.

2.1.2. Model II

This model also was presented earlier in detail [13,14]. Assuming that the CCPL molecule having amphoteric character is involved in acid-base equilibria with both H^+ and OH^- ions, the following relationships can be written:



Based on the above expressions, it can be concluded that the CCPL molecule can exist in four different forms: $CCPLH^+$ with H^+ adsorbed, $CCPLOH^-$ with OH^- adsorbed, $CCPLHOH$ with both H^+ and OH^- ions adsorbed on the surface and a free CCPL i.e. with no ions adsorbed. It is assumed that the CCPL bilayer is composed of these four forms.

The surface concentrations of the groups postulated in Model I can be written depending on the forms of the CCPL molecule postulated in Model II:

$$C_{A^-} = C_{CCPL} + C_{CCPLOH^-} \quad (10)$$

$$C_{AH} = C_{CCPLH^+} + C_{CCPLHOH} \quad (11)$$

$$C_{B^+} = C_{CCPL} + C_{CCPLH^+} \quad (12)$$

$$C_{BOH} = C_{CCPLOH^-} + C_{CCPLHOH} \quad (13)$$

where:

C_{CCPL} , C_{CCPLOH^-} , C_{CCPLH^+} , $C_{CCPLHOH}$ [$mol m^{-2}$] – the concentrations on the membrane surface of the membrane components, respectively.

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