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The reassembled behavior of bilayer lipid membranes supported by Pt electrode

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Abstract

The article examines membrane permeability and reassembled behavior due to the surfactant hexadecyl trimethyl ammonium bromide (HTABr) addition. The influence of HTABr on s-BLMs was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The experimental results show that the HTABr appeared to be an effective ion carrier to facilitate the transmembrane transportation of ferrocyanide/ferricyanide. The permeability of s-BLMs changes with time and concentration of surfactant addition. At the same time, it is interesting to note that phosphatidylcholine molecules can self-assemble again on the surface of Pt electrode within limitative time and/or concentration of surfactant addition. The phenomenon of transmembrane transportation of ferrocyanide/ferricyanide disappeared in the absence of the surfactant hexadecyl trimethyl ammonium bromide.

Keywords: Reassembled; Hexadecyl trimethyl ammonium bromide; Surfactant; Cyclic voltammetry; Impedance spectroscopy

1. Introduction

The ion permeation between extracellar and intracellar through bilayer lipid membrane (BLMs) plays an important role in biological activity and has been extensively investigated. Presently, much attention has been paid to the research of ion permeation processes of self-assembled membrane, which are made of amphiphilic molecules containing diverse ion carriers or other electrochemical active substance [1–7]. The advantageous feature to these membrane systems is selective recognition and permeation to some ions. Many researchers are interested in this field because the ion permeation processes facilitated by ionophore or channel-forming peptides have potential not only for the basic research of biomembrane energetics and electrochemistry, but also for the development of biosensers and bioelectronic devices [8–11].

Although a BLM represents a high-energy barrier for hydrophilic ion, the studies on the BLMs adsorbed at the interface between two immiscible electrolyte solution have shown that the ion permeation occurs easily when ion transporters exist in the BLMs. Some researchers believed that the current for ion permeation was attributed to the transfer of ions associated with the transporters. The membrane systems could concentrate hydrophobic ions spontaneously into their lipid phases and even hydrophilic ions when the BLMs contain hydrophobic complexing agents [12].

Surfactants are known to dissolve lipid bilayer membrane and denature proteins [13], because the chemical structures of surfactant and lipid molecules are similar. That is to say, they are amphiphilic molecules and easily reacted with biomembrane. Subsequently, membrane permeability is changed. Despite a great number of studies on surfactant-induced lipid membrane permeabilization, the mechanism of the process is still far from being understood. Different experimental results can be observed even with the same surfactant/lipid system. Regarding membrane permeabilization, many questions are still open [14].

In this paper, we are mainly concerned with membrane permeability changes induced by surfactant hexadecyl trimethyl ammonium bromide and choose ferrocyanide/ferricyanide (1:1) as marker ions. Cyclic voltammograms and electrochemical

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impedance spectroscopy for ion permeation were recorded under various conditions. The study was undertaken in an attempt to better understand the molecular mechanism of ion permeation through the BLMs. From the experiment, we found that HTABr could react with $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ to form ion pairs, which facilitated probe molecules crossing the s-BLMs. Moreover, we presented the evidence that lipid membrane can reassemble on the surface of Pt electrode within limitative time and/or concentration of surfactant addition. When the surfactant concentration exceeded a critical value, the reassembled behavior of the lipid membrane disappeared.

2. Experimental

2.1. Materials

L-α-Phosphatidylcholine (PC) from fresh egg yolk and cholesterol were purchased from Sigma (USA). Hexadecyl trimethyl ammonium bromide and all other chemicals were of analytical grade and were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). All chemicals were used without further purification. Obtained by means of a Arium 611 (Sartorius, Germany) water purification set, pure water was used throughout (18.2 MΩ cm).

2.2. Method for supported lipid layer formation

The material preparation and formation of s-BLMs on Pt electrode surfaces were followed as per the procedure in reference [7]. A Pt electrode of 1.0 mm diameter was used as a solid substrate.

2.3. Electrochemical measurement

All cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were carried out on an electrochemical working station 273A (EG&G, Princeton Applied Research, USA) and frequency response detection FRD100 ((EG&G, Princeton Applied Research, USA). For a.c. impedance measurements, a 5 mV amplitude sine wave was applied to the electrode. The frequency range was from 0.1 Hz to 10 kHz. Impedance data were fitted to an equivalent circuit by using a commercial program from FRD 100.

3. Results and discussion

3.1. Impedance measurement of Pt electrode supported lipid membranes

Impedance spectroscopy is an effective method for probing the features of a surface-modified electrode [15,16]. The experimentally obtained impedance data may be analyzed by a relatively equivalent circuit consisting of ideal and non-ideal electrical analogs to the real physical and chemical processes. Fig. 1 illustrates the results of impedance spectroscopy of a bare electrode (a) and a electrode modified with supported membranes

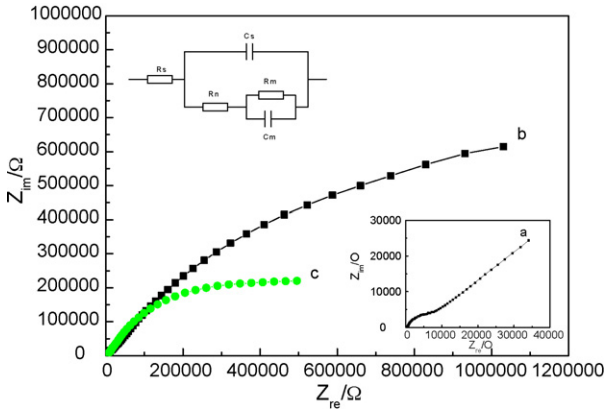

Fig. 1. Impedance spectra of bare Pt electrode (a), Pt electrode modified with supported bilayer lipid membrane (b) and after interaction with 5.0 mmol^{-1} HTABr for 10 min in 1.0 mmol l^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) solution containing 0.1 mol l^{-1} KCl. Inset shows the equivalent circuit.

(b) in the presence of 1.0 mmol l^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) solution containing 0.1 mol l^{-1} KCl. It can be seen that the bare Pt electrode exhibits an almost straight line that is the characteristic of a diffusional limiting step of the electrochemical process. However, with the presence of the bilayer lipid membrane, a significant difference in the impedance spectra is observed. The semicircle located near the origin is probed by higher frequencies, which means that the dynamics of electron transfer in higher frequency range could be observed and the current due to voltage excitation is under kinetic control [17]. The obvious semicircle of modified electrode indicates the s-BLM hindered the electron transfer of marker ions.

To get more detailed information about the impedance property of the membranes, a modified Randle's equivalent circuit (inset in Fig. 1) was chosen to fit the measured results. The total characteristic of impedance was determined by several parameters, where R_s is the electrolyte resistance, R_m the membrane resistance, C_m the membrane capacitance, R_n the non-membrane resistance and C_s is the distributing capacitance for the entire circuit. The value of C_m and R_m of s-BLMs were determined directly from the impedance spectroscopy using Randle's equivalent circuit as 3.11×10^{-7} F cm^{-2} and 9.31×10^5 Ω cm^{-2}, respectively.

It is known that the capacitance C_m depends on the membrane thickness according to the following relation:

$$C_m = \frac{\varepsilon\varepsilon_0}{d} \quad (1)$$

where d is the thickness of s-BLMs, ε the relative dielectric permittivity of the lipid (8.85×10^{-14} F cm^{-1}) and ε_0 is the dielectric permittivity of the free space (2.05 under our experimental [18]). From Eq. (1), we know that the thickness of the lipid membranes is ~5.8 nm. It is very close to the value of 4–10 nm, which is the thickness of the bilayer of PC [19,20]. It is clear that the s-BLMs have formed on the surface of Pt electrode.