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Novel modeling of electrical potential oscillation across a water/octanol/water liquid membrane

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Abstract

An oscillating electrical potential across a liquid membrane is studied as a model of a biological system. The oscillating potential is caused by repeated surfactant adsorption and desorption at the interface. The surfactant desorption process was simulated using both Fick's diffusion equation and the Langmuir-Hinshelwood equation. A water/octanol/water liquid membrane containing sodium dodecyl sulfate (SDS) was used and the effect of NaCl was studied. Calculations agree closely with experimental results, supporting the validity of the model we propose. Adsorption rate constants were obtained by comparing the experimental and calculated results. The addition of NaCl increased adsorption rate constants and decreased desorption rate constants. Calculations suggest that surfactant desorbs mainly into the octanol phase and this desorption is not affected by the addition of NaCl. The disordering of potential oscillations by NaCl addition may be caused by decreased SDS accumulation in the octanol phase close to the interface. A lower adsorption rate of the surfactant from the octanol phase onto the water/octanol interface leads to an oscillating electrical potential across the liquid membrane.

Keywords: Electrical oscillation; Liquid membrane; Octanol; Adsorption kinetics; Biomimetics

1. Introduction

The oscillation of an electrical potential across liquid membranes has been studied as a model of biological processes, using as an oscillator a water/oil/water liquid membrane containing surfactant in one water phase [1–5]. The liquid membrane oscillator has the advantages of regularity and reproducibility. Several organic solvents, such as nitrobenzene [6], octanol [7], and nitromethane [8], have been used for liquid membrane.

A taste sensor is a typical example of a biomimetic application of this electrical oscillation [8–12]. The addition of taste substances to the water phase changes the pattern of electrical oscillation, which varies with the taste category, distinguishing salty, sweet and bitter. In particular, the octanol liquid membrane is analogous to biological receptors in its response to a mixture of two taste substances [13]. Furthermore, an octanol liquid membrane has been reported to behave similarly to a biomembrane in the estimation of drugs [14]. These analogies suggest that an understanding of the electrical oscillation across an octanol liquid membrane can lead to an understanding of, and a model for, biological membranes.

The oscillation of an electrical potential across a liquid membrane has been explained by the repeated adsorption and desorption of surfactant at water/oil interface [1]. The mechanism of electrical oscillation has been discussed by many authors [15–17]. Nowadays it is known that the electrical oscillation occurs at the water/oil interface of the side initially without SDS [18,19]. Since the pioneering work of Yoshikawa et al. [9], some authors have reported the simulation of electrical oscillation across a nitrobenzene liquid membrane [18,20]. But the mechanism of electrical oscillation, including the adsorption and desorption of surfactant, is still unclear. To clarify the mechanism of electrical oscillation, analysis of surfactant movement is needed that includes a kinetic model of the liquid membrane and interface.

In the octanol liquid membrane, surfactant (generally sodium dodecyl sulfate (SDS) is used) initially constructs a stable monolayer at one water/oil interface whose molecules are repeatedly

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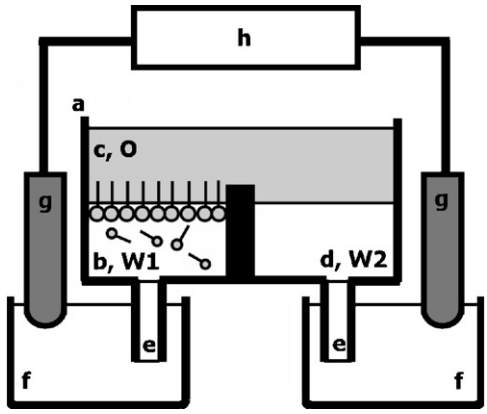

Fig. 1. Experimental setup for measurement of electrical potential across a liquid membrane: (a) fluoroplastic cell, (b, W1 phase) left water phase, (c, O phase) octanol phase, (d, W2 phase) right water phase, (e) salt bridge, (f) 3 M KCl, (g) Ag/AgCl electrode, (h) electrometer.

adsorbed and desorbed at the other water/oil interface [7]. The sudden adsorption process is probably caused by the Marangoni instability and a change in interfacial form [21,22]. Because of the complication of surfactant movement during the adsorption process, preliminary study of surfactant kinetics and surfactant concentration close to the interface is needed. On the other hand, the desorption process of the surfactant is concentration dependent. The desorption of surfactant, therefore, consists of two processes [23,24]; diffusion of the surfactant from the bulk water to near the interface, and adsorption and desorption of the surfactant at the interface.

The objective of the present paper is to construct a model of surfactant movement in the desorption process during the electrical oscillation across the octanol liquid membrane, to evaluate the effect of adding a salt (NaCl) as a taste substance, to obtain the kinetic constants of adsorption by comparing experimental and calculated values, and to identify which factors determine how the electrical potential oscillates by the estimation of surfactant concentration close to the interface.

2. Experimental and analytical

2.1. Measurement of electrical potential across an octanol liquid membrane

The electrical potential across a water/octanol/water liquid membrane was measured using the apparatus shown in Fig. 1 [7]. A fluoroplastic cell (a) was used for measurements. The water phase on the left (b, W1 phase) was 1.1 ml of distilled water containing 8 mM SDS and 5 M ethanol. The octanol phase (c, O phase) was 1.6 ml of 1-octanol containing 5 mM tetrabutylammonium chloride. The water phase on the right (d, W2 phase) was 1.1 ml of distilled water or 100 mM NaCl solution. Salt bridges (e) were directly connected under the cell. The other ends of the salt bridges were each immersed in a 3 M KCl solution (f). Using Ag/AgCl electrodes (g) each immersed in a 3 M KCl solution, the electrical potential was measured with an electrometer (h, Keithley 6517A). Data were stored on a personal computer. All experiments were performed at room temperature (293–298 K). All reagents were obtained from Wako Pure Chemicals and used as received without further purification.

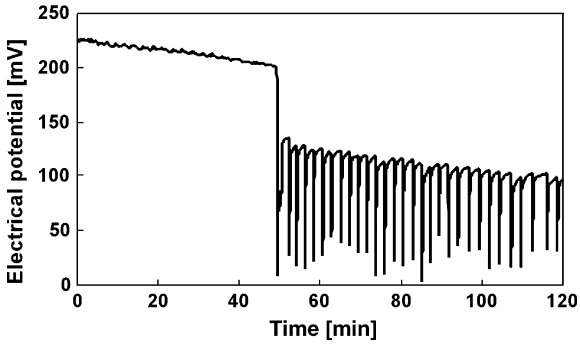

Fig. 2. Oscillation of electrical potential across an octanol liquid membrane (W1: 8 mM SDS, W2: distilled water).

3. Results and discussion

3.1. Oscillating electrical potential

Oscillations of the electrical potential between aqueous phases are shown in Figs. 2 and 3. The mechanism of the electrical oscillation across an octanol liquid membrane was explained as below [7].

The surfactant initially added to W1 phase is adsorbed onto W1/O interface. This adsorption of surfactant generates an initial potential of approximately 200 mV. The surfactant diffuses through O phase to the region close to W2/O interface. When the surfactant concentration reaches a critical value, the surfactant is adsorbed onto W2/O interface and suddenly generates an electrical potential at W2/O interface. Because the potential at W2/O interface depresses that across W1/O phase, the total electrical potential across the liquid membrane decreases. The sudden adsorption of the surfactant causes an excess surfactant density (over equilibrium) at W2/O interface. Formation of this excess is followed by desorption of the surfactant to W2 phase. As a result of desorption, the electrical potential at W2/O phase decreases and the liquid membrane potential recovers. When the surfactant concentration near W2/O interface again reaches the critical value due to transport from W1 phase, the surfac-

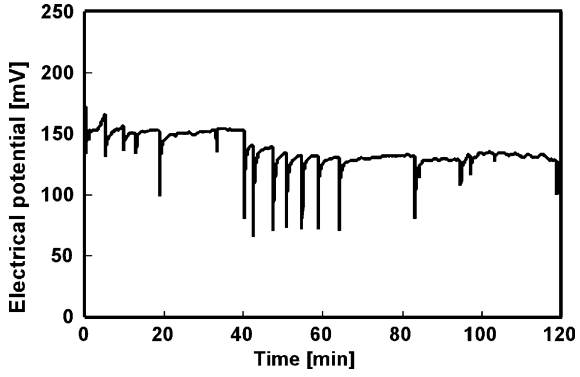

Fig. 3. Oscillation of electrical potential across an octanol liquid membrane (W1: 8 mM SDS, W2: 100 mM NaCl).