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OSCILLATION OF ELECTRICAL POTENTIAL IN A POROUS MEMBRANE DOPED WITH GLYCEROL α-MONOOLEATE INDUCED BY AN Na^+/K^+ CONCENTRATION GRADIENT

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The electrical potential across a fine-pore membrane doped with glycerol α-monooleate and separating aqueous solutions of 0.5 M NaCl and 0.5 M KCl was studied. It was found that this system showed rhythmic and sustained oscillations of electrical potential. These oscillations may be due to the phase transition of glycerol α-monooleate molecules within the fine pores. In relation to this, it is shown here that Na^+ and K^+ have different effects on the aggregation of glycerol α-monooleate. This oscillatory phenomenon is very interesting because in biological nervous membrane an Na^+/K^+ concentration difference across the membrane is essential for excitability.

1. Introduction

This paper reports that sustained potential oscillations occurred spontaneously across a porous membrane without any external stimulus such as pressure, voltage or electrical current. The membrane was placed between aqueous solutions of NaCl and KCl and the difference between the ion compositions of these aqueous phases on the right and left induced the oscillations. A concentration difference between Na^+ and K^+ is known to be essential for excitability of nervous membranes, but we know of no report about excitation of an artificial membrane by an Na^+/K^+ concentration gradient.

2. Materials and methods

The apparatus used in this study is shown schematically in fig. 1. Porous polytetrafluoroethylene filter paper of 10 μm nominal pore size (PF2) was obtained commercially from Toyo Roshi, Tokyo. The filter paper was soaked in monoolein (glycerol α-monooleate) for 72 h. The quantity of monoolein absorbed was adjusted to

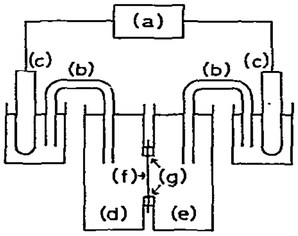

Fig. 1. Diagram of the experimental apparatus. (a) Millivoltmeter, (b) KCl salt bridge, (c) Ag/AgCl electrode, (d) 0.5 M KCl aqueous solution (7 ml), (e) 0.5 M NaCl aqueous solution (7 ml), (f) membrane, (g) silicon rubber gasket having a bore of 8 mm diameter.

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about 3 mg/cm^2. All experiments were carried out at room temperature (28 ± 1°C). The voltage across the membrane was measured with a Hitachi-Horiba F-7 pH/mV meter connected by two salt bridges to two Ag/AgCl electrodes. All reagents were commercial products.

3. Results and discussion

Typical traces of oscillation of the electrical potential are shown in fig. 2, where an upward change indicates an increase in the positive charge in the KCl solution. The oscillations started abruptly 10–120 min after the filter paper was placed between the solutions of 0.5 M NaCl and 0.5 M KCl. The observed oscillations could be classified into the three types shown in fig. 2 (a, b and c, d). In fig. 2a the resting potential was about +5 mV and spikes with an amplitude of 130 mV were generated successively at intervals of 2 min. Fig. 2b and c shows that the upward and downward changes of the electrical potential were generated mutually, i.e., transitions between two steady states occurred repeatedly. In fig. 2d the resting potential was about +8 mV and downward spikes were generated at intervals of about 20 s. All these types of oscillations were observed, but though we have carried out more than 100 experiments with porous membranes doped with monoolein, we have not yet succeeded in determining the experimental conditions necessary to produce a certain type of oscillation. This may be due to the uncertainty as to the state and quantity of monoolein molecules present within many pores, although we tried to ensure that the quantity of monoolein absorbed in the filter paper remained as constant as possible. This uncertainty may also be related to the variation of the amplitude (from several to 100 mV). It is also noted that sometimes one type of oscillation changed abruptly to another during an experiment.

Further insight into the oscillations was obtained by examining the effects of Na$^+$ and K$^+$ on the state of monoolein. Fig. 3 shows the changes of transmittance of light of 700 nm by aqueous solutions of monoolein of various concentrations in a cell of 10 mm light path. In pure water the transmittance decreased monotonically with increasing monoolein concentration. In contrast, in NaCl and KCl solutions the transmittance changed nonmonotonically with concentration. Fig. 3 shows that the effects of Na$^+$ and K$^+$ on the aggregation of monoolein were markedly different. This result suggests that Na$^+$ and K$^+$ interact differently with the molecules of monoolein at the interface

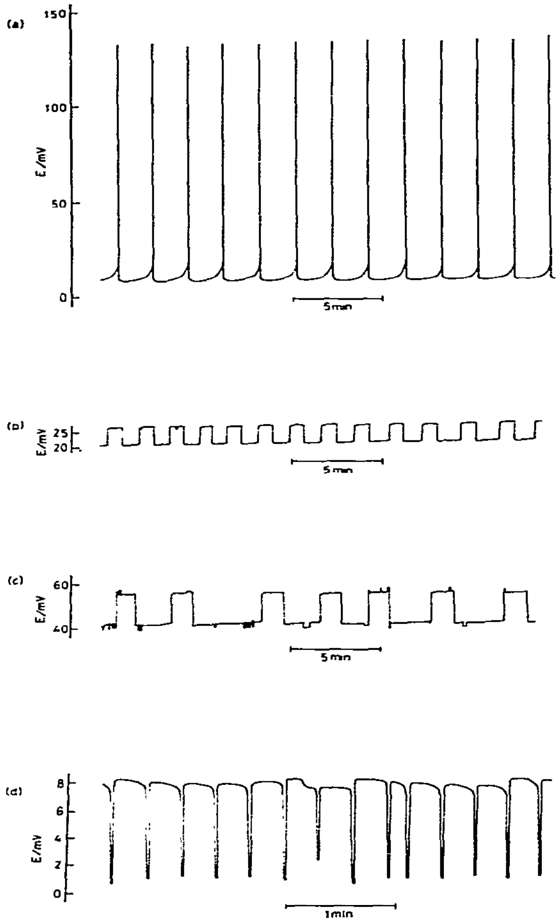

Fig. 2. Oscillations of electrical potential between the two aqueous phases. Experiments were performed at 28°C.

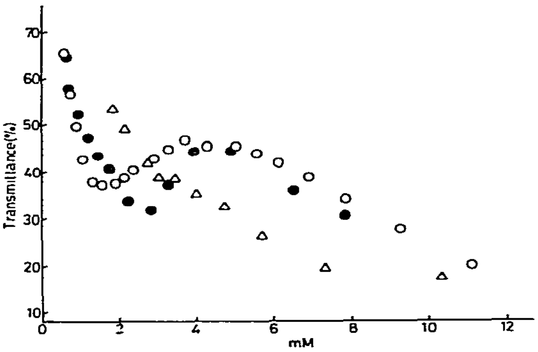

Fig. 3. Concentration dependence of the transmittance of light of 700 nm by monoolein in a cell of 10 mm light path. (○) 0.5 M KCl, (●) 0.5 M NaCl, (△) pure water.

between the aqueous and organic phases. The nonmonotonic behavior of the transmittance may be related to a phase transition, probably from an isotropic to a lamellar phase [1–3]. It is well established that such nonmonotonic behavior of a system is connected with oscillatory phenomena in general [4,5]. Thus, the abrupt transition of the electrical potential shown in fig. 2 may be related to this nonmonotonic behavior of the aqueous solution of monoolein. In addition, the changes of NaCl and KCl concentrations, together with the concentration of water, in the pores, i.e., the change of the states of the organic phase, may be the most important factors influencing the oscillation. In order to clarify the origin of the oscillation, we are now trying to obtain a phase diagram of monoolein with variation of the concentrations of water, KCl and NaCl.

It is also interesting to note that the NaCl solution is negative with respect to the KCl solution throughout the measurements (fig. 2). As the anion is Cl^- for both aqueous solutions, the membrane potential should result from the difference in the mobilities of Na^+ and K^+ within the membrane. The negative charge in NaCl solution suggests greater mobility of Na^+ than that of K^+. Hopfer et al. [6] reported that a bilayer membrane made from diglucosyldiglyceride showed cation selectivity, i.e., the mobility of Na^+ is greater than that of K^+. This is in accordance with our experimental result. The presence of hydroxyl groups in a hydrophobic region seems to be important for the preference of Na^+ over K^+.

Recently, we found that electrochemical oscillations occur spontaneously even in a simple two-phase system consisting of an organic solution of picric acid in nitropropane and an aqueous solution of cetyltrimethylammonium bromide [7]. We also studied an artificial liquid membrane consisting of an oil layer, nitrobenzene containing picric acid, placed between two aqueous phases, one containing cetyltrimethylammonium bromide and ethanol [8]. We found that this system also shows rhythmic and sustained oscillations of electrical potential. Further experimental and theoretical studies on oscillatory phenomena in porous and liquid membranes are in progress.

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