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A Novel Explanation for the Mechanism of Electrical Oscillation across a Liquid Membrane

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While studying electrical oscillation across a water-nitrobenzene-water liquid membrane, data that conflict with the explanation of Yoshikawa et al.[1] were found. The mode of electrical oscillation across this membrane is quite similar to that between an organic and aqueous phase to which no detergent has previously been added. A new explanation is given for the mechanism of oscillation.

Recently, excitable liquid membranes have been studied extensively. Yoshikawa and his coworkers [2] examined in detail electrical oscillation across a liquid membrane comprised of an organic layer, nitrobenzene containing 2,4,6-trinitrophenol (picric acid), interposed by two aqueous layers, using the U-shaped glass tube shown in Fig. 1. One of the aqueous layers (left arm of the tube in Fig. 1) contained hexadecyltrimethylammonium bromide (CTAB) and ethanol. The oscillation was explained as the repetitive formation and abrupt destruction of a monolayer structure of hexadecyltrimethylammonium (CTA) cations on the interface between the organic and aqueous phases in the left arm of the tube. However, while observing electrical oscillation under the same conditions, the present authors obtained data in conflict with this explanation, as follows: 1) Yellowish substances appear immediately on the left interface on contact of the organic phase with the two water phases. Just when these substances reaches the right interface, electrical oscillation begins. 2) With a drop in potential during oscillation, a small area of the surface layer of the organic phase occured ruptures at the right interface. Light yellowish substances then become suspended about the interface in the water phase. These findings prompted the authors to clarify in further detail the mechanism for electrical oscillation.

This study was conducted using essentially the same equipment as that by Yoshikawa et al.,[1] unless otherwise stated. A solution (4 ml) of

nitrobenzene containing 1.5 mM (1 M = 1 mol dm^{-3}) picric acid was placed at the bottom of the U-shaped glass tube as the organic phase. Two 10 ml portions of aqueous solutions were poured simultaneously into both arms of the cell on the organic phase without stirring. The left aqueous phase contained 5 mM CTAB and 1.5 M ethanol and the right one, 0.1 M sucrose. The potential across the liquid membrane was measured using two Ag/AgCl electrodes with a Beckmann SS-2 or Hitachi-Horiba M-7 pH/mV meter at 25±1 °C.

Figure 1 shows electrical potential oscillation across the liquid membrane and a schematical illustration of the diffusion of yellowish substances in the U-shaped cell. Oscillation first began immediately after the substances reached the right interface. The induction period, the period up to the time of the first oscillation, became shorter on lessening the distance between the two interfaces or adding CTAB to the organic phase after its contact with water phases. The potential drop in oscillation occurred synchronously with the rupture of a small area of the surface layer at the right interface.

Potential differences between the organic and water phases at the left and right interfaces were measured simultaneously. As shown in Fig. 2, two small tubes to serve as the salt bridges(f) and (g), connected to Ag/AgCl electrodes (b) and (c) were placed in the organic phase to monitor its potential. Electrical potential oscillation patterns obtained at the left and right interfaces are shown in Fig. 2 as (B) and (C), respectively. Oscillation of the liquid membrane was also observed and the data (A) in Fig. 2 are given for comparison. The rhythmic oscillation mode in Fig. 2 (C) is quite similar to that in Fig. 2 (A), with respect to period and

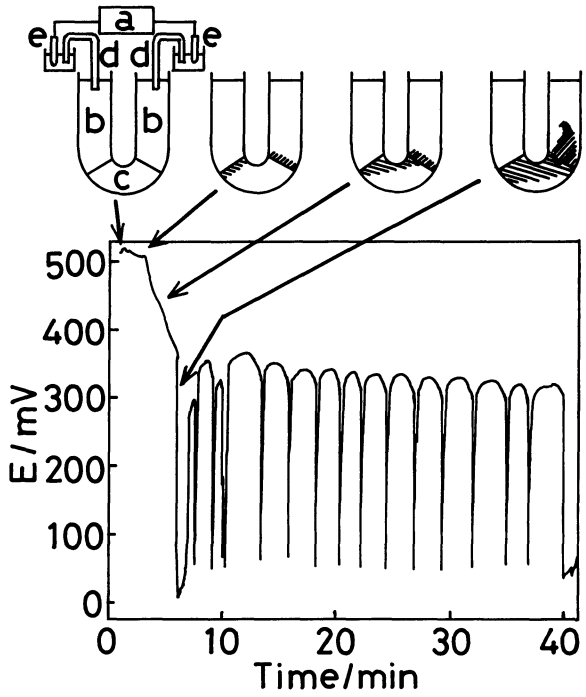

Fig. 1. Electrical potential oscillation across a liquid membrane and schematically illustrated features of the diffusion of yellowish substances in the U-shaped cell: (a) millivolt meter, (b) water phase, (c) organic phase, (d) salt bridge, (e) Ag/AgCl electrode.

amplitude of oscillation but differs marked with that in Fig. 2 (B). It is thus quite evident that electrical potential oscillation across the liquid membrane is generated at the right interface.

The diffusion potential in the organic phase was less than 30 mV, which is much less than that of the electrical potential of the liquid membrane. Phase-boundary potentials between the water and organic phases, as determined roughly in two systems consisting of an aqueous solution of 1.5 M ethanol and a nitrobenzene solution of 1.5 mM picric acid in the presence and then absence of CTAB, were 300 mV and -200 mV, respectively. Figure 1 shows the electrical potential of the liquid membrane to be about 500 mV just when the organic phase makes contact with the two water phases. The electrical potential of the liquid membrane is conceivably the algebraic sum of two phase-boundary potentials between the organic and water phases on the left and right interfaces. Although (A) in Fig. 2 was not recorded simultaneously with (B) and (C) but successively, they demonstrate that such a sum should be nearly the same as that of the electrical potential of the liquid membrane. Since the electrical potential of the liquid membrane becomes nearly zero at the bottom of an oscillation, the potential across the right interface just following rupture of the surface

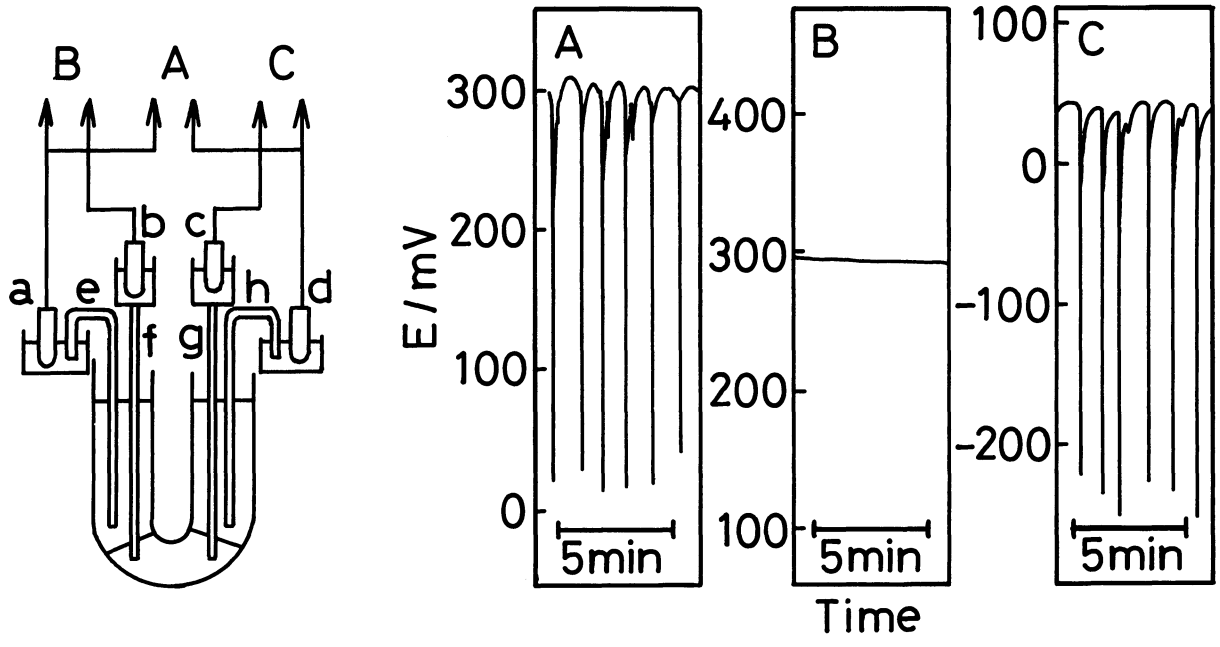

Fig. 2. Electrical potential oscillation across a liquid membrane (A), and between the organic and water phases in the left (B) and the right (C). All data were obtained using the U-shaped cell : (a), (b), (c), and (d) Ag/AgCl electrodes, (e), (f), (g), and (h) salt bridges.

layer would likely equal the potential across the left interface. The structure of the surface layer of the right interface following the rupture should thus resemble that of the left interface; that is, the monolayer of CTA cations is still in existence. Spectrophotometric determination of CTA cation indicated about 10 nmol of CTA cation to move toward the aqueous phase in the right arm by one oscillation. The amounts of CTA cations may correspond to many micelles.

The yellowish substances, which initially appeared near the left interface and diffused to the right in the organic phase, may be an inverted-micelle containing water, ethanol and CTA cations, with picrate anions. Electrical oscillation started immediately on their reaching the right interface, and a small area of the surface layer of the organic phase ruptured synchronously with the potential drop in the electrical oscilation of the liquid membrane. Consequently, a new mechanism for electrical oscillation across the liquid membrane should be proposed to explain the present findings. CTA cations, present in the left aqueous phase, adsorb on the interface, and picric acid molecules dissolve in the aqueous phase on contact of the organic phase with aqueous phase, followed by the formation of ion-pairs of CTA cations and picrate anions. The ion-pairs dissolve as inverted-micelles in the organic phase and move toward the right interface. After the micelles have reached the right interface, the monolayer of CTA cations is formed at the interface and the micelles become concentrated near the surface. On attaining a critical concentration, the micelles suddenly proceed to the right aqueous phase (State I), whereupon there occur the potential drop in the electrical oscillation of the liquid membrane and rupture the surface layer occur. Following a decrease in their concentration, the micelles depart from the organic phase (State II) and come to the surface. States I and II occur repeatedly in this manner.

This mechanism is consistent with the findings observed in this study and may serve as a basis for developing sensors that use liquid membranes.

References

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2) K. Yoshikawa and Y. Matsubara, Biophys. Chem., 17, 183 (1983); K. Yoshikawa, T. Omochi, and Y. Matsubara, ibid., 23, 211 (1986); K. Yoshikawa, T. Omochi, Y. Matsubara, and H. Kourai, ibid., 24, 111 (1986).

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