Observation of Self-Oscillation of Electrical Potential Difference in Organic Phase of Water-Oil-Water Liquid Membrane System

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Electrical potential differences were measured between two points in an organic phase of a water-oil-water liquid membrane system in which self-oscillations of an electrical potential difference across the three-phases-liquid membrane were observed. The electrical potential difference between two points in the organic phase was oscillated in the same way as did that across the three phases.

Self-oscillation of an electrical potential difference across an oil-water interface was first observed by Dupeyrat et al.,[1] and was observed also in a water-oil-water liquid membrane system first by Yoshikawa et al.[2] This three-phases system has been studied on mechanism of the self-oscillation,[2–6] and was applied to the method to analyze various substances such as tastes,[7] drugs,[8] and metal ions.[9,10] Various mechanisms have been proposed on the bases of the formation-deformation of the electrical bilayer at the interface,[2–4] ion transfer across the interface,[3,6] and dynamics of the interface.[5] The features of the self-oscillation were reported to depend on the features of the cell used such as largeness and material.[11] Yoshidome et al. proposed the H-shaped cell with high-reproducibility of the self-oscillation, and applied it to the analyses of metal ions.[9,10] In the present study, the electrical potential differences were measured between two points in the organic phase of the water-oil-water system. Self-oscillations were observed on the time course of the electrical potential difference, which indicates that the self-oscillations are not only caused by chemical and physical phenomena at the interface, but also by those in the organic phase. This is the first report of the self-oscillations of the electrical potential difference in the organic phase.

The experimental set-up used was the same as that reported before.[9] 3.2 ml of nitrobenzene solution of 1.5 mM picric acid was first placed in the cell to form the organic phase. An aqueous solution was placed on one surface of the organic phase to form W1 phase; and a pure water, on the other of the organic phase to form W2 phase. The W1 phase contained 10 mM hexadecyl trimethyl ammonium bromide as a surface active substance and 0.5 M 2-butanol. The electrical potential of the W1-phase hand was measured in reference to the W2-phase hand.

Figure 1(a) shows typical time course of the electrical potential difference between the two aqueous phases. The potential difference slightly fluctuated around −320 mV for the first 1400 s. Next sharp pulses of about 300-mV amplitude appeared at regular time intervals up to 3200 s, and continued at longer and irregular time intervals up to 4000 s. The potential difference subsequently approached 0 mV gradually after the pulses disappeared.[9] Figure 1(b) shows typical time course of the electrical potential difference between two points in the organic phase. The potential difference was measured at about center of each side of the organic phase through a couple of salt-bridges. The salt-bridges were inserted into the organic phase across each oil-water interface, and were 35 mm away from each other. The salt-bridges were formed in glass tubes, and the glass tubes for Figure 1(b) were covered with Teflon tubes. Self-oscillations were observed in Figure 1(b) in the same way as those in Figure 1(a). Figure 1(a) and (b) were not results of a simultaneous measurement, but the self-oscillations of the electrical potential difference in the organic phase are thought to be synchronized with the potential difference between two aqueous phases.

The salt-bridge is a gel of an agar containing KCl, that is, a kind of aqueous phase. The self-oscillations observed in Figure 1(b) might be those of the electrical potential difference across the interface between the agar-gel and the organic phase. A couple of carbon rods of 2 mm diameter covered with the Teflon tubes were next used instead of the salt-bridges. Figure 2(b) shows a part of the time course observed. Figure 2(a) is a part of Figure 1(b) for comparison. The features were almost similar between (a) and (b) of Figure 2, which means that the self-oscillations observed in the organic phase were not those of the electrical potential difference

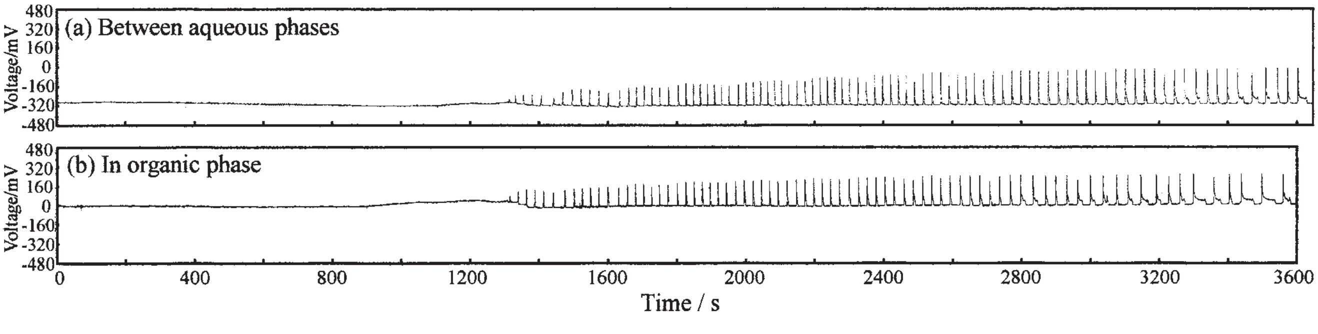

Figure 1. Typical time courses of the electrical potential difference between the two aqueous phases (a) and between two points in the organic phase (b).

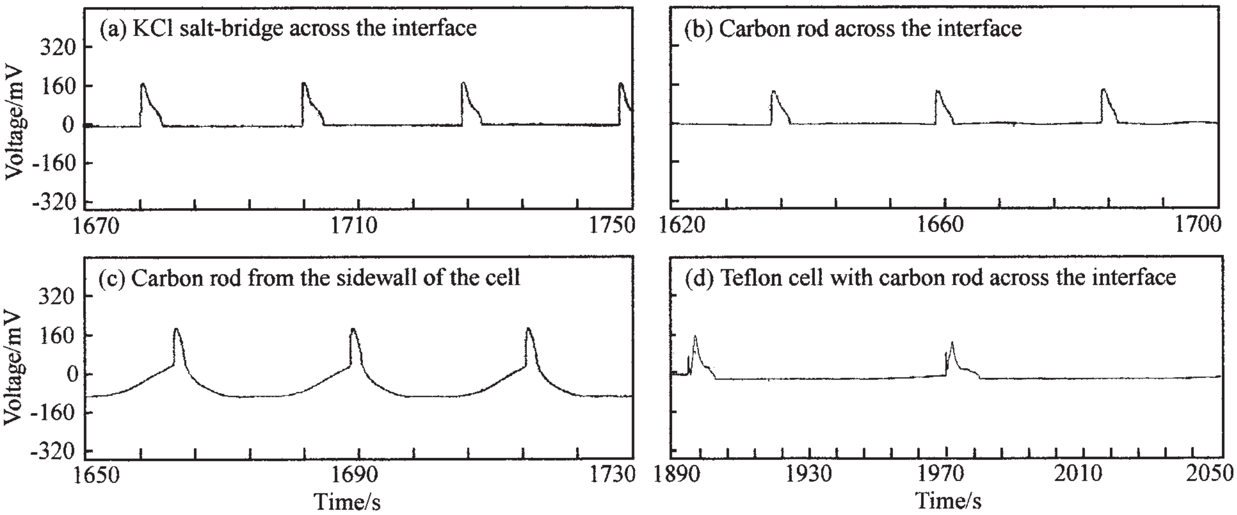

Figure 2. Parts of the time courses of the electrical potential difference between two points in the organic phase obtained with the use of the salt-bridges formed in the Teflon-covered-glass tubes across the interfaces (a), the Teflon-covered-carbon rods across the interfaces (b), the Teflon-covered-carbon rods inserted from the sidewalls of the cell (c), and the Teflon cell with the Teflon-covered-carbon rods across the interfaces (d).

across the interfaces of the agar-gel/organic-phase, nor of the carbon-rod/organic-phase.

Both the salt-bridges and the carbon rods were set across the oil-water interface. Influence of this penetration across the oil-water interface on the self-oscillation was investigated by the use of a couple of carbon rods inserted into the organic phase from the sidewall of the cell without any penetration across the oil-water interface. Figure 2(c) shows a part of the time course observed. The self-oscillations were surely observed though the features were different in shape of the pulses from those seen in Figure 2(a) and 2(b). The carbon rods inserted were not covered with Teflon tube, and a tip of an about 10 mm length of the carbon rods inserted was exposed to the organic phase, which leads the measurement of the electrical potential at this 10-mm-length area. On the other hand, the electrical potentials for the others of Figure 2 were measured at only a few-mm^2 area of the tip of the salt-bridge or of the carbon rod. The features of Figure 2(c) may be resulted from a spatial distribution of the electrical potential in the organic phase.

The cell used for the experiments mentioned above is made of glass. Similar experiments were next carried out with the use of a H-shaped cell made of Teflon. A part of the time course of the electrical potential difference in the organic phase is shown in Figure 2(d). The self-oscillations were observed though the features were different from those of the others of Figure 2. The time course of the electrical potential difference between the aqueous phases observed with the use of this Teflon-H-shaped cell was similar to that seen in Figure 2(d) (not shown). Teflon changed the time course of the electrical potential difference as shown in Figure 2(d). Thus, the observation of the self-oscillations in the organic phase was independent of the kind of the material of the H-shaped cell.

Thus, the self-oscillations of the electrical potential difference in the organic phase were first observed. Some physical phenomena in the organic phase, such as diffusion process of chemical substances, are thought to cause the self-oscillations. Any self-oscillation of the electrical potential difference in the organic phase has not been so far observed with the use of any type cell. The self-oscillations observed here in the organic phase are thought to be characteristic of the H-shaped cell used. Further experiments, such as simultaneous measurements and cell dependence, are being prepared for investigations of the mechanism.

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References

1 M. Dupeyrat and E. Nakache, *Bioelectrochem. Bioenerg.*, **5**, 134 (1978).
2 K. Yoshikawa and Y. Matsubara, *J. Am. Chem. Soc.*, **105**, 5967 (1983).
3 H. Yoshihisa, K. Miyamura, and Y. Gohshi, *Chem. Lett.*, **1997**, 1031.
4 K. Arai, S. Fukuyama, F. Kusu, and K. Takamura, *Electrochim. Acta*, **40**, 2913 (1995).
5 H. Suzuki and T. Kawakubo, *Biopyhs. Chem.*, **45**, 153 (1992).
6 K. Maeda, S. Nagami, Y. Yoshida, H. Ohde, and S. Kihara, *J. Electroanal. Chem.*, **496**, 124 (2001).
7 K. Yoshikawa, T. Omochi, and Y. Matsubara, *Biophys. Chem.*, **23**, 211 (1986).
8 K. Arai, S. Fukuyama, F. Kusu, and K. Takamura, *Bioelectrochem. Bioenerg.*, **33**, 159 (1994).
9 T. Yoshidome, T. Higashi, M. Mitsushio, and S. Kamata, *Chem. Lett.*, **1998**, 855.
10 T. Yoshidome, T. Higashi, and S. Kamata, *Chem. Lett.*, **2000**, 550.
11 H. Yoshihisa, S. Sutou, K. Miyamura, and Y. Gohshi, *Anal. Sci.*, **14**, 133 (1998).