Biophysical Chemistry 40 (1991) 149–153
Elsevier Science Publishers B.V., Amsterdam

BIOCHE 01563

A short period oscillation in a water / oil / water system

Hitoshi Suzuki *, Yoshimi Tsuchiya and Tatsuyuki Kawakubo
Department of Applied Physics, Tokyo Institute of Technology, Oh-okayama, Meguro, Tokyo 152, Japan

Received 30 August 1990
Revised manuscript received 24 November 1990
Accepted 27 November 1990

Water/oil interface; Potential oscillation

A new kind of potential oscillation with a short period of 7.5 s was found to occur in a water/oil/water system which consisted of an aqueous solution of surfactant, nitrobenzene and an aqueous solution of NaCl. A long period (~ 10 min) oscillation previously reported was also found to be superposed on the new oscillation. The power spectrum of the short period oscillation has been measured.

1. Introduction

Self-sustained oscillations in an artificial membrane system were discovered by Teorell [1]. Using salt solutions with different concentrations separated by a porous membrane, he observed undamped oscillations of the potential, the water pressure between two cells and the membrane resistance under the condition of d.c. current application. Kobatake [2] found an oscillation in another membrane system which consisted of a Millipore filter impregnated with dioleyl phosphate.

Similar oscillations in a water/oil interface system were observed by Nakache and Dupeyrat [3]. They observed oscillations of the interfacial tension, pH and the potential in an aqueous solution of octadecyltrimethylammonium chloride which was poured on nitrobenzene containing potassium picrate. Yoshikawa and Matsubara [4] obtained a stable oscillation in a three-phase system composed of an aqueous solution of surfactant (cetyltrimethylammonium bromide) with alcohol, nitrobenzene containing picric acid and an aqueous solution of sugars which were settled in a U-shaped tube and reported that the frequency and the shape of the oscillation depend on the concentration and the kind of alcohols. Yoshikawa et al. [5,6] also observed the same kind oscillatory behavior in another three-phase system which consisted of an aqueous solution of sodium oleate and alcohol as the solution of surfactant, nitrobenzene with 2,2′-bipyridine and an aqueous solution of NaCl and reported that the characteristics of oscillation such as frequency and amplitude were different for four taste stimuli — salty, sour, sweet and bitter – which were due to substances added to the solution of surfactant. They pointed out that the three-phase system was used as a taste sensor which distinguished the four tastes from each other. Kawakubo and Fukunaga examined the surfactant concentration dependence of the stability of oscillation on the same system [7] and further investigated the effect of a constant voltage or a constant current application on the oscillation [8]. They found that there was a range of applied voltage or current where the stable oscillation appears. The period of the oscillations they measured was of the order of 10 min.

It is supposed that a conformational transfor-

---

* To whom correspondence should be addressed.

0301-4622/91/$03.50

mation of surfactant such as the formation of inverted micelles near the water/oil interface causes the oscillatory behavior. However, the relation between such a transformation and the oscillations has not yet been demonstrated experimentally. We have no idea which of the chemical components of the system is the most essential for the mechanism of oscillation. In the present experiment, we have studied the same system as used by Yoshikawa et al. [5,6] and Kawakubo and Fukunaga [7] except that 2,2′-bipyridine was omitted in order to simplify the system. A new type of oscillation with a short period as well as the long period oscillation previously reported [5–7] was found to occur.

2. Experimental and results

2.1. Experimental procedure

The experimental cell was a U-shaped tube, 12.5 mm in diameter as shown in fig. 1. The water/oil/water interface system was composed as follows; distilled nitrobenzene (5 ml) was placed in the bottom of the cell, one side of the cell was filled with an aqueous solution of a mixture of surfactant sodium oleate (0.4 mM) and 1-propanol (20% v/v) and another side was filled with an aqueous solution of NaCl (0.5 M). All of the chemicals were purchased from Kanto Chemicals and were used without further purification except nitrobenzene.

For the electrical measurement, the two aqueous phases were connected via salt bridges to vessels where Ag/AgCl electrodes were placed and the electrode on the side of NaCl was grounded. The potential difference between the two electrodes was fed into a differential amplifier through an impedance converter. The experimental cell and the electrode vessels were placed in a metal box to shield them from electrostatic disturbance. The experiments were performed at room temperature (about 300 K) without any temperature control, because the experimental results did not seem to be sensitive to the environmental temperature in the present experiment. We sampled the amplified voltage at an interval of 0.5 s with a digital voltmeter (Keithley DMM196) and stored it on a disk with a microcomputer (NEC,

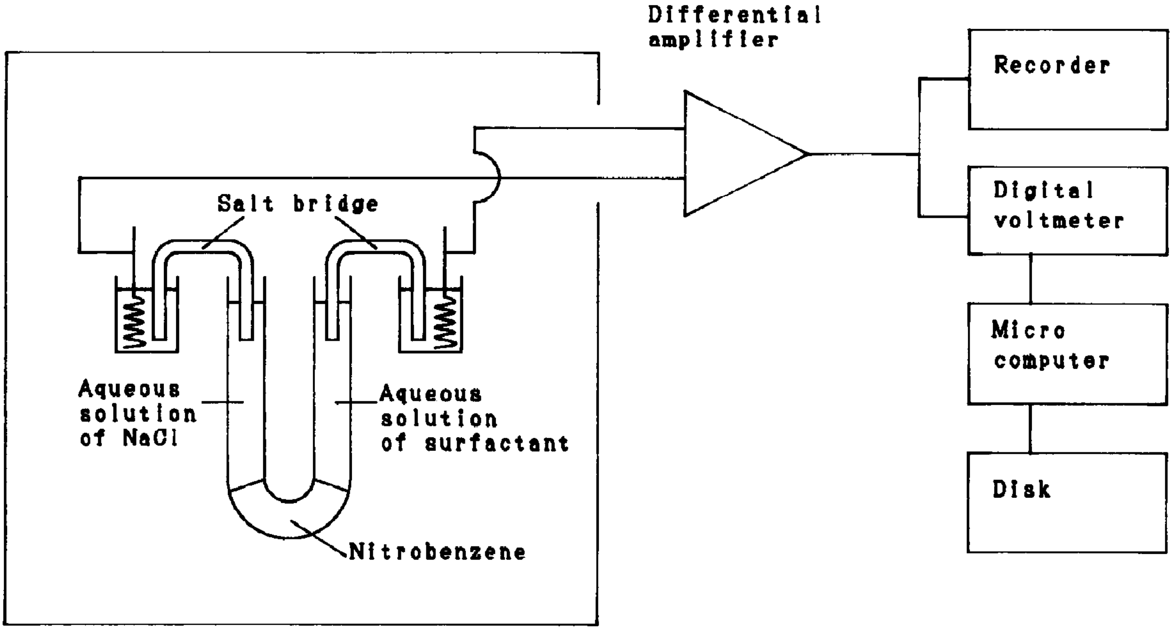

Fig. 1. Block diagram for measurement of potential oscillations.

PC-9801). A recorder was used for monitoring the amplified voltage during the experiment. The power spectrum of the potential was obtained from the data of 512 s with the fast Fourier transform method.

2.2. Results

Figures 2(a–c) show three parts of a successive time series of a typical potential variation. The

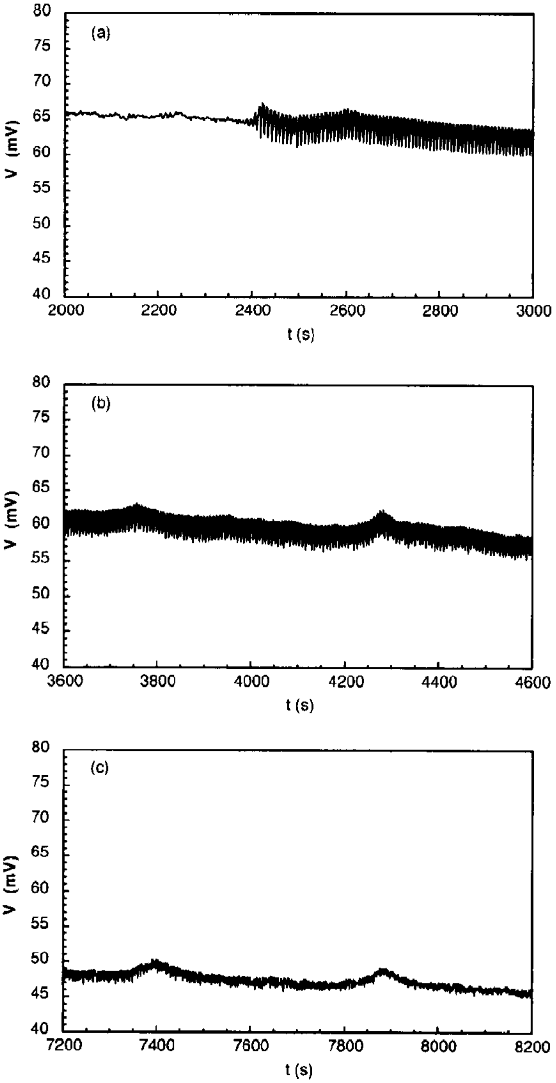

Fig. 2. Time series of potential oscillation. The ordinate represents the potential difference between the two aqueous solutions. The abscissa is the time measured after composing the water/oil interface.

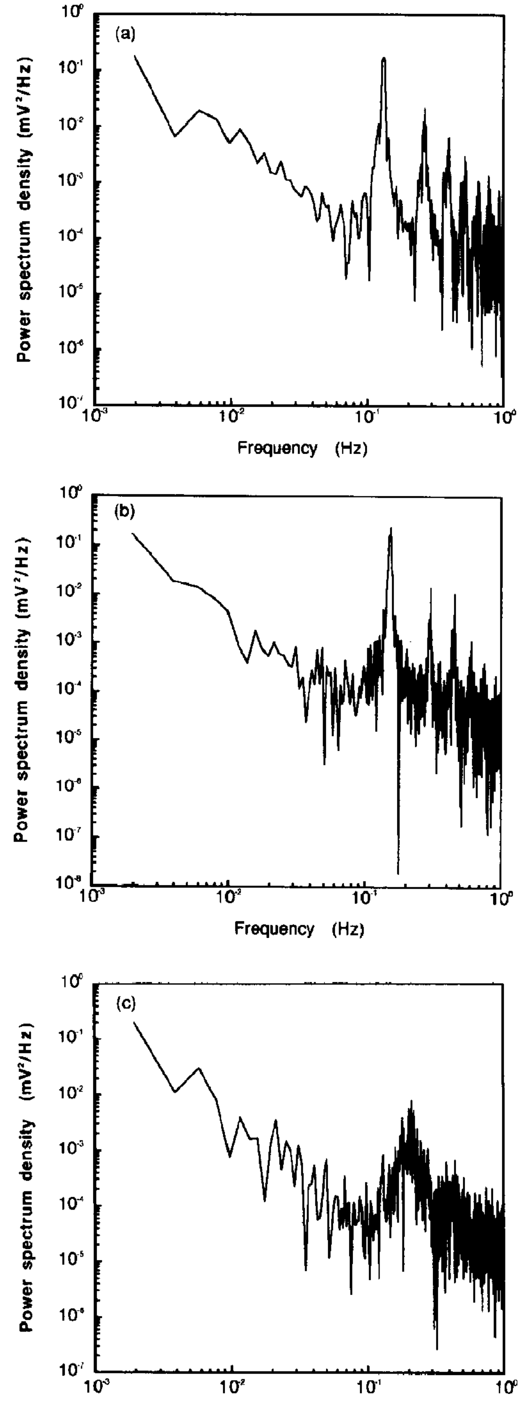

Fig. 3. Typical power spectra of potential in the time ranges corresponding to fig. 3. These are obtained from the data which were sampled for 512 s at intervals of 0.5 s.

voltage V denotes the potential difference between the electrodes at time t after pouring the solution of surfactant on the nitrobenzene. Fig. 2a shows that a short period oscillation started at about 2400 s after pouring the solution of surfactant on the nitrobenzene. The amplitude was about 5 mV and the period was 7.5 s during the initial stage, but gradually variations became evident, i.e., the amplitude decreased and the period became irregular in the course of time (fig. 2b and c). The duration of the oscillation is about 1.5 h.

In fig. 2b, two broad peaks (at 3750 and 4300 s) reflecting a long period oscillation can be seen, whose interval is about 9.2 min. A similar wave form of the oscillation is observed in fig. 2c with a period of 8.3 min. The duration of the oscillation was about 7 h. The period and the duration agree with those previously reported by Kawakubo and Fukunaga [7].

It is remarkable that the long period (~ 10 min) oscillation is superposed on the short period oscillation (fig. 2b) and remains after the short period oscillation ceases (fig. 2c), i.e., the period and the amplitude of the long period oscillation in fig. 2b are about the same as in fig. 2c, while those of the short period oscillation have entirely changed.

Typical examples of the power spectrum of the potential are given in fig. 3a–c, which were obtained from the data corresponding to fig. 2a–c, respectively. The power spectra in fig. 3a and b are proportional to f^{-2} in the frequency range below 0.1 Hz and have many peaks in the higher frequency range. The peak at 0.13 Hz represents the short period oscillation and other peaks are its harmonics. In fig. 3c, the trend in the frequency range below 0.1 Hz is similar to that in fig. 3a and b, but the many peaks in the higher frequency range disappear and only one broad peak remains at about 0.2 Hz. The appearance of the broad peak in fig. 3c shows that the short period oscillation has become irregular.

3. Discussion

A new oscillation with a short period of the order of 10 s was found in the water/oil/water system, in addition to the long period oscillation previously reported [5–7]. The experimental conditions in the present study differ from those previously employed in that the concentration of 1-propanol mixed in the aqueous solution of sodium oleate was doubled and 2,2′-bipyridine was not dissolved in nitrobenzene. It is not certain, however, whether the lack of 2,2′-bipyridine is essential for the short period oscillation. Stability of oscillation strongly depends on the concentrations of sodium oleate and 1-propanol. In particular, at low concentrations of 1-propanol, the short period oscillation did not occur and at high concentrations the oscillation again disappeared. The concentrations of sodium oleate and 1-propanol chosen in the present experiment are those which give the highest stability for the short period oscillation.

We suppose that the oscillation is caused by following processes.

(1) Oleate anions in the aqueous solution diffuse to the water/oil interface and form a monolayer at the interface. Molecules of 1-propanol also have a tendency to diffuse from the aqueous phase to the interface and to enter the oil phase. The concentrations of these substances near the interface increase gradually.

(2) The two kinds of substances on the interface aggregate form inverted micelles when the concentrations of the two substances exceed some threshold. Then, the micelles move into the oil phase and the oleate anions near the interface suddenly vanish.

(3) New oleate anions diffuse from the bulk of the aqueous solution to the interface and the same cycle is repeated.

Thus, the concentration near the interface and the flux through the interface of the oleate anion change periodically. The process is a reaction-diffusion system, which may be described by multivariable nonlinear differential equations. A multivariable nonlinear dynamic system can exhibit various oscillatory behaviors including single period oscillation, double period oscillation and chaotic motion [9]. In the present study, the occurrences of the double periodic and single periodic oscillation depend on the concentration of surfactant and/or alcohol, so that the earlier decay of the short period oscillation compared with the long period one may be caused by a decrease in the concentration of substances essential for the short period oscillation. There is insufficient evidence available as yet to establish the mechanism of the two kinds of oscillations described above. Direct measurements of the changes in concentration of molecules near the interface would be desirable.

Acknowledgment

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

1 T. Teorell, J. Gen Physiol. 42 (1959) 831.

2 Y. Kobatake, Adv. Chem. Phys. 29 (1975) 319.

3 M. Dupeyrat and E. Nakache, Bioelectrochem. Bioenerg. 5 (1978) 134.

4 K. Yoshikawa and Y. Matsubara, J. Am. Chem. Soc. 106 (1984) 4423.

5 K. Yoshikawa, M. Shoji, S. Nakata, S. Maeda and H. Kawakami, Langmuir 4 (1988) 759.

6 K. Yoshikawa, S. Maeda and H. Kawakami, Ferroelectrics 86 (1988) 281.

7 T. Kawakubo and K. Fukunaga, Ferroelectrics 86 (1988) 257.

8 T. Kawakubo and K. Fukunaga, Biophys. Chem. 35 (1990) 113.

9 D. Ruelle and F. Takens, Commun. Math. Phys. 20 (1971) 167.