Entrained Responses of the Current Oscillation of Polymer Gels to Sinusoidal Stimulation

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The responses of the current oscillation of the water-swollen polymer gels generated by dc current to the sinusoidal stimulation were investigated. The current oscillation was semiquantitatively analyzed by fast Fourier transform and the phase diagram was made up from power spectra. It was found that the entrainment of oscillation occurred in the polymer gels when the frequency of sinusoidal stimulation was closed to that of parent current oscillation. It was also found that the stronger sinusoidal voltage caused the entrainment in wider frequency range.

Recently a variety of spatial- and time-ordered structures (dissipative structure) have been experimentally and theoretically investigated in many nonlinear and nonequilibrium systems. Action potential of nerves occurred by external electrical stimulation is the representative example.[1] In the chemical reaction systems, Belousov-Zhabotinsky reaction whose the reactor concentration changes periodically by means of the autocatalytic process is well-known.[2] More recently, banding pH pattern surrounding the root and the corresponding current pattern was investigated by Toko et al.[3]

The ordered structure is often generated by synchronizing many rhythms consisting the system and this effect is called entrainment. For example, the self-sustained oscillation with a frequency of 145 Hz occurs in the squid giant axon by exchanging seawater for mixture of seawater and 550 mM NaCl solution (1 M=1 mol dm^{-3}). When the external sinusoidal current frequency is closed to 145 Hz, the forced firing frequencies that is the firing frequencies under the sinusoidal current, are entrained to the sinusoidal frequencies.[4] Away from these frequency ranges and in the case of weak sinusoidal current, the amplitude modulation upon the repetitive spikes is only observed. Some chaotic behavior is observed in the forced repetitive spikes when a strong ac is applied.

On the contrary, the artificial oscillating systems consisting of porous polyelectrolyte membranes are the simple artificial model for these oscillative systems observed in biological systems and they were made by Teorell,[5] Kobatake,[6] Seno,[7] Mounier,[8] Shashoua,[9] Katchalsky,[10] and others. For example, Teorell demonstrated that a system consisting of polyelectrolyte membrane, separating two electrolyte solutions of different conductance shows oscillation with a frequency as low as 5×10^{-4} Hz, when a dc flows through the membrane. The oscillatory phenomena was explained as an electroosmotic process causing periodic resistance changes of the membrane. The generation of pulses superimposed on dc was observed by Seno in ion-exchange membranes dipped in an aqueous sodium chloride solution. The phenomenon was associated with the formation of a salt-depletion diffusion layer. Shashoua reported the generation of current oscillations under constant dc electric field in the membranes consisting of polymeric acid-base composite facing each other. In these cases the presence of salt on both sides of the membrane was one of the requirements in order to generate spikes. Katchalsky explained the appearance of these oscillative phenomena as follows: the current flow through the membrane induces salt accumulation in the polymer membranes, which, at a certain concentration, leads to the shrinkage of the membrane and a breakdown region is formed. The excess ions are washed off to reestablish the original state of the membrane.

An electrically activated mechanochemical system made of polyelectrolyte gels was recently reported[11,12] and a variety of electro-mechanical conversion devices were developed.[13–15]

In the course of this study, We found that the repetitive current oscillation occurred in the gel[11,16] when a dc was applied through electrodes and the semiquantitative analyses of the oscillation were made by use of fast Fourier transform (FFT). The Lorentz plot of the current of the gel obtained by plotting each amplitude against the preceding one resulted in a convergent set around a point on the line of slope 1 indicating that the frequency of the repetitive oscillation fluctuates around this peak and any irregular oscillation can be attributed to a quasi-periodic motion. In fact, the Lorentz plot of the gel currents formed a closed line. Different from the membranes described, the oscillation of our gels is not induced neither by change in gradient of the transmembrane concentration of the ions nor by the periodical response of specific chemical reagents like liquids,[17–19] but induced by the amorphous and homogeneously swollen polyelectrolyte gels. The application of constant electric potential, higher than a certain threshold value, is the only requirement for the generation of periodical oscillations.

The purpose of this paper is to report the effects of external sinusoidal voltage upon the current oscillation of the gel. It was found that the entrainment of current oscillation occurs when the frequency of the sinusoidal stimulation become close to that of parent current oscillation and that the stronger sinusoidal voltage caused the entrainment in wider frequency range.

Experimental

Materials. Gel from alginic acid was prepared by immersing a visking tube (diameter 42 mm) containing 1.1% of sodium salt solution of alginic acid in a large amount of 1.0% calcium chloride solution for 2 days. Crosslinked water-swollen gels of poly(methacrylic acid)(PMAA) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) were prepared by radical polymerization of 5.0 mol% aqueous solutions of corresponding monomers in the presence of 5×10^{-2} mol% *N,N′*-methylenebis(acrylamide) (MBAA) which was used as a crosslinking agent. In these cases polymerization was carried out at 60 °C under vacuo, and 5×10^{-2} mol% of potassium peroxodisulfate was used as an initiator. The obtained gels were then immersed in water at least for 1 week to remove excess salt. The degree of swelling $DS=(W_s-W_d)/W_d$ was calculated by weighing the weights of dry (W_d) and water-swollen (W_s) gels, respectively.

Method of Measurement. A piece of water-swollen cylindrical polymer gel, 11 mm long and 24 mm in diameter, was placed in a Petri dish containing water of ca 10 mm depth. A pair of platinum wire electrodes 20 mm long and 0.2 mm in diameter were inserted in the gel with a distance of 10 mm and 10 mm in depth. A dc voltage (V_o=5 V) was applied in order to induce the current oscillation through the platinum wire electrodes. A stable current oscillation with a frequency of f_o, was observed after a certain induction period. The sinusoidal voltage, $V_o+V\sin 2\pi f_i xt$ was then applied by the same platinum wire electrodes. In these cases the current supply was delivered to the electrodes from Hokuto 501 potentiometer. The oscillative response of the gel was recorded on a data recorder (Hitachi 561) and the response of the current oscillation to the sinusoidal stimulation (f_i) was analyzed by a personal computer (NEC, model PC 9801 Vm2). The oscillation was simultaneously sampled at intervals 500 ms and in the range of $0.005<f_i<1$ Hz and $0.005<V<2$ V depending on the nature of oscillation and was used for computer analysis.

Measurement of the oscillation was carried out at 25 °C. Water used in these experments had an electric conductivity in the range $1-5\times10^{-7}\ \Omega^{-1}\ cm^{-1}$.

Results and Discussion

Figure 1(A) shows a repetitive curve and its power spectrum of the gel when dc (7 V) was applied to the calcium alginate gel. As reported in the earlier paper[16] the oscillatory current appeared after a certain induction period, and this oscillation occurred undamped for more than several hours and more. There existed a "threshold" value of potential, below which (in this experiment about 3 V cm^{-1} or below) practically no oscillation appeared. During the induction period, the undamped oscillations appeared in every crosslinked water-swollen polymeric gel, provided they possess ionized moieties, regardless of strong or weak polyelectrolytes. The power spectrum of this oscillation shows a main peak at the frequency of 0.013 Hz (f_o) with higher harmonics. The magnitude of the main peak was about 9.80% of that of total energy within a range of 0.5 Hz. The maximum amplitude of the current oscillation was about 0.22 mA.

Entrainment by Sinusoidal Voltage. Figure 1 B—D shows the effects of external sinusoidal voltage upon the current oscillations and the power spectra when the ac frequencies (f_i) from 0.005 through 0.03 Hz and amplitude (V) of 2 V were superimposed afterward to the oscillation induced by dc voltage (V_o=5 V). Thus, the electric field by dc+ac does not exceed the value applied by dc. When the ac with the frequency of 0.005 Hz was applied to this oscillating gel, the response of the current oscillation became chaotic as shown in the power spectrum (Fig. 1(B)). The magnitude of this ac was about 0.08 mA and this value was much lower than that induced by dc 5 V. The power spectrum in this case has many peaks but the peak induced by dc (f_o) also remained at 0.013 Hz. The magnitude of f_o is about 0.85% of the total energy and that of frequency of ac (f_i) is about 0.63%. The frequency of the main peak was shifted to 0.15 Hz and magnitude of this peak was about 1.30%.

Figure 1(CI) shows the response of current oscillation and its power spectrum when the ac with a frequency of 0.01 Hz was applied. The power spectrum has a sharp peak at the frequency of 0.01 Hz but there is no peak of f_o this time. The magnitude of this peak is large and comprises about 28.8% of that of total within the range of 0.5 Hz. This suggests the 1:1 entrainment of current oscillation occurred. The response of this current oscillation gradually changed with time. As shown in the spectrum of Fig. 1 (CII); the frequency of main peak changed to that of ac in the course of experiment and after 17 min (1026 s) the entrained frequency changed from 0.01 Hz to 0.02 Hz. This shows that the frequency of the entrained oscillation became twice of that of sinusoidal stimulating oscillation (2 : 1 entrainment).

When the ac of 0.03 Hz was applied to the gel, a complete change of the oscillation was observed as shown in Fig. 1 (D). There is no peak of f_o any more, but only the repetitive oscillation with a frequency of f_i (0.03 Hz) was observed. The magnitude of the peak corresponding to 0.03 Hz was as large as 94% of that of total within a range of 0.5 Hz, clearly showing that the current oscillation induced by dc was completely entrained to the oscillation induced by ac even the magnitude of the latter was much lower. Thus, it was demonstrated that the entrainment of oscillation occurs in the gel when ac with certain frequency is

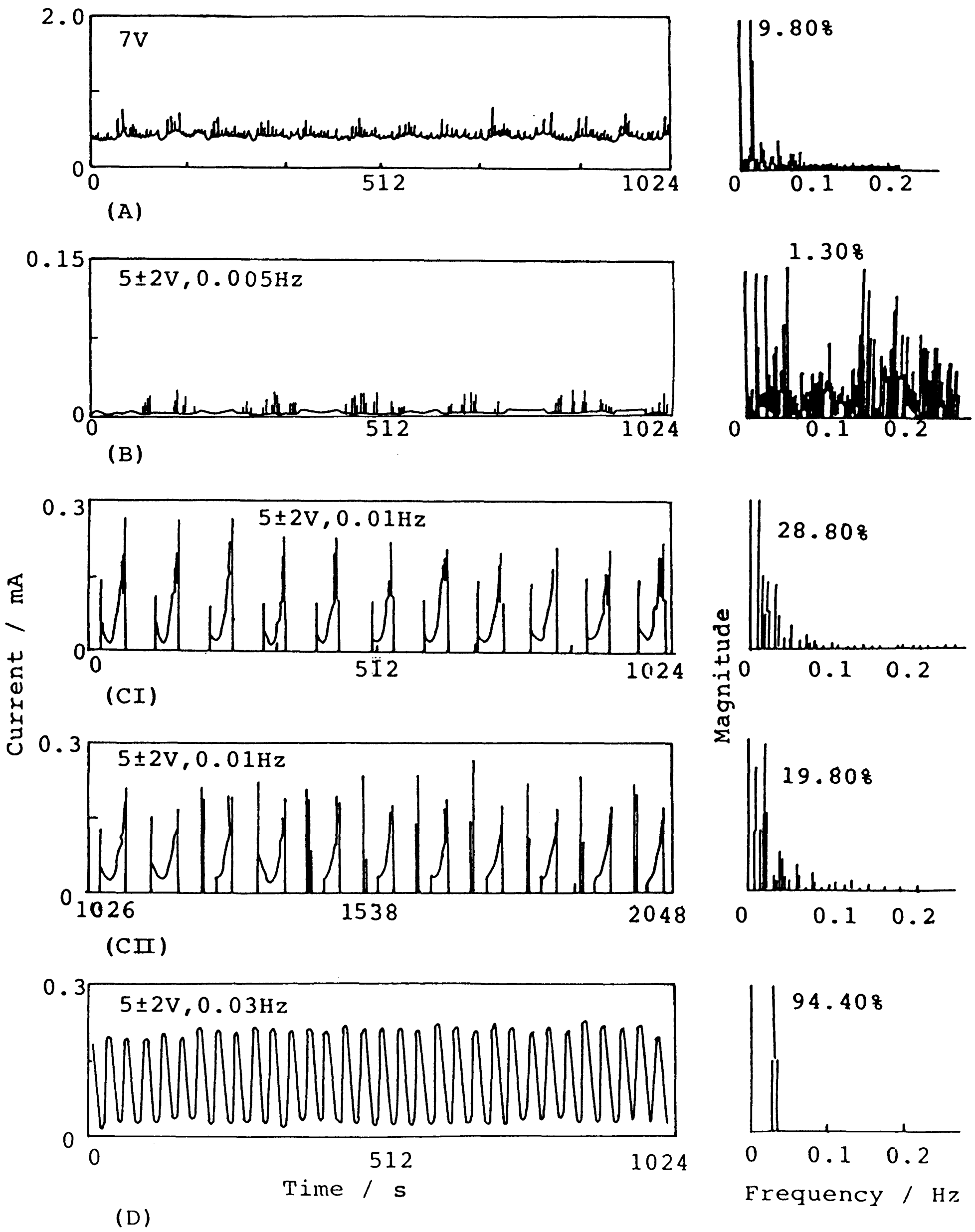

Fig. 1. The effects of frequency of external sinusoidal voltage upon the current oscillation. Gel: calcium alginate, 24 mm in diameter, 11 mm long, DS: 40, electrode distance: 10 mm.
(A) dc: 7 V, (B) dc: 5 V, ac: 0.005 Hz, 2 V, (CI, CII) dc: 5 V, ac: 0.01 Hz, 2 V, (D) dc: 5 V, ac: 0.03 Hz, 2 V. Figures denoted in the power spectra indicate percent magnitude of the main peak of total energy generated within a range from 0 to 0.5 Hz.

imposed, and the phenomena were observed repeatedly for various polymer gels.

Effect of ac Frequency of Sinusoidal Voltage. The dependence of the magnitude of f_o and f_i on the frequency of f_i for various polymer gels is shown in Fig. 2(A—C). In the case of calcium alginate gel (Fig. 2(A)), magnitude of f_o decreased quickly with increasing ac frequency and the oscillation with a frequency of f_o completely disappeared at the value f_i=0.01. This fact indicates that the entrainment of current oscillation was completed at this frequency, and suggests that there exists the threshold ac frequency in this case in order to cause an entrainment.

The entrainment of the oscillation was also observed in other polyelectrolyte gels regardless of weak (PMAA) or strong (PAMPS) polyelectrolyte. The examples are shown in Fig. 2B and 2C, respectively. The threshold frequency in order to induce an complete entrainment was 0.05 Hz for PMAA gel and the magnitude of the peak at 0.05 Hz was 80.5% as shown in Fig. 2B. As shown in Fig. 2B the magnitude of the oscillation corresponding to f_o decreased

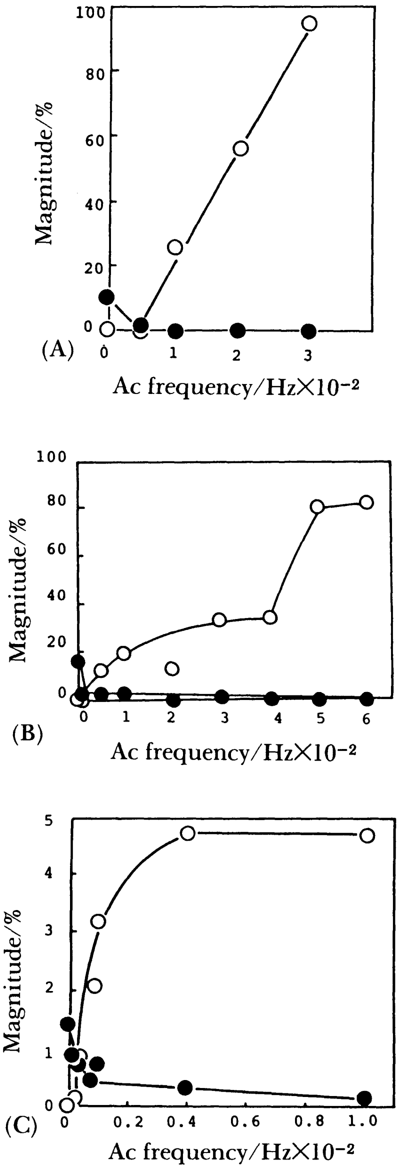

Fig. 2. Dependence of magnitude of f_o(●) and f_i (○) on the frequency of f_i.
Polymer gels: (A) calcium alginate: 26 mm in diameter, 12 mm long, DS: 40, electrode distance: 5 mm, dc: 5 V, ac: 2 V. (B) PMAA: 14 mm in diameter, 10 mm long, dc: 10 V, electrode distance: 7 mm, dc: 5 V, ac: 1 V. (C) PAMPS: 12 mm in diameter, 17 mm long, DS: 50, electrode distance: 7 mm, dc: 5 V, ac: 1 V.

quickly when ac with a frequency (f_i) of 1×10^{-3} Hz was imposed. A gradual decrease of magnitude of f_o was then observed whereas the magnitude of f_i increased rather rapidly. A complete entrainment occurred when f_i was larger than 0.04 Hz. A sudden and steep increase in magnitude of f_i was simultaneously observed.

In the similar manner the magnitude of parent oscillation f_o of PAMPS gel decreased rapidly when ac was imposed (Fig. 2C). However, a complete entrainment was not observed within a range of 1 Hz.

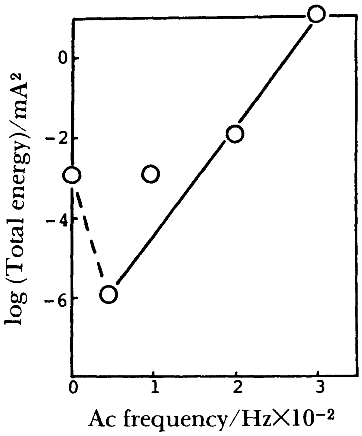

Fig. 3. Dependence of total energy whthin a range from 0 to 0.5 Hz on the frequency of f_i. gel: calcium alginate, 24 mm in diameter, 11 mm long, DS: 40, electrode distance: 10 mm, dc: 5 V, ac: 2 V.

The magnitude of f_i was not large comparing preceding two examples and the value was only 5% or less. Figure 3 shows the dependence of total energy on the ac frequency f_i. Total energy is defined as an integral calculus of the power spectrum within a certain frequency range. It is seen from Fig. 3 that the total energy calculated within 2.5 Hz is extremely low as 10 mA^2 when ac with a frequency of 0.05 Hz was imposed. However, it increased exponentially with increase in ac frequency and the total energy of the oscillation entrained by ac with a frequency of 0.03 Hz, was 10^6 times larger than that entrained by ac 0.005 Hz. We cannot clarify the reason at present, but as reported in the previous paper, PAMPS is a strong polyelectrolyte and exhibits intensive oscillation with many higher harmonics. The different characteristics of entrainment observed in PAMPS gel should be explained with this different nature of the oscillation.

Effect of Amplitude of Sinusoidal Voltage. Complete entrainment could be observed when the frequency of sinusoidal stimulation was kept constant but ac voltage was altered. Figure 4 shows the effects of external sinusoidal voltage upon the current oscillation of calcium alginate gel. Here, the ac frequency (f_i) was kept constant at 0.03 Hz, while amplitude was varied as 0.05, 0.08, 0.13, 0.82, 2.0 V, respectively. Figure 4(A) corresponds to repetitive oscillation curve and its power spectrum of the gel when dc (5 V) was applied. It was found from Fig. 4A that the frequency of the current oscillation induced by dc was about 0.038 Hz and the amplitude of this oscillation was about 0.1 mA.

The current of ac in the gel at 2 V ac was 0.04 mA and this value was less than 50% that of current oscillation induced by dc. Thus, the current oscillation induced by dc is not covered by the ac imposed afterward. When ac voltage (0.03 Hz) as low as 0.05 V

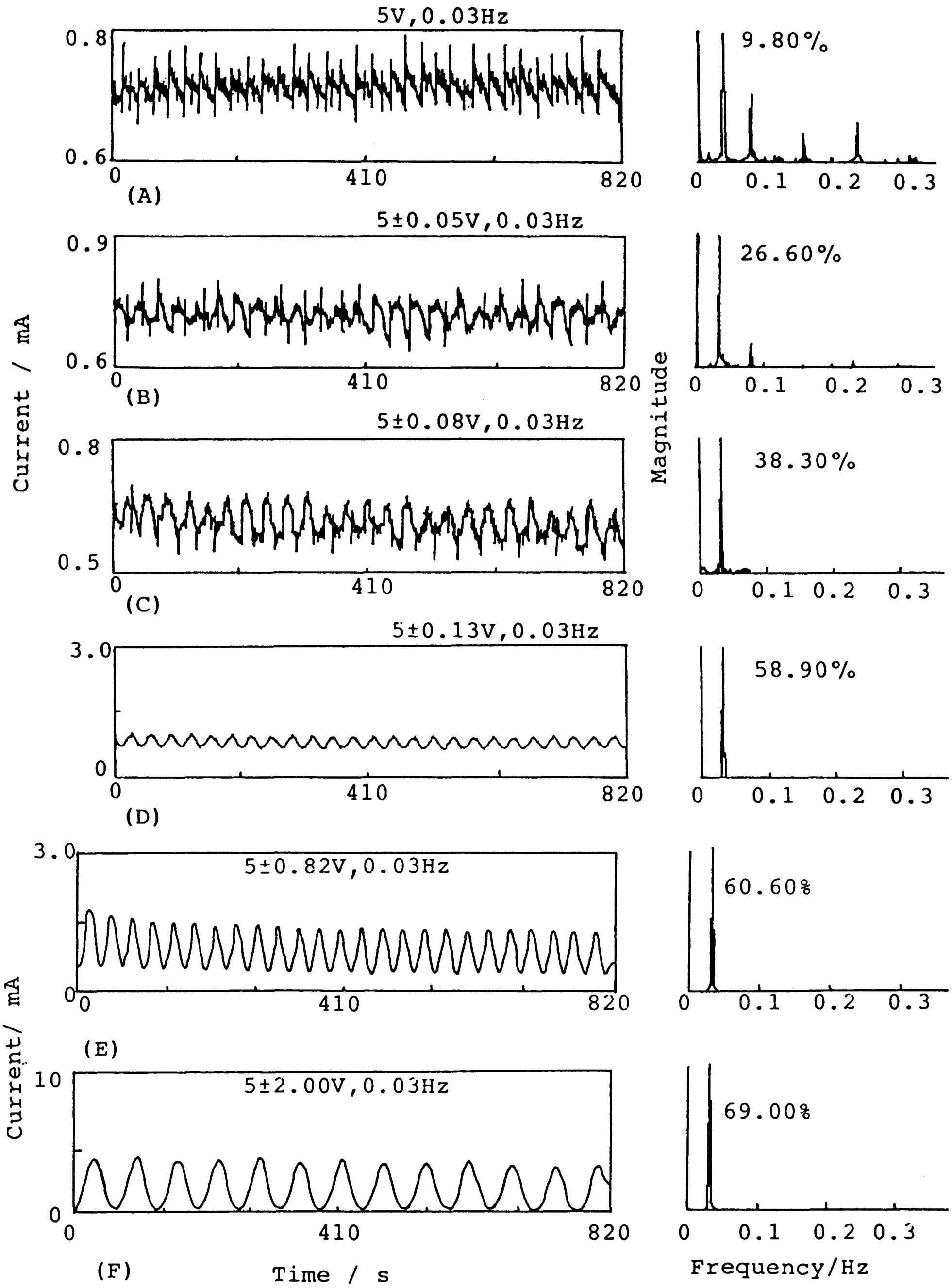

Fig. 4. The effects of amplitude of external sinusoidal voltage upon the current oscillation. Gel: calcium alginate, 26 mm in diameter, 12 mm long, DS: 40, electrode distance: 5 mm.
(A) dc: 5 V, (B) dc: 5 V, ac: 0.05 V, 0.03 Hz, (C) dc: 5 V, ac: 0.08 V, 0.03 Hz. (D) dc: 5 V, ac: 0.13 V, 0.03 Hz, (E) dc: 5 V, ac: 0.82 V, 0.03 Hz, (F) dc: 5 V, ac: 2.00 V, 0.03 Hz. Figures denoted in the power spectra indicate percent magnitude of the main peak of total energy generated within a range from 0 to 2.5 Hz.

or 0.08 V was applied, magnitude of f_0 induced by dc decreased from 9.80% to 0.73%. Instead, a new peak corresponding to f_i (0.03 Hz) appeared and this is clearly seen in their power spectra (Fig. 4B and 4C). When the ac amplitude is as high as 0.13 V, the parent oscillation completely disappeared and new ac current having only one peak of f_i was observed (Fig. 4D, 4E, and 4F). Magnitude of this peak is about 58.9%. Further increase in ac voltage up to 0.82 V or 2.0 V (Fig. 4E and 3F) lead to additional increase of magnitude of the oscillation consisting of only one peak of f_i(0.03 Hz). From these results it is seen that the 1:1 entrainment of the current oscillation occurs at the amplitude from 0.13 V to 2.0 V and chaotic behavior appears when the ac amplitude is less than 0.13 V. Figure 5 shows the dependences of magnitude of spec-

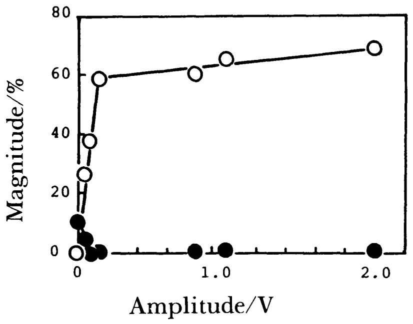

Fig. 5. Dependence of magnitude of f_o and f_i on ac amplitude. gel: calcium alginate, 26 mm in diameter, 12 mm long, DS: 40, electrode distance: 5 mm.

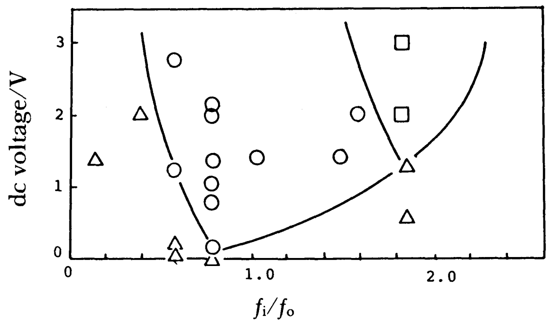

Fig. 6. The phase diagram of the current oscillation under the sinusoidal stimulation. Gel: calcium alginate, 24 mm in diameter, 11 mm long, dc: 40, electrode distance: 10 mm. ○: 1 : 1 entrainment, □: 2 : 1 entrainment, △: chaotic.

tra of f_o and f_i on ac amplitude. The magnitude of the peak at the frequency of 0.038 Hz (f_o) decreased quickly by imposing ac current and disappeared completely at the voltage as low as 0.13 V. Simultaneously, the magnitude of a peak corresponding to 0.03 Hz (f_i) increased until ac voltage becomes 0.13 which then changed almost plateau. It should be noted again that after entrainment only one peak corresponding to 0.03 Hz was seen in the power spectra. Thus, in the similar manner as changed ac frequency (Fig. 2A and 2B), the threshold amplitude of ac was required in order to make an entrainment of current oscillation.

Phase Diagram. The phase diagram of the response of the current oscillation to the sinusoidal stimulation in the case of calcium alginate gel is shown in Fig. 6. When the f_i/f_o is 0.8 or higher, the entrainment of current oscillation was observed in the wide range of dc from 0.1 to 2 V. If the dc voltage is increased, the entraiment occurs in lower f_i/f_o. At higher dc voltage and higher f_i/f_o, a 2 : 1 entrainment preferably occurs. From this figure it is seen that an entrainment of the oscillation induced by dc occurs more easily when the ac frequency was close to that of parent oscillation. It is also seen the stronger sinusoidal voltage cause the entrainment in wider frequency range. Away from these frequency ranges and weak ac amplitude, the chaotic behavior was observed.

Our preliminary hypothesis of the oscillation in the gel is that nonlinear ion transport causes a periodic electrostatic as well as osmotic potential owing to change in charge densities on a local level. One of the experimental evidences is that the pH oscillation occurred in the gel[20] for a prolonged period of time after the electric field was turned off; as reported previously[20] a constant potential was applied to the PAMPS gel for 40 min, thereafter the electrodes were removed, instead a specific micro-pH electrode was inserted. No periodic oscillation or fluctuation of pH appeared for the first 50 min, however, intensive and clear oscillation accompanied with some satellite peaks suddenly appeared.

The obtained results indicate that many ion transport process can be ordered and syncronized by superimposing ac. This fact means that the factors which may cause the nonlinear ion transport have many degree of freedom and are flexible and it is possible to be able to synchronize to external stimulation. To our knowledge, there has been no study on such periodical nature of oscillations in the water-swollen homogeneous gels having no ion gradient and may be of interest in relation to many rhythmic systems and "deterministic chaos".

There has been an increasing interest in the rhythmic systems appeares in the individuals in biology such as oscillation of heart, circadian rhythms, the cellular fussion. Entrainment phenomena observed in the hydrated gel may provide the simplest and suitable model for understanding syncronized rhythmic system in biology.

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