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Self-Sustained Nonlinear Oscillation of Hydrogen Ions in the Polyelectrolyte Gels

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Long-term, self-sustained oscillations of hydrogen ions were detected in the water-swollen polyelectrolyte gels when an electric potential was applied for certain period of time and then turned off. A hypothetical nonlinear ion transport mechanism was proposed.

Systems exhibiting the self-sustained[1-3] and the forced oscillation[4-7] behaviors attracted considerable attention in a wide variety of combinations of chemical components. However, physicochemical mechanism of those oscillations associated with the chemical and physical nature of the component substances has not been fully investigated. Previously we reported that water swollen polyelectrolyte gels contract under the influence of direct current (DC)[8,9] and some mechanochemical devices were shown.[10] In the course of this study we also found that the repetitive oscillation occurred in the gels when a constant electric potential was applied.[8] Power spectra and Lorentz plots were obtained and semiquantitative analyses were made using fast Fourier transformation(FFT).[11] The aim of this paper is to propose a hypothetical mechanism that self-organized nonlinear diffusion of electrolytes, particularly, that of hydrogen and hydroxyl ions can induce the periodical oscillations in the polyelectrolyte gels. The basis of this mechanism is the fact that the long-term, self-sustained repetitive oscillation of hydrogen ion is detected in the gel after electric potential was turned off.

The measurement of oscillation and preparation of gels were carried out in the similar manner as described previously.[8,11] Figure 1 shows a typical repetitive oscillation curve appeared in the gel of 2-acrylamido-2-methyl-1-propanesulfonic acid(AMPS) and 2-hydroxyethyl methacrylate(HEMA) copolymer(poly(AMPS-co-HEMA)) while applying 5V through a pair of platinum wire electrode. The power spectrum of the oscillation showed a main peak at the frequency of 3.1 x 10^{-2} Hz with many higher harmonics. The magnitude of the main oscillation was about 3% of that of total within a range of 1 Hz, and the amplitude of this main peak gradually decreased with time. The Lorentz plot of the oscillation of the gel obtained by plotting each amplitude against the preceeding one suggested that the frequency of the oscillation fluctuated around this main peak.

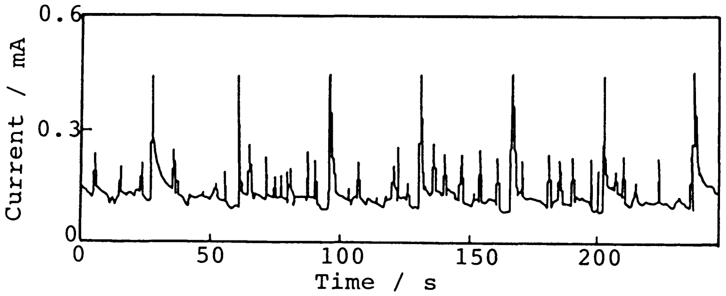

Fig.1. Current oscillation of poly(AMPS-co-HEMA) gel.

Gel: 9 mm long, 33 mm in diameter, degree of swelling(DS) , 20 times of the dry weight,
DC: 5 V electrode distance(ED) : 7 mm

Extremely interesting result here is that the self-sustained oscillation with less frequency is appeared for prolonged period of time after the electric potential was turned off. The poly(AMPS) gel, 11.5 mm wide, 9.4 mm high, 23.4 mm long initially showed a constant pH of 1.75. A constant potential of 18 V was then applied to the gel for 40 min through a pair of platinum plates(10 mm x 10 mm) by a 23.4 mm gap from each other. Thereafter, the electrodes were removed, instead a specific pH electrode(Micro-combination pH electrode, 1.2 mm in diameter, MI 410, Microelectrode. Inc.) was inserted to the gel in 3 mm depth near cathode with 3mm distance. The gel showed pH of 1.7-2.0 at this time and no periodic oscillation or fluctuation of pH appeared for the first 50 min. However, intensive and clear oscillation suddenly appeared as shown in Fig.2A. Frequency of the oscillation was low and the main peak had a frequency of 1.6 x 10^{-3} Hz which was accompanied with some satellite peaks. The amplitude of the oscillation was quite large, especially in the initial period and different of pH in this region attained 2-3 order of magnitude. The oscillation became rather stable after a certain period of time and repetitive oscillation with a frequency of 1.4 x 10^{-3} Hz and with a amplitude of approximately one order of pH appeared. Figure 2B shows other example of oscillation appeared in a crosslinked polyacrylic acid(PAA) gel swelled in 10 mM NaCl solution . Similarly to the case of Fig.2A, the gel showed pH of 1.5-2.2 and no oscillation appeared for the first 20 min. Intensive oscillation again appeared whose periods and amplitudes were, however, different from those observed in the earlier case. The frequency and amplitude of the oscillation in this case increased which abruptly transformed to the oscillation with less frequency and less amplitude. The frequency of the oscillation in the very initial period was 1.5 x 10^{-2}Hz and that in the period of 80-120 min was about 2.9 x 10^{-3}Hz. The oscillation suddenly ceased at 170 min from the beginning of the experiment. The gel prepared from polymethacrylic acid (PMAA) containing no additional salt exhibited spike-like oscillation with very low frequency (Fig.2C). Thus, the oscillation seemed to be dependent on the charge density in the gel.

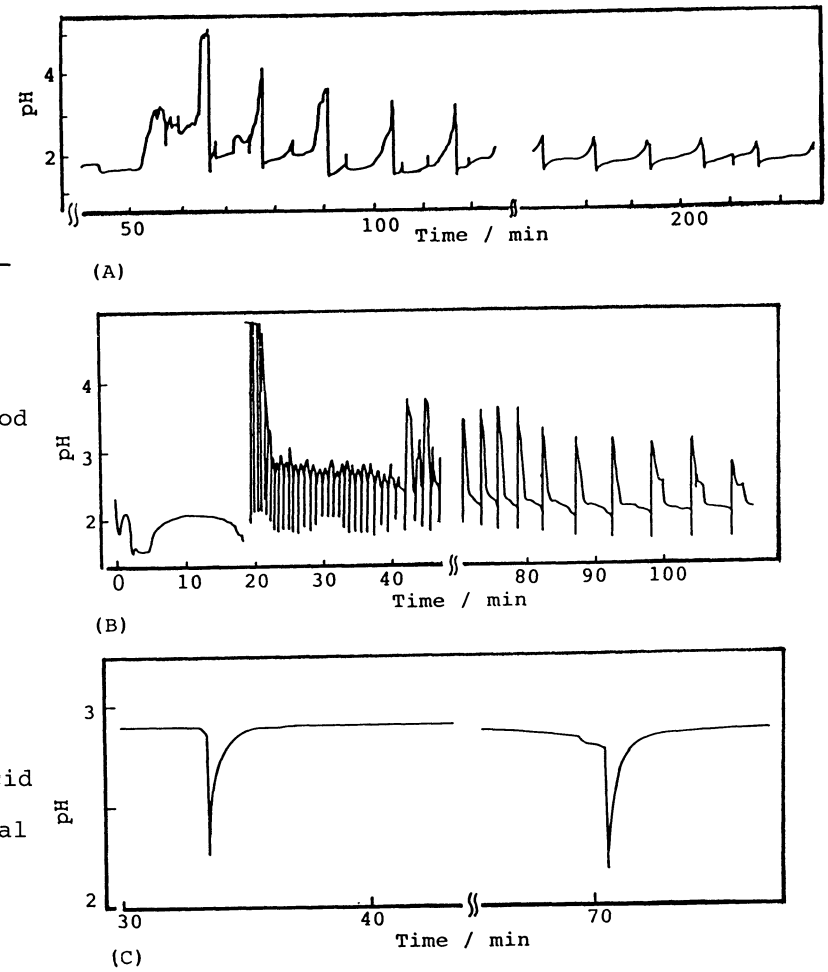

Fig. 2. Oscillation of pH in the polyelectrolyte gels.
(A) Poly(AMPS): 11.5 mm wide, 9 mm high, 23.5 mm long: 18 V(142 mA) of DC was applied for 40 min: DS, 20, ED, 23.5 mm
(B) PAA swelled in 10 mM NaCl soln.: 16.3 mm in diameter, 8.8 mm long: 20 V(52 mA) of DC was applied for 30 min: DS, 3, ED, 8.8 mm
(C) PMAA: 13.0 mm in diameter, 13.5 mm long: 18 V(14 mA) of DC was applied for 20 min: DS, 5, ED, 13.5 mm

Our Preliminary hypothesis of the oscillation in the gel is that nonlinear ion transport, particularly that of hydrogen(H^+) and hydroxyl inos(OH^-), travelling in the polyelectrolyte gel causes the periodic electrostatic and osmotic potential owing to change in charge densities of these ions. When an electric potential is applied for a certain period of time, H^+ and OH^- are produced near cathode and anode in the gel as a result of hydrolysis of water. After turning off the potential, these ions start to diffuse in the gel. The driving force of the transport of those ions is the concentration gradient of ions produced near the electrode. The nonlinear oscillation of pH would occur in the course of this diffusion process which, probably form a self-organized, disspative structure. The system must obtain parameters which give the critical condition in order to induce the nonlinear diffusion of ions and this should be associated with the induction period observed. In general nonlinear diffusions of the fluids and nonlinear thermal transfer (convection) are rather well-investigated phenomena.[12)] Kobatake, Fujita[13)] as well as M. Suzuki[14)] demonstrated experimentally and theoretically how the nonlinear oscillations induced by electro-osmotic effect, appeared in the capillary or in the U-type tubes. In our case, the nonlinear flow of ions may possibly be caused on coupling between the diffusional flow of H^+ and the dynamical movement of charged network since the oscillation can be observed only in the polyelectrolyte gels and not in the polymer or in the low molecular salt solution at all. The spikes or oscillations observed in the polyelectrolyte membranes, separating two electrolyte solutions of different concentration[4-7)] may be explained by the same reasoning. Thus, the ion transport process in the gels can play an essential role to appear the oscillation both in the forced (oscillation appeared by electric potential) and the self-sustained (oscillation after turning off the electric potential) oscillations. The only difference is that the ion transport of the former is carried out by electrokinetic (electro-osmotic) process and the latter is by the concentration gradient of ions produced by hydrolytic reaction.

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