Self-Excitable Molecular-System towards the Development of Neuro-Computer, Intelligent Sensor and Mechanochemical Transducer

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Abstract

Utilizing the exotic characteristics in nonlinear, nonequilibrium conditions, various "vital" artificial systems have been developed; (1) Spatio-temporal self-organization in coupled chemical oscillators, (2)Life-phenomena in cellular automata simulation, (3) Intelligent chemical sensor with self-excitable transducer, (4) Novel engine driven by the direct conversion of chemical energy.

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1. Introduction

Excitable or rhythmic phenomenon is one of the central aspects of life. Various biological systems exhibit rhythmic phenomena, e.g., circadian rhythms, beating heart, breathing, developing embryo, oscillation of nervous cells, etc. Life is connected with rhythms in general. The driving force of these rhythmic phenomena in living organisms originates from the dissipation of chemical energy. In relation to these rhythmic phenomena, there remain many unsolved problems on the mechanism of exotic biological functions, such as informational processing in brain, chemical recognition in taste and olfaction, chemical engine as in muscle, etc. We believe that these dynamic functions concern deeply with the nonlinear characteristics of dissipative system. In the present paper, we would like to describe new strategy to develop artificial "vital systems", based on the idea to utilize *spatio-temporal self-organization in far-from-equilibrium, nonlinear conditions.*

2. Network Dynamics in Coupled Chemical Oscillators

We have studied on coupled oscillators, with special attention to three-coupled oscillators in a triangle arrangement. Both for the coupled CSTR's in the Belousov-Zhabotinsky reaction (Yoshikawa *et al* 1990) and coupled salt-water oscillators (Yoshikawa *et al* 1991), tri-phasic mode with the phase difference of $2\pi/3$ was found to exist. The stability of the tri-phasic mode has been discussed (Yoshinaga *et al* 1991, Yoshimoto *et al* 1992, Yoshimoto *et al* 1993) in analogy with the interacting spin system. It has been shown that the concept of "frustration" in the interacting Ising spins is useful to predict the stability of various dynamic modes of entrainment, including the tri-phasic mode (Yoshimoto *et al* 1993). The tri-phasic mode is bistable in its intrinsic nature, clockwise or anticlockwise (Yoshikawa *et al* 1991). The tri-phasic mode becomes monostable when the interacting parameters become asymmetric, i.e., when the diffusive parameters become asymmetric between the neighboring oscillators (Yoshinaga *et al* 1991, Yoshimoto *et al* 1992). With an appropriate design of the interacting parameters, one can obtain either one of the bistable triphasic modes, clockwise and anticlockwise.

The above results indicate that "chiral symmetry-breaking" in the dynamic mode of entrainment is realized with the introduction of symmetry-breaking or asymmetry into the "boundary condition".

3. Life Phenomena in Computer

Recently, life phenomena in intelligence and evolution by celluar automata have been extensively studied by several researchers (Bak, P. *et al* 1990, Bennet, C. *et al* 1990 , Langon, C. G. 1990, etc.). In order to elucidate the logic of self-organization in life phenomena, we have carried out the studies on cellular automata simulations at the edge of chaos (Yonezawa 1993). Between the models of "ordering of the chaos" and "regeneration of the chaos", there exist intermediate type, i.e., self organization as in life has appeared near the threshold of chaos generation. We will show that such a systems exhibits stronger unpredictability than typical bio-chaotic systems, and consequently that almost nothing can be said about their long-term behavior.

Natural life systems are expected to be interpreted along with the mechanism of nonlinear dynamics including chaos and limit cycle.

Using Cellular automata simulation, we are further investigating the time development in implemented self-excitable oscillators at the edge of chaos.

4. Chemical Sensing with Nonlinear Transducer

In taste and olfaction, the information on chemical species is transformed into the information of impulses in nervous cells connected to the receptor cells. As the excitation and pulse-generation in nervous cells are regarded to be a typical nonlinear phenomenon, it may be of value to study how the "nonlinear characteristics" concern with the transformation of the information. We have been studying on the new kind of chemical sensor based on the strategy to utilize nonlinear dynamics into chemical sensing.

i) It has been found (Yoshikawa *et al* 1983, 1984, 1988, Yoshikawa 1990) that self-pulsing phenomenon is observed at an oil-water interface in the presence of various kinds of surfactants. In this system, one can observe pulsations of electrical potential. It has been demonstrated that the time-series of the electrical pulses contain abundant information on chemical substances present in the aqueous phase. Through the mathematical analysis of the oscillatory pattern, one can distinguish and also quantitate many chemical species even with a single detector.

ii) The origin of the nonlinearity of impedance in an electrochemical system, composed with electrodes and an aqueous solution, has been discussed based on various experimental results. It was found (Nakata *et al* 1989) that the nonlinearity of the impedance, in other words, the voltage-dependence of capacitance and conductance of an electrochemical system, changes markedly depending on the chemical nature of the substance present in the aqueous solution. In relation to this, we have proposed

(Nakata *et al* 1992) a new sensing method based on the information on the mode of entrainment in an electrochemically forced oscillator.

We have also studied (Nakata *et al* 1992) on the dynamic response of a ceramic gas sensor with periodic change of the temperature. From the measurement on the non-linear "dynamic response" of the ceramic sensor, one can simultaneously distinguish and quantitate various gases in the environment (Fig.1).

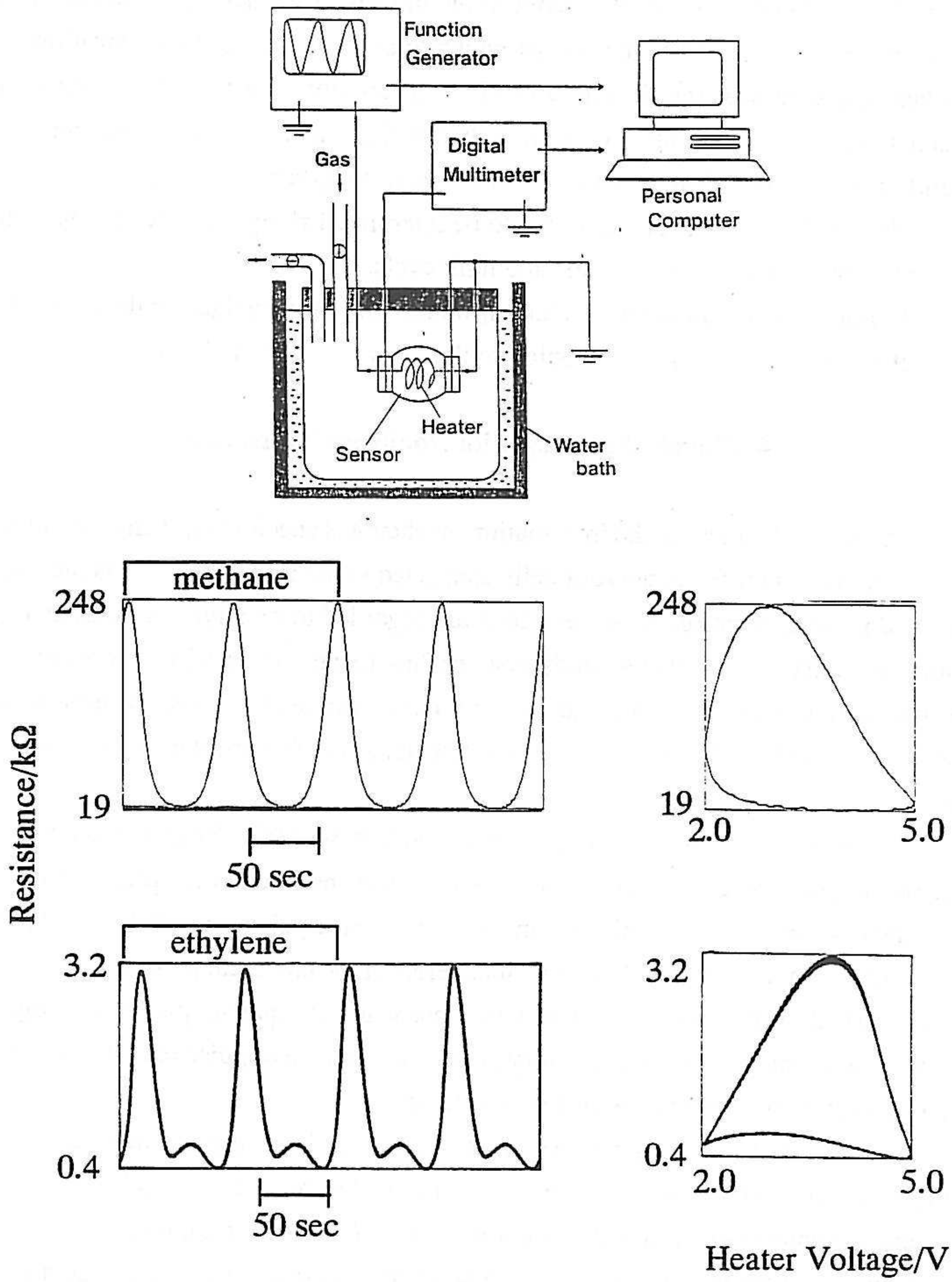

Fig. 1 Upper figure: Experimental apparatus for detecting the nonlinear characteristics of a gas sensor. Lower: Dynamic response in sensor resistance and phase portrait of the resistance *vs.* heater voltage.

5. Novel Motor Directly Driven by Chemical Energy

In 1970's, Dupeyrat and Nakache (Dupeyrat *et al* 1978) found quasi-periodic variation of electrical potential and interfacial tension in an oil-water system. Using the similar experimental system, Kai, et al. observed (Kai *et al* 1985) an exotic movement of the interface. We have found the followings: 1) Periodic oscillation, or limit cycle oscillation, is generated with good reproducibility (Yoshikawa *et al* 1983,1984); 2) The driving force of these phenomena is the difference of chemical potential of the solutes, surface active compounds, between the two phases (Yoshikawa *et al* 1988); 3) Oscillations are observed in the presence of various kinds of surfactant (Yoshikawa 1990); 4) The mechanism of oscillation and self-movement of the interface is periodic formation and destruction of the surfactant monolayer at the interface (Yoshikawa *et al* 1988, Yoshikawa 1990). As an extension of these studies, we will show the spontaneous movement of the oil-water system in the present paper.

Figs.2 and 3 show the spontaneous rotational movement of an oil-water system, where a cationic surfactant initially presents only in the aqueous phase. When the vessel, i.e., the boundary condition, is double concentric cylinder, the direction of movement of oil droplet is random (Fig.2). On the other hand, with the introduction of a chiral "screw" made from aluminum foil, the oil-water system rotates only one direction, clockwise or anti-clockwise (Fig.3). The direction of the rotational motion can be controlled as one wants, i.e., the chiral asymmetry of the "screw" determines the direction of the rotational movement. In living organisms, vectorial process such as force in muscle and active transport in biomembrane, is generated through the direct conversion of chemical energy. The above experiment demonstrates that coupling between chemical energy and vectorial process is quite possible in a nonlinear dynamical system with the boundary condition of broken chiral symmetry.

We have also found that a periodic mechanical force is generated at an air-water interface of an aqueous Belousov-Zhabotinsky medium. Fig. 4 shows the schematic representation of the experimental apparatus. The BZ medium was continuously stirred in order to generate the chemical oscillation all-in-phase throughout the whole solution. To minimize the effect of convection on the surface tension, we used the cylindrical Wilhelmy plate made of thin platinum sheet (0.1 mm thickness, 15 mm diameter). The redox potential was measured between a platinum and a Ag/AgCl reference electrode, using a K_2SO_4 salt-bridge. Fig. 5 shows the time trace of the surface tension ($\Delta\gamma$) and the redox potential (ΔE). In Fig. 5, A and C, it is clear that the surface

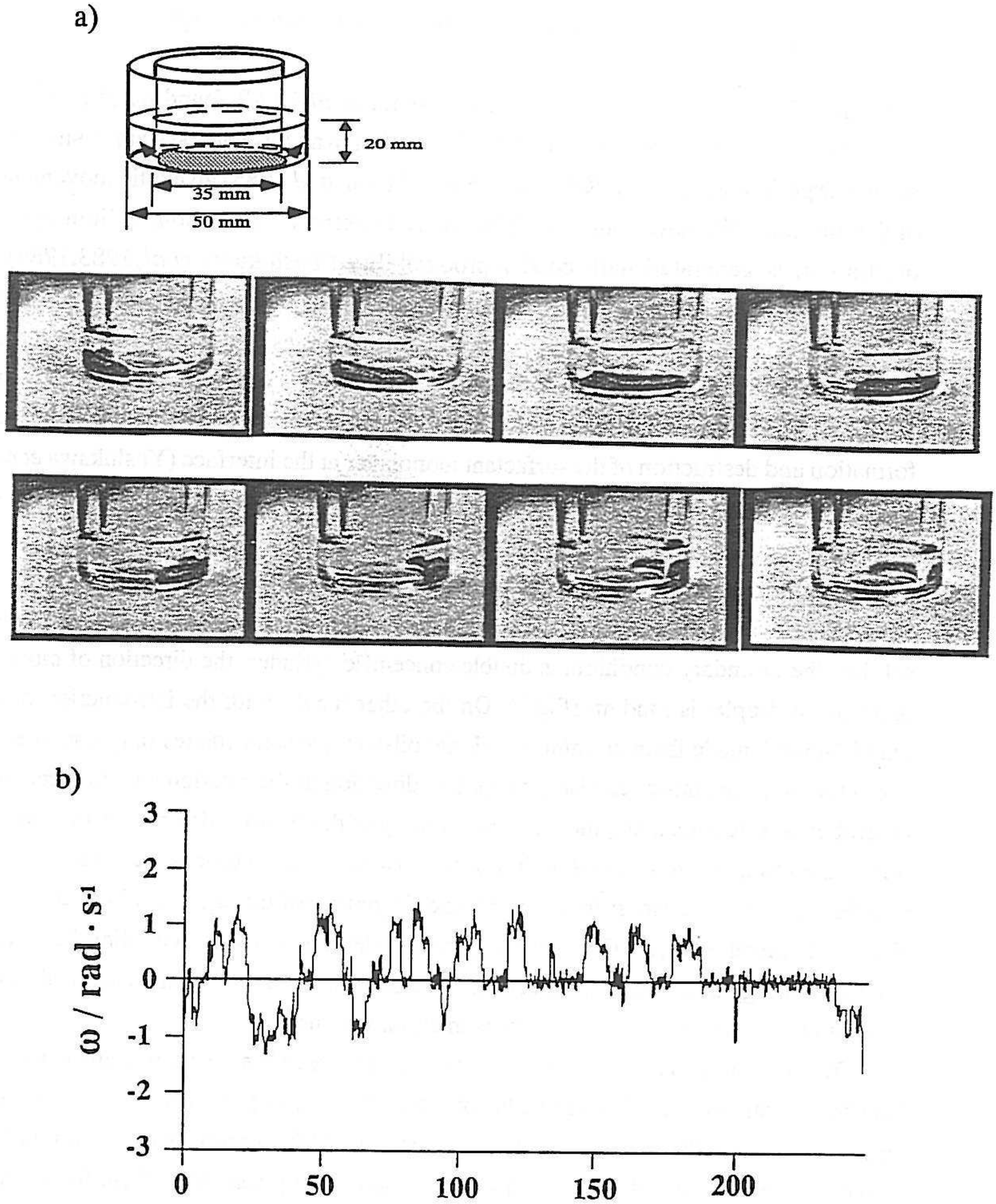

Fig. 2 a)Random movement of an oil droplet in an aqueous solution in a double concentric cylindrical vessel. The interval between the photographs is 0.3 sec. b) The time trace of angular velocity of the oil droplet. Aqueous phase: 1 mM trimethylstearylammonium chloride solution, and organic phase: 2 mM I_2 in nitrobenzene saturated with KI.

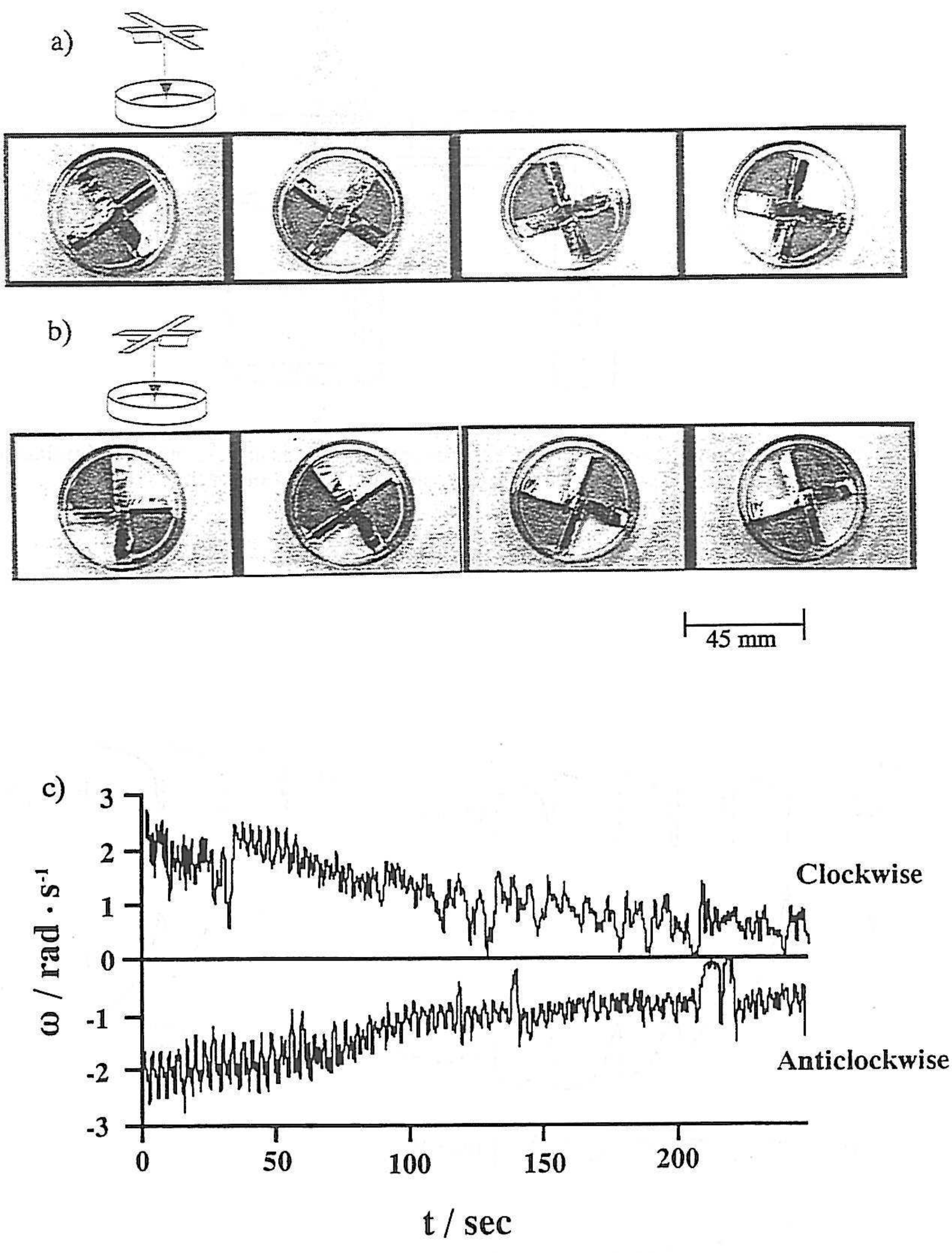

Fig. 3 a) Clockwise and b) anti-clockwise self-rotational movement of the oil-water system in an petri dish with an alminum rotor. The chirality in the structure of the aluminum foil, respectively, determines the direction of the rotation. The time interval is 0.3 sec. The conocentrations of solutions are the same as in Fig. 2. c) Time trace of angular velocity for the system of a) and b).

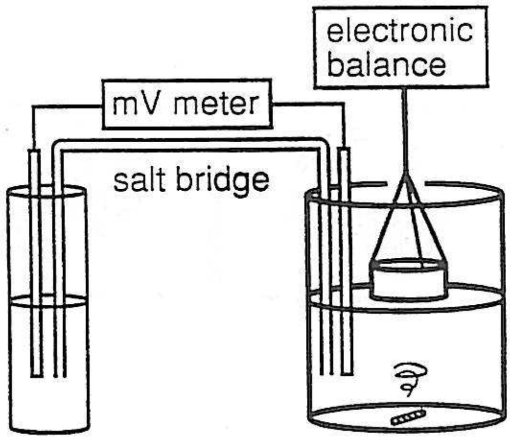

Fig. 4 Schematic representation of experimental apparatus used to monitor simultaneously the periodic changes of surface tension and redox potential.

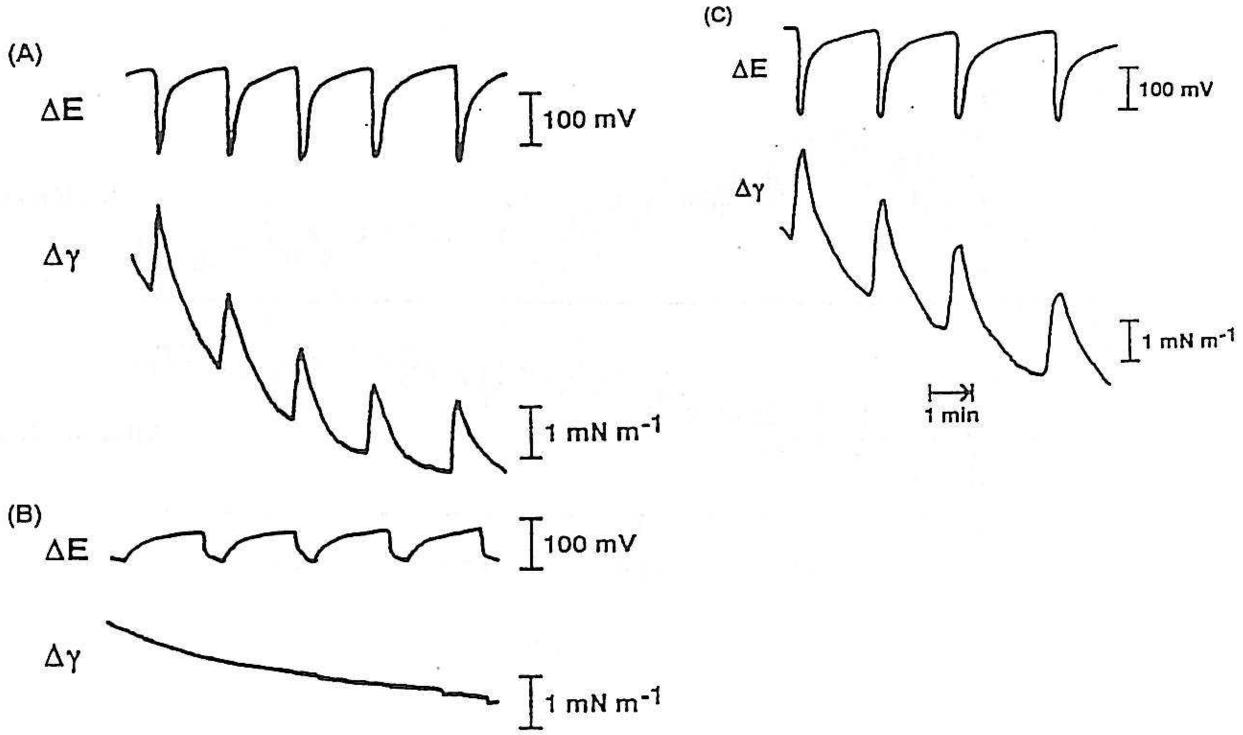

Fig. 5 Rhythmic changes of surface tension ($\Delta\gamma$) and redox potenyial (ΔE). [malonic acid] = 0.05 M, [H_2SO_4] = 0.3 M, [$NaBrO_3$] = 0.15 M, [NaBr] = 0.03 M. Catalysts are (A) 6 mM ferroin, (B) 6 mM Ce^{4+} and (C) 6 mM ferroin plus 6 mM Ce^{4+}.

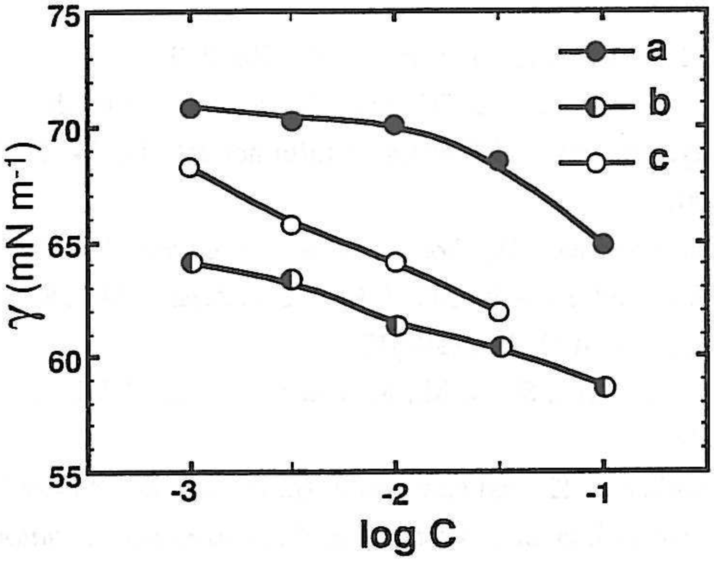

Fig. 6 Concentration (molarity) dependence of surface tension (γ) of the iron complex in aqueous solution at 25°C. (a)$[Fe(phen)_3]^{2+}$, (b)$[Fe(phen)_3]^{2+}$ in 0.15 M $NaBrO_3$ (reduced form; red), (c) prepared from $[Fe(phen)_3]^{2+}$ in 0.15 M $NaBrO_3$ and 0.3 M H_2SO_4 (oxidized to ferriin; blue).

tension changes in a rhythmic manner synchronized with the oscillation of the redox potential. When the catalyst is cerium ion without ferroin as shown in Fig. 5B, the surface tension does not exhibit rhythmic change. It is therefore expected that Fe(II) ions complexed with 1,10-phenanthroline are the root of the rhythmic change of surface tension. It is supposed that the surface activity between Fe(III) and Fe(II) complexes should be different because of the difference in solvation or hydrophilicity. In order to make clear the effect of the iron-complex on the surface tension, we have carried out the measurement of surface tension for the solution with Fe(II) and Fe(III) complexes as shown in Fig. 6. The surface activity is markedly increased in the presence of sodium bromate as shown in Figure 6b. It is also clear that the surface activity of the Fe(II) complex (Fig. 6b) is larger than that of the Fe(III) complex (Fig. 6c). In correspond to these experimental trends in the static systems, in Fig. 5, A and C, the surface tension is low when the redox potential is low, that is, when the complex exists as the form of Fe(II) in the reacting solution.

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