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ON THE OSCILLATORY PHENOMENON IN AN OIL/WATER INTERFACE

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A simple theoretical model is presented for simulating the self-sustained oscillations of electric potential and pH at an oil/water interface appearing in a two-phase system composed of 2-nitropropane solution containing picrate acid and an aqueous solution of cetyltrimethylammonium bromide. In the present model, a well-known condition necessary for the occurrence of self-sustained oscillations, i.e., the presence of a positive feedback process far from equilibrium, is taken into account in a set of kinetic equations to describe simplified characters of the following two processes: (i) a cooperative formation of ion pair complexes at the interface, and (ii) supply of picrate anions and cetyltrimethylammonium cations to the interface accompanied by release of ion pair complexes to the organic phase. The numerical solutions of the present equations are shown to reproduce fairly well the characteristic properties of the oscillation of electric potential and pH such as wave forms and frequencies.

1. Introduction

Recently, Yoshikawa and Matsubara [1] found self-sustained oscillations of electric potential and pH without any external force such as pressure, electric current or voltage, in a two-phase system of a solution of picric acid in 2-nitropropane and an aqueous solution of cetyltrimethylammonium bromide (CTAB). They also studied an artificial liquid membrane consisting of an oil layer of nitrobenzene containing picric acid, imposed between two aqueous phases, one containing CTAB and an alcohol [2]. This sytem showed rhythmic and sustained oscillations of electric potential within the range 150–300 mV with an interval of 0.5–30 min.

Prior to the finding of these oscillating phenomena, Dupeyrat and Nakache [3,4] reported that spontaneous hydrodynamic instabilities occurred at the interface between an aqueous solution of potasium chloride and an organic solution of octadecyltrimethylammonium picrate in nitrobenzene when an electric field was applied between the two phases. Quasi-periodic variations of a relaxation type were also observed for the interface tension and electric potential of a system composed of solutions of hexadecyltrimethylammonium chloride in water and picric acid in nitroethane or nitrobenzene. They proposed a mechanism involving an ion pair complex between the hexadecyltrimethylammonium cation (CTA^+) and the picrate anion (Pi^-) to explain the interfacial movement. On the basis of a theoretical consideration, however, Sanfeld et al. [5] claimed that no interfacial motion could occur by the mechanism proposed by Dupeyrat and Nakache. This is because no cooperative or autocatalytic process was involved in their mechanism. Such a process is considered to be essentially important to cause dissipative structures based on the thermodynamic theory concerning nonlinear, nonequilibrium states. Instead of their mechanism, Yoshikawa et

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al. [1] have proposed a mechanism including cooperative movement of CTA^+, from the aqueous phase to the interface and from the interface to the organic phase. While a tentatively simulated result on this mechanism has reproduced the observed result rather well as far as the wave form is concerned, their model is too simple to result in any instability of the system bringing about self-oscillations, i.e., hard-mode instabilities [6].

In this paper we shall provide an advanced model for simulating the above self-sustained oscillations of electric potential and pH by taking account of the well-known condition necessary for the occurrence of hard-mode instabilities to result in self-oscillations, i.e., the presence of a autocatalytic process far from equilibrium. Whereas the present model is composed of a set of equations describing only a rather simplified behavior of the real process, the simulated results are shown to reproduce fairly well the various characteristics of the observed results. This kind of study may be important not only from the theoretical point of view but also in obtaining deeper understanding of biological periodic phenomena such as excitable membrane pulses, circadian, cardiac and brain rhythms.

2. Experimental

2.1. Materials and methods

All reagents were commercial products. Picric acid was dried in vacuo. 2-Nitropropane was purified by distillation. Measurements were made after bringing 2 ml of the aqueous phases, a solution of CTAB, into contact with an upper phase of 1.5 ml of the organic solvent containing picric acid in a test tube (13 mm diameter). Experiments were carried out without stirring and the temperature was maintained at 18°C during the measurements. The pH of the aqueous phase and the electric potential between the organic and aqueous phases were measured with a Hitachi-Horiba F-7 pH/mV meter. The pH was monitored with an Ingold combinated mini-electrode (catalog no. 603002) situated about 5 mm from the interface. The electric potential was monitored with two bright platinum probes (wire) situated on either side of the interface, and about 3–5 mm from it. Other experimental conditions were the same as in the previous study [1].

For the experiment of oscillatory phenomenon in a liquid membrane (water/oil/water system), a U-shaped glass tube (12 mm inner diameter) was used. A solution (4 ml) of 1.5 mM picric acid in nitrobenzene was placed in the base of the U cell. Aqueous solutions (10 ml) were each introduced simultaneously into the arms of the U cell above the organic phase without stirring. The aqueous solution in the left arm contained 5 mM CTAB and 1.5 M ethanol and that in the right arm 0.1 M sucrose. Measurement was carried out at 18°C. The voltage across the liquidmembrane was measured with a Hitachi-Horiba F-7 ph/mV meter connected by two salt bridges to two Ag/AgCl electrodes. Other experimental procedures were the same as in the previous report [2].

2.2. Experimental results

Fig. 1a shows the whole profile of the change in pH in the aqueous phase after contact of the organic and aqueous phases. The solid line in fig. 1a represents the self-oscillation when the aqueous and organic phases contain CTAB and picric acid, respectively. It is noted that oscillations did not occur in the absence of either CTAB or picric acid. This implies that the interaction between CTAB and picric acid is essential to induce the oscillations.

Fig. 1b shows the oscillations of pH in the aqueous phase and of the electrical potential between the two phases in a system of a solution of picric acid in 2-nitropropane and an aqueous solution of CTAB. The oscillations of pH and electrical potential showed a constant period and nearly constant amplitude, and as seen in fig. 1b, they were synchronized.

Fig. 1c shows the oscillations of the voltage across a liquid membrane consisting of an oil layer, nitrobenzene containing 1.5 mM picric acid, between two aqueous phases, 5 mM CTAB plus 1.5 M ethanol on the left and 0.1 M sucrose on the right. The oscillations continued for more than 1 h. The amplitude of the oscillations was between

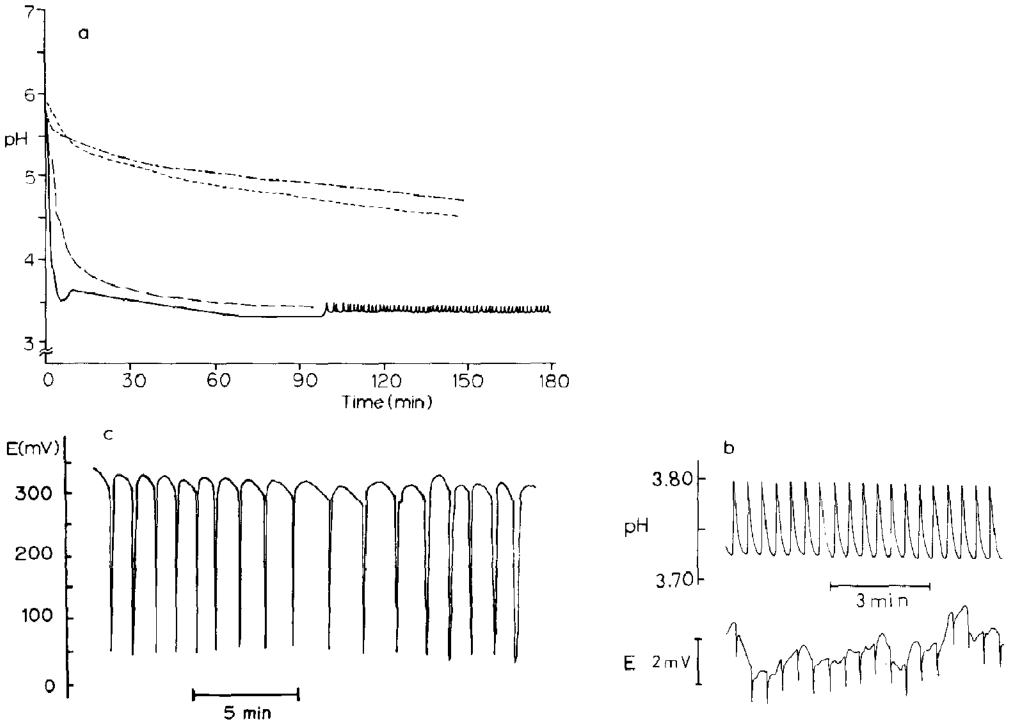

Fig. 1. (a) pH variation after contact of the two phase. (———) Picric acid in the organic phase and CTAB in the aqueous phase. (— — —) In the absence of CTAB. (·—·—·) In the absence of picric acid. (- - - - -) In the absence of CTAB and picric acid. (b) Oscillation of pH in the aqueous phase and electrical potential E between the aqueous and organic phases. (c) Oscillation of electrical potential between the two aqueous phases in a liquid membrane.

250 and 300 mV. No oscillations were observed in the absence of ethanol or CTAB.

It is interesting that a similar oscillatory phenomenon was observed in both a two-phase system and a liquid membrane, and that the amplitudes of the oscillations in the latter system was as much as two orders of magnitude more than that in the former system. For measurement of the electrical potential in the two-phase system, two platinum probes were dipped directly into the oil and aqueous phases. The potential thus observed does not seem to be so reliable at least with respect to its absolute value, because the surface potential between the platinum probes and the solutions should be affected markedly through the interactions of the platinum probes with the molecules of solvent, CTA^+ and Pi^-. Therefore, the observed magnitude of the potential may be reduced significantly in the two-phase system. In contrast, the potential between the two aqueous phases in the three-phase system (liquid membrane) may be reliable enough, as the above problem accompanied by the measurement of the potential in the two-phase system has been eliminated in this system. It thus seems reasonable to consider that the magnitude of the oscillation of the electrical potential is of the order of 100 mV for the two-phase system, similar to that for the three-phase system.

Fig. 2 shows the oscillation of pH in the aqueous phase when CTAB was replaced by 1-laurylpyridinium chloride, indicating that the manner of oscillations becomes somewhat irregular.

The amplitude of the observed pH oscillation depended on the position of the glass electrode, and was less when the glass electrode was far from the interface. Though we have tried to study the relationship between the magnitude of oscillation and the location of the glass electrode, we have not yet succeeded in obtaining a quantitative result, because any movement of the electrode, even if it

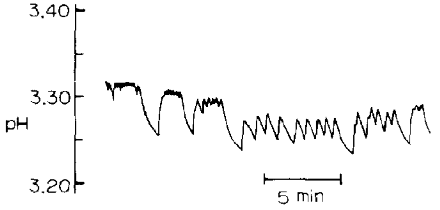

Fig. 2. pH variation in a two-phase system. Organic phase: 1.25 mM picric acid in 2-nitropropane. Aqueous phase: 5 mM 1-laurylpyridinium chloride.

is as small as possible, affects the manner of oscillation. There is another problem in the pH measurements: the magnitude of the oscillation also depended on the arrangement of the glass electrode and the reference electrode, i.e., the location of the latter also has some influence on the oscillation.

3. Theory

3.1. A theoretical model

Fig. 3 illustrates a situation where CTA, Pi^- and their ion pair complexes coexist at the interface and in the organic and aqueous phases. We do not describe spatial variations of concentrations of these substances, since this simplification, called a zero-dimensional approximation, may be sufficiently useful for explaining the occurrence of self-sustained oscillations [7–9]. Let us denote x, y and z as the concentrations of Pi^- near the oil/water interface, CTA^+ and ion pair complexes $CTA \cdot Pi$ at the interface, respectively. The concentration of Pi^- concerns that in the region usually called an equilibration layer, of several hundred ångstroms in width near the interface [10,11]. The concentrations at the interface are defined as the number of molecules contained in the average surface area per molecule at the critical micelle concentration.

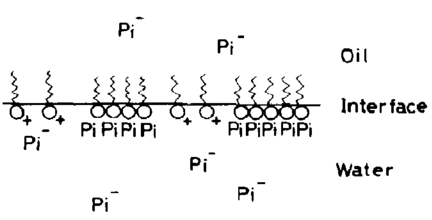

Fig. 3. Illustration of situation in an oil/water interface. The tightly packed monolayer of CTA·Pi is formed while CTA^+ distributes rather sparsely at the interface.

These concentrations may obey the following phenomenological equations:

$$\frac{dx}{dt} = j_x - k_x x - \epsilon_x z, \tag{1a}$$

$$\frac{dy}{dt} = j_y + k_y y - \epsilon_y z, \tag{1b}$$

$$\frac{dz}{dt} = k_z xy + \frac{\gamma z^n}{\theta + z^n} - \beta z, \tag{1c}$$

where j_x, k_x, ϵ_x, j_y, k_y, ϵ_y, k_z, θ, γ, n and β are the numerical parameters; their physical meanings are described below.

Eq. 1a describes the change in concentration x. The terms composed of first and second terms represent diffusion of Pi^- within the frame of the zero-dimensional approximation [7–9]. The values of j_x and k_x can be estimated from the period and wave form of self-oscillation of electric potential and pH. The third term expresses the reduction of x through the transformation to ion pair complexes. This effect may be relatively small, since Pi^- is ample in both phases. This term is also related to the barrier effect of complexes at the interface, which may prohibit Pi^- from diffusing rapidly across the interface.

Eq. 1b concerns CTA^+. The first two terms express the property of adsorption on the interface, with the second proportional to y representing a weak cooperativity of adsorption [12]. The presence of ion pair complexes at the interface, however, reduces the surface area effective for adsorption of CTA^+. Furthermore, the transformation to $CTA \cdot Pi$ may also decrease the number of CTA^+. The excluded volume effect and the reaction to produce $CTA \cdot Pi$ are expressed by the final term. Thus, the coefficient ϵ_y may be larger than ϵ_x.

Eq. 1c describes the formation of ion pair complexes $CTA \cdot Pi$ at the interface and the release into the organic phase. The first term is concerned with the formation of complexes from CTA^+ and Pi^-, the second expressing the strong cooperativity of subsequent formation of tightly packed monolayer. The escape of ion pair complexes from the interface to the oil phase is expressed by the last term. The cooperative formation of a CTA · Pi monolayer is considered as relatively strong. The CTA^+ monolayer-formative process, on the other hand, can be weakly cooperative because of the repulsive electric interaction between positively charged heads, as usual [13,14]; the coefficient γ is large compared with numerical parameters in eq. 1a for x and eq. 1b for y, with n also fairly large. This leads to a large value of β, i.e., fast release to the oil phase, as will be understood from fig. 5.

Eqs. 1a–c are the basic equations for describing the behavior of Pi^- near the oil/water interface, CTA^+ and ion pair complexes CTA · Pi at the interface. Let us next give the expressions for the electric potential E and pH in terms of these quantities. We assume the measured electric potential reflects the surface electric potential near the oil/water interface [12]:

$$E = \frac{2k_B T}{e} \sinh^{-1} \frac{\sigma}{\sqrt{2\epsilon_W k_B T c/\pi}} \tag{2}$$

where k_B denotes the Boltzmann constant, T the absolute temperature, e the positive elementary charge, ϵ_W the dielectric permeability of water, and c the bulk concentration of picric acid. Since CTA^+ is positively charged, the surface charge density σ may be given by

$$\sigma = ey/A, \tag{3}$$

where A is the molecular surface area at the critical micelle concentration.

The pH measured may be directly related to x. When the Pi^- concentration in the equilibration layer touching the interface increases abruptly, the Pi^- concentration relatively far from the interface may decrease. The pH measured reflects the H^+ concentration dissociating from picric acid in this region, since the pH electrode is placed about 5 mm from the interface. Thus, the pH may be given by

$$pH = -\log(x_0 - x) + pH_0 \tag{4}$$

where x_0 and pH_0 are the adjustable parameters for the origin of the pH value.

3.2. Theoretical results

Fig. 4 shows an example of numerical calculations in eqs. 1 with eq. 2 for E and eq. 4 for pH. The adopted parameter values are detailed in the figure caption. The wave forms, period and amplitudes of self-oscillations of electric potential and pH may reproduce fairly well the observed data in fig. 1.

The present theoretical model gives the nonoccurrence of self-oscillation, when the parameters j_x, k_x and ϵ_x for x or j_y, k_y and ϵ_y for y are put to zero. This agrees with the experiment that oscillations did not occur in the absence of either CTAB or picric acid. This implies that two coexisting kinds of species participate in this phenomenon.

A mechanism of the present self-oscillation can be understood as follows: Pi^- diffuses slowly to the region near the oil/water interface, and at the same time, CTA^+ tends to accumulate on the interface. This leads to the formation of ion pair complexes CTA · Pi. Because of the strong cooperative process, the CTA · Pi monolayer is built up spontaneously. As a consequence, the total concentration of CTA^+ and CTA · Pi at the interface becomes too large, and hence CTA · Pi can no longer remain there so as to escape to the oil phase. During the last process, Pi^- and CTA^+ continue to be consumed through the change to CTA · Pi. It follows that the concentrations of Pi^-, CTA^+ and CTA · Pi decrease to recover the starting step. Again, Pi^- and CTA^+ accumulate near and at the interface. The above-mentioned processes can, therefore, be repeated provided sufficient Pi^- and CTA^+ exist in the experimental system.

This mechanism may suggest that the supply rate of Pi^- and CTA^+ is intimately balanced with the release rate of CTA · Pi. The present model expresses the supply rate as j_x and j_y, and the release rate as β. Fig. 5 shows a phase diagram on the j ($= j_x = j_y$) and β plane, according to a linear stability analysis for examining the appearance of an oscillation (details are given in the appendix). Fig. 5 reveals that the self-sustained oscillation appears in a limited region of values of j and β. In fact, the stirring in the aqueous phase prohibits

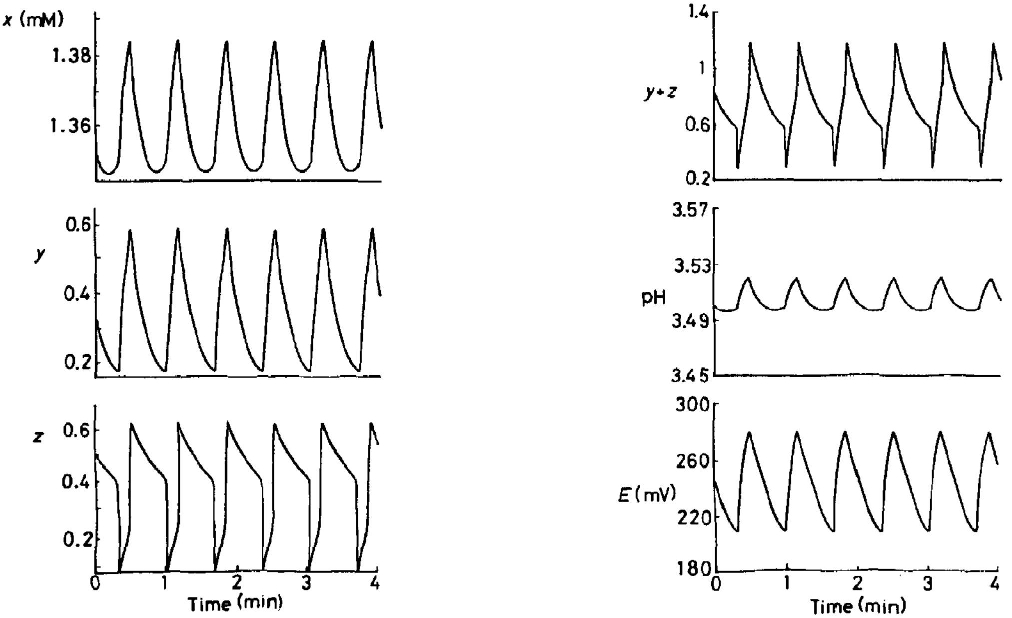

Fig. 4. Results of computer simulation. Numerical parameters chosen as $j_x = j_y = 3.33$ (mM/min), $\epsilon_x = 1$ (min^{-1}), $\epsilon_y = 10$ (min^{-1}), $k_x = 2.5$ (min^{-1}), $k_y = 1$ (min^{-1}), $k_z = 150$ (min^{-1} mM^{-1}), $\gamma = 190$ (min^{-1}), $n = 10$, $\theta = 3^{-10}$, $\beta = 500$ (min^{-1}), $A = 25$ (Å^2), $x_0 = 3.0$ (mM) and pH$_0$ = 4.0. Adopted parameter values belong to the oscillatory region in fig. 5. If the parameter values are selected outside this region, the oscillation can no longer appear.

the oscillation [1]. The diffusion speeds of Pi$^-$ and CTA$^+$ (expressed by j) and the escape speed of CTA · Pi (expressed by β) can be considered as altered drastically to result in the nonoccurrence of oscillation, whereas a delicate role of the interface structure also cannot be ignored. The burst-like oscillations shown in fig. 2 will be explained by a slight modification of the present theoretical model, as has been done for the burst of membrane potential observed in an artifial membrane [8]. More detailed comparison with observed data may need further definite experiments and improvement of the theoretical model to take account of experimental situations.

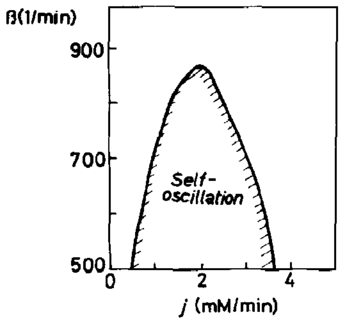

Fig. 5. Phase diagram at the j-β plane. Other numerical parameters are the same as in fig. 4.

4. Discussion

In the present paper the self-sustained oscillations of electric potential and pH in the oil/water interface were studied. The theoretical model revealed that the self-oscillation occurs mainly through two factors: (i) A cooperative formation of ion pair complexes at the interface and (ii) supply of Pi$^-$ and CTA$^+$ to the interface accompanied by release of CTA · Pi into the organic phase. The former point suggests the participation of a positive feedback mechanism. The latter means that the present system is subject to strong non-equilibrium situations. Both are well known as conditions necessary for the occurrence of self-oscillations [15].

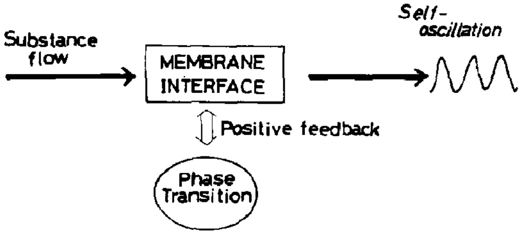

Fig. 6. A self-oscillation in systems composed of membrane or interface.

Self-oscillations of membrane potential have also been observed in a system composed of an artificial membrane separating two aqueous phases [7,8,16,17]. This membrane is constructed from a Millipore filter, whose pores are filled with a lipid analogue, dioleyl phosphate (DOPH). While it exhibits self-oscillations with long period of several minutes to a few hours only under a salt-concentration difference, oscillations with a short period of the order of 1 s appear under a salt-concentration difference, pressure difference and/or electric current. Theoretical analysis [7,8,16–18] shows that the oscillation occurs through the phase transition of DOPH molecules among oil droplets, micelles and multilayers within the pore, which are intimately coupled with salt flow. It quite resembles the oscillation at the oil/water interface. Fig. 6 illustrates the mechanism of self-oscillation in these kinds of systems. A recent study [19] also reveals that the frequency of oscillation in DOPH-Millipore membrane changes drastically in the presence of chemicals such as $CaCl_2$ and sucrose. This result suggests a new type of chemical sensor utilizing a self-sustained oscillation of electric potential. Self-sustained oscillation induced by an Na^+/K^+ concentration gradient has also been reported for a porous membrane doped with various lipids [20–22]. The study of oscillatory phenomena in model membranes may be of use for deeper understanding of biological rhythms.

Appendix

A linear stability analysis can examine the stability of a nonoscillatory steady state: If the steady state becomes unstable, a self-oscillation can appear. In the present case, the concentrations x, y and z must be expanded around the steady state expressed by x_s, y_s and z_s, respectively, as

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x_s \\ y_s \\ z_s \end{pmatrix} + \begin{pmatrix} \delta x \\ \delta y \\ \delta z \end{pmatrix} \tag{A1}$$

where δx, δy and δz are the small quantities. Substituting eq. A1 into eqs. 1, we then obtain the linearized equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} \delta x \\ \delta y \\ \delta z \end{pmatrix} = \begin{pmatrix} -k_x & 0 & -\epsilon_x \\ 0 & k_y & -\epsilon_y \\ k_z y_s & k_z x_s & \dfrac{n\gamma\theta z_s^{n-1}}{(\theta + z_s^n)^2} - \beta \end{pmatrix} \begin{pmatrix} \delta x \\ \delta y \\ \delta z \end{pmatrix}, \tag{A2}$$

with x_s, y_s and z_s given by

$$x_s = (j_x - \epsilon_x z_s)/k_x,$$
$$y_s = (\epsilon_y z_s - j_y)/k_y,$$
$$k_z x_s y_s = \frac{\gamma z_s^n}{\theta + z_s^n} - \beta z_s. \tag{A3}$$

The small quantities δx, δy and δz can take the form:

$$\begin{pmatrix} \delta x \\ \delta y \\ \delta z \end{pmatrix} = M e^{\lambda t}, \tag{A4}$$

where M is the three-component vector, and λ the eigenvalue. The substitution of eq. A4 into eq. A2 leads to the secular equation:

$$\lambda^3 + p\lambda^2 + q\lambda + r = 0, \tag{A5}$$

where the coefficients p, q and r are given by

$$p = k_x - k_y - \Gamma,$$
$$q = -k_x k_y + (k_y - k_x)\Gamma + k_z(\epsilon_y x_s + \epsilon_x y_s),$$
$$r = k_z(k_x \epsilon_y x_s - k_y \epsilon_x y_s) + k_x k_y \Gamma, \tag{A6}$$

with Γ defined by

$$\Gamma = \frac{n\gamma\theta z_s^{n-1}}{(\theta + z_s^n)^2} - \beta. \tag{A7}$$

Eq. A5 has three solutions: λ_1, λ_2 and λ_3; their formal expressions for the present interesting case are

$$\lambda_1 < 0,$$
$$\lambda_2 = d + i\omega,$$
$$\lambda_3 = d - i\omega. \tag{A8}$$

As is well known, the nonoscillatory steady state is stable if d takes negative values. When d is positive, however, the steady state becomes unstable so that oscillatory solutions can appear. The point given by $d = 0$, therefore, is an instability point. The solid line shown in fig. 5 corresponds to the line of $d = 0$, across which the stability change occurs.

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