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ARTICLES

Oscillation in Penetration Distance in a Train of Chemical Pulses Propagating in an Optically Constrained Narrowing Channel

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A chemical wave train propagating in a narrowing excitable channel surrounded by a nonexcitable field is investigated by using a photosensitive Belousov−Zhabotinsky (BZ) reaction. The considered geometry is created as a dark triangle surrounded by an illuminated area where the reaction is suppressed by the light-induced generation of bromide ion. For a low illumination level, a pulse train terminates at a constant position. However, as the light intensity increases, the position at which subsequent pulses disappear changes periodically, so that the period-doubling of penetration depth occurs. Two-dimensional simulations based on a modified Oregonator model for the photosensitive BZ reaction reproduce the essential features of the experimental observation.

1. Introduction

Propagation of waves in reaction-diffusion systems is one of the most interesting issues in nonlinear science. This phenomenon is associated with a large class of problems, including those concerned with the function of the brain and the nervous system, since the propagation of pulses in nerve channels can be qualitatively described with relatively simple models based on reaction-diffusion equations, such as the FitzHugh−Nagumo ones.[1,2] A pulse or a train of pulses in a neuron network appears to be a manifestation of nonequilibrium constraints in a thermodynamically open system. There have been numerous experimental and theoretical studies on nerve dynamics. However, some of the generic features that characterize the nonequilibrium behavior of an excitable medium, and especially information processing in a reaction-diffusion process, can be discovered by investigating simple models for rather complex systems. In such studies, the Belousov−Zhabotinsky (BZ) reaction can play an important role because it is often considered as a standard medium for experiments on reaction-diffusion systems.[3−6] The qualitative features of time evolution of a spatially distributed medium where this reaction proceeds can

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be successfully simulated by using the Oregonator model.[7,8] For example, if the parameters in the equation are properly adjusted, this model reproduces the transition between oscillatory, excitable, and nonexcitable states, as well as spatiotemporal patterns (such as target patterns and spiral patterns).

There have been numerous studies on chemical wave propagation on fields of various shapes, such as a circular ring, a sphere, a small droplet, a narrowing area, and other peculiar geometries.[9−14] Among these, the chemical wave propagation from a narrower channel to a larger area, and that from a larger area to a narrower channel, seem to be closely related to pulse propagation in a neuronal system,[15,16] where a large cell body is linked to other cells by narrow nerves. In our previous studies, we investigated chemical wave propagation in a narrowing glass capillary. When a chemical pulse propagates toward the narrower area, it slows down, and finally stops and disappears.[16] The mechanism of this slowing and stopping of the chemical pulse can be explained as the charge effect of the glass surface. Since the physical chemistry near the glass surface is a complex phenomenon, the extent to which we can apply a description based on a system of reaction-diffusion equations with standard boundary conditions is still unclear.

The BZ reaction catalyzed by a Ru-complex is known to be photosensitive. The mechanism of this photosensitivity can be explained as follows: The ruthenium catalyst absorbs light and gets excited. The ruthenium catalyst in the excited state reacts with bromomalonic acid and then causes the production of bromide ion, an inhibitor of the BZ reaction.[17−21] By using a photosensitive BZ reaction and inhomogeneous illumination to generate a geometric pattern of excitable and nonexcitable areas, one can easily increase the complexity of propagating chemical waves and control their evolution in time.[22−30]

In the present article, we report our results regarding pulse propagation in a narrowing excitable channel generated using the photosensitive BZ reaction (cf. Figure 1). The optical constraints can be seen as an alternative to a glass capillary, but with well-defined boundary conditions. In our experiments, the light intensity in the illuminated area around the channel is used as a control parameter. We considered a periodic train of pulses propagating toward the channel tip and observed the position at which a pulse disappears. We found that the character of pulse propagation depends on the intensity of light. For a low light intensity all pulses of the train disappear at the same point. If the light intensity increases, we observe oscillations in penetration depth. Two-dimensional simulations using a modified Oregonator for photosensitive BZ reaction qualitatively reproduce the experimental observations.

2. Experimental Setup

All chemicals were analytical grade reagents and used without further purification. Water was purified with a Millipore Milli-Q system. The BZ medium was composed of 0.45 mL of 1.5 M sodium bromate ($NaBrO_3$), 0.1 mL of 3.0 M sulfuric acid (H_2SO_4), 0.2 mL of 1.0 M malonic acid ($CH_2(COOH)_2$), 0.05 mL of 1.0 M potassium bromide (KBr), and 0.2 mL of 8.5 mM ruthenium bipyridyl chloride ($Ru(bpy)_3Cl_2$). The system is excitable with these reagents at the concentrations listed above. We mixed all of the reagents except for the ruthenium catalyst, and the solution turned brown due to the generation of bromine. After bromine reacted with malonic acid to produce bromomalonic acid and the solution turned colorless, the ruthenium catalyst solution was added. A cellulose-nitrate membrane filter (Advantec, A100A025A; pore size of 1 μm) was soaked in the BZ solution and placed on a glass plate (Matsunami, Slide glass; 76 × 52 × 1.2 mm). The surface of the membrane filter was completely covered with 0.7 mL of silicone oil (Wako, WF-30) to prevent it from drying and to protect it from the influence of oxygen. All experiments were carried out at room temperature (20 ± 3 °C). The required geometry of excitable and nonexcitable areas was introduced by nonhomogenous illumination. In some experiments, the required geometry was generated on a computer as a screen with different gray levels and directly projected on a membrane filter. In other experiments, the capillaries were printed on a transparent film that was placed below the uniformly illuminated membrane. The propagation of chemical pulses was recorded from above through a blue filter with a maximum transparency at 410 nm (Asahi Techno Glass, V-42) with use of a digital video camera (Sony, DCR-VX700). A schematic representation of the experimental setup is shown in Figure 1 A. The light intensity of bright areas was selected so that they were nonexcitable (excitations died out rapidly), and thus the chemical pulses could propagate only in the dark areas. To compare results obtained for chemically identical medium, we performed experiments for two identical optical capillaries with different background illumination. The geometry of optical capillaries used in experiments is illustrated in Figure 1B. The channels are 1.5 mm wide. Excitations are introduced with a silver wire (diameter 1 mm) that touches the membrane in the middle of right vertical channel. The illumination in the back regions is 2 klx. The background illuminations of the upper and lower capillaries are 57 and 37 klx, respectively.

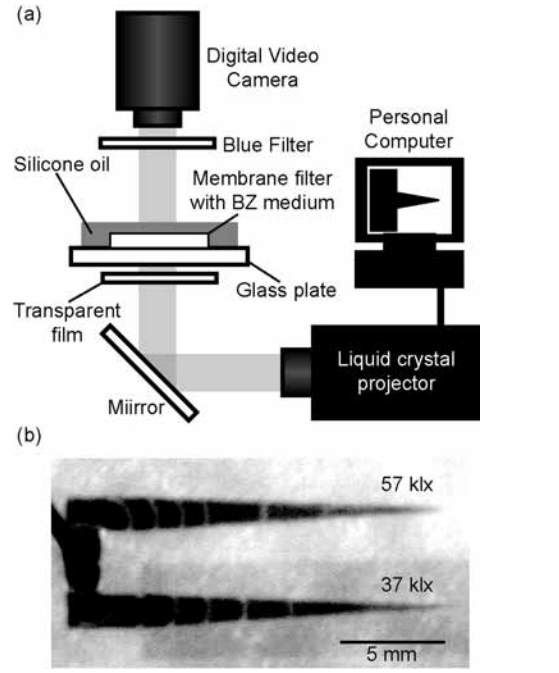

Figure 1. (a) The schematic representation of the experimental setup. The shape of the reaction field is projected onto the membrane filled with reagents. (b) The geometry of the optical capillaries used in experiments presented in Figures 2 and 3. The black channels are 1.5 mm wide. Excitations are introduced with a silver wire (diameter 1 mm) that touches the left vertical channel. The illumination of the back regions is 2 klx. The background illuminations of the upper and lower capillaries are 57 and 37 klx, respectively.

3. Experimental Results

Snapshots and spatiotemporal plots of a train of chemical pulses propagating on a triangular reaction field are shown in Figures 2 and 3. Pulses moving from the triangle base disappeared as they approached the tip. When the light intensity

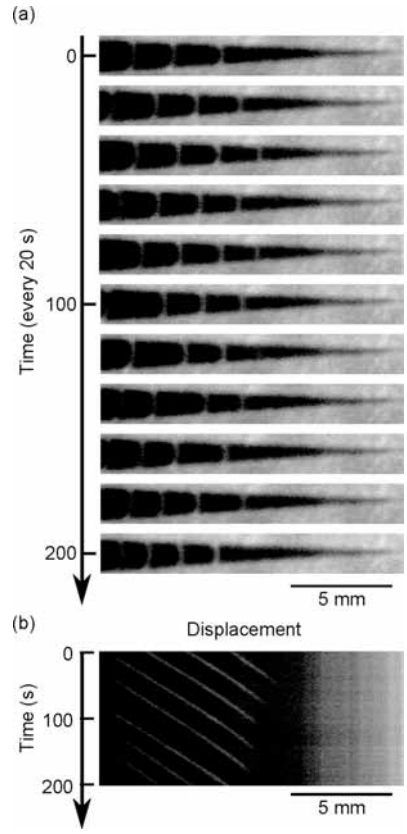

Figure 2. Experimental results for chemical wave propagation on a triangular reaction field. The surrounding area had lower light intensity (37 klx). (a) Snapshots every 20 s and (b) spatiotemporal plots made by aligning the images along the symmetry axis of the triangular channel.

in the brighter and that in the surrounding area was low (37 klx), all pulses disappeared at the same point, as shown in Figure 2. The disappearance of excitation pulses before the tip of the dark triangular region can be explained by a combination of two effects. The maximum concentration of activator in a pulse decreases when a pulse moves toward the narrow part because its diffusion into the illuminated areas becomes more important. On the other hand, the diffusion of inhibitor from illuminated areas (its concentration is higher there) increases and makes the system less excitable. At a certain propagation depth the activator concentration drops below the level necessary to propagate excitation and the pulse terminates. However, when illumination was higher (57 klx), the point at which excitation pulses disappeared changed with a period of two, as shown in Figure 3. The period doubling can be explained by uncompleted medium relaxation perturbed by high-frequency spikes. In a pulse, the propagating maximum of activator responsible for excitation of medium before the spike is followed by a maximum of inhibitor forcing the return to the rest state. If the frequency of arriving spikes is high, the triangle tip does not relax after a deep penetrating pulse and the subsequent excitation terminates earlier. However, when the next pulse arrives, it finds the tip more relaxed and so its penetration is deeper. Next the scenario repeats. In experiment the properties of the reaction field changed with time, since the system is a batch reactor and reagents are consumed. Nevertheless, this characteristic periodic penetration pattern was maintained for a few minutes.

4. Discussion

There have been several experimental and theoretical studies on the periodic penetration of a wave train. Almost all of these studies considered a field where the parameters were changed in a stepwise manner. For example, Bär et al. reported periodic transmission in a numerical model for the oxidation of carbon monoxide (CO) at a platinum plate.[31] Sielewiesiuk and Górecki reported *N*:*M* transmission through a passive gap with a numerical calculation using the FitzHugh−Nagumo model.[32] On the other hand, Kettunen et al. studied chemical wave propagation for the BZ reaction in a uniform straight capillary and reported 1:*N* transmission. They discussed the observed phenomena based on aging of the BZ reaction.[33] In our system, the character of medium continuously changes along the direction of pulse propagation. Thus, we investigated the mechanism of the periodic penetration of a wave train based on a continuous change in parameters in a mathematical model.

Bromide ion, as an inhibitor of the BZ reaction, is produced by light illumination through the processes: the excitation of ruthenium catalyst, and the reaction between excited catalyst and bromomalonic acid. Thus, the Oregonator model describing the standard BZ reaction is modified to take this effect into account:[18]

$$\frac{\partial u}{\partial t} = \frac{1}{\epsilon}[qv - uv + u(1 - u)] + D_u\nabla^2 u \qquad (1)$$

$$\frac{\partial v}{\partial t} = \frac{1}{\epsilon'}[-qv - uv + fw + \phi] + D_v\nabla^2 v \qquad (2)$$

$$\frac{\partial w}{\partial t} = u - w + D_w\nabla^2 w \qquad (3)$$

where u, v, and w are dimensionless variables that correspond to the concentrations of the activator ($HBrO_2$), bromide ion (Br^-), and oxidized catalyst ($[Ru(bpy)_3]^{3+}$), respectively. f, ϵ, ϵ', and q are positive parameters that determine the nature of the BZ reaction. D_u, D_v, and D_w are the diffusion constants for u, v, and w, respectively. ϕ is a variable that is proportional to the light intensity.

On the basis of eqs 1 to 3, numerical simulations in a two-dimensional space were performed. We considered two values of parameter ϕ, which corresponds to the light intensity: $\phi = 0$ in the dark region and $\phi = \phi_0$ in the illuminated area. For the considered parameters describing the dark medium, the shortest period of propagating pulses was 4.45 time units. Chemical waves were initiated every T time units at the wider end by setting $u = 0.8$. Our simulations depended on three parameters: ϕ_0, T, and the angle θ at the tip of triangular dark area, as illustrated in Figure 4a. The spatial and temporal grid sizes were set as $\Delta x = \Delta y = 1$ and $\Delta t = 10^{-4}$. The initial conditions for u, v, and w were set to u_0, v_0, and w_0, which were the values at a steady state without illumination. The Neumann boundary condition was adopted at the edges of the calculated field.

The results of the numerical simulation are shown in Figure 4b. For small ϕ_0 ($\phi_0 = 0.1$), the position at which the consecutive pulses of the train stop does not change. When $\phi_0 = 0.2$, we observe oscillations in the penetration depth. These numerical results correspond to the experimental observations as given in Figures 2 and 3. By the numerical simulation with the change in θ, the periodic penetration can be seen when θ is smaller than a critical value θ_c (when $\phi_0 = 0.20$, $\theta_c \approx 0.055$ rad). We also investigated the dependency of the penetration doubling on T and θ as shown in Figure 3c. With an decrease in θ, the penetration doubling occurs if the period of the traveling waves T is larger. Thus, the numerical results indicate that the inflow

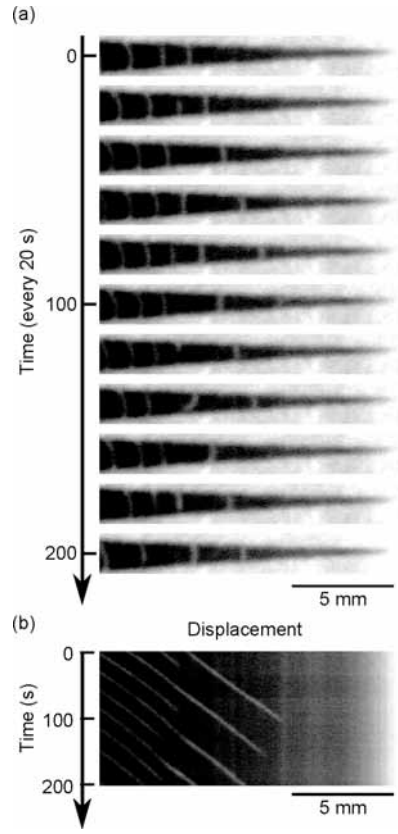

Figure 3. Experimental results for chemical wave propagation on a triangular reaction field. The surrounding area had a greater light intensity (57 klx). (a) Snapshots every 20 s and (b) spatiotemporal plots made by aligning the images along the symmetry axis of the triangular channel.

of inhibitor produced by light illumination in the surrounding area plays an essential role in the penetration doubling. When the light intensity becomes higher, the amount of inhibitor produced is greater. As a result, the chemical wave is affected more significantly. This causes the periodic penetration.

5. Conclusion

Chemical wave propagation was investigated in a narrowing excitable channel controlled by light illumination. The present results showed that the nature of pulse propagation depends on the intensity of light and changes from wave-disappearance at a constant position for a low light intensity to oscillations in penetration depth for a higher light intensity. The experiments also indicated that more complex penetration patterns can exist, but they are less stable in batch conditions. Numerical simulations showed that this phenomenon can be explained by the diffusion of activator generated in the excitable channel to the neighboring nonexcitable region and by the reverse diffusion of inhibitor produced in the illuminated area. This phenomenon shows that the geometrical distribution of excitable and nonexcitable areas can modify the propagation of a train of pulses in a complex manner that is strongly dependent on small changes in the control parameters.

If the reaction field is X-shaped (two triangles joined at the tips), we could expect that every other pulse could cross through the gap. Thus, this can be regarded as a "low-pass filter". In the experiments, we confirmed that an X-shaped reaction field allows only every other wave to pass through. By changing the light intensity, every wave can pass through or every wave disappears (data not shown). By using the flow reactor, we will

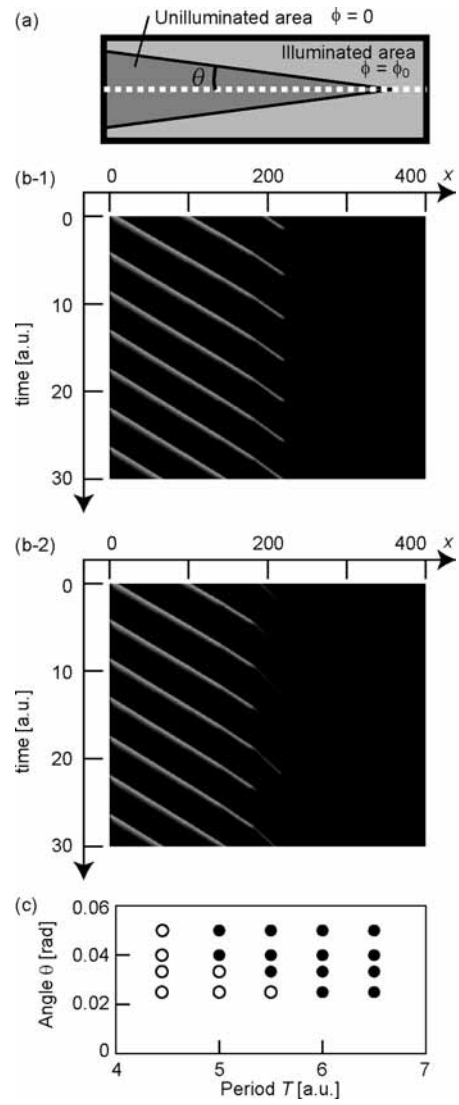

Figure 4. Numerical results represented by spatiotemporal plots based on eqs 1 to 3. The parameters are $f = 3$, $\epsilon = 4 \times 10^{-2}$, $\epsilon' = 1 \times 10^{-4}$, $q = 8 \times 10^{-4}$, and $D_u = D_v = D_w = 10$. (a) Geometrical scheme adapted for the simulation. (b-1 and b-2) Spatiotemporal plots constructed from time-successive images along the broken white line in panel a with the angle at the tip of dark area $\theta = 0.025$ rad and the period of propagating pulses $T = 4.45$ (the shortest period): (b-1) for $\phi_0 = 0.1$ and (b-2) for $\phi_0 = 0.2$. (c) Presence of periodic penetration as the function of T and θ. Open and closed circles correspond to the presence and absence of periodic penetration, respectively. The parameters are the same as those in panel b-2.

be able to control the characteristics of the chemical wave more easily and more accurate control will be capable in the near future. By tuning the parameters, such as the light intensity or the excitability, a one-in-three mode, a two-in-three mode, and other modes can also be realized. In our experiments, a one-in-three mode was observed, but it was not stable enough to maintain for a long time. More delicate tuning and modification of the theoretical framework should be addressed in future works. We hope that the characteristic manner of pulse transmission depending on the channel geometry may inspire further studies to understand the mechanisms that underlie informational processing in living systems, which shows remarkable adaptation in contrast to that in existing electronic computers.

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