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ARTICLES

Propagation of Chemical Waves at the Boundary of Excitable and Inhibitory Fields

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The photosensitive Belousov−Zhabotinsky (BZ) reaction with $Ru(bpy)_3^{2+}$ catalyst has been used to study wave propagation and annihilation at the boundaries of excitable and inhibitory regions of an active medium. Depending on the degree of excitability of the two areas, waves can either penetrate into the inhibitory region or collapse in the excitable zone. The experimental trend can be reproduced semiquantitatively with a numerical calculation based on the three-variable Oregonator model modified for the light sensitivity of the reaction. These results suggest that the photosensitive BZ medium may be a useful model for studying the effects of the geometric arrangements between areas of different excitability.

Introduction

It was recently recognized that the boundary of an excitable medium can significantly affect wave propagation. It may serve as a source of wave front instability, resulting in the accumulation of wave breaks and the multiplication of rotating spiral waves,[1] and as a modulator of speed and morphology in such spiral rotation.[2,3] The boundary may also cause wave-train suppression or rhythm transformation;[4] thus, it acts as a "natural" inhomogeneity in a confined medium. A specific layer is formed around the boundary, which can significantly change the efficiency of the wave propagation, when the area of the excitable medium is small, resulting even in the complete blockade of propagating waves.[5,6] In these previous studies, the boundary had the role of separating active and inactive parts, i.e., regions of autocatalytic reaction and diffusion and that of diffusion only within the medium. The boundary can be either no-flux- or sink-type; in other words, the reaction components could not or could diffuse into the inactive area of the medium with no reaction inside.

In this work we study a system where the boundary separates two regions of different excitability. As an experimental model, we use the photosensitive version of the Belousov−Zhabotinsky (BZ) reaction,[7,8] where the light illumination results in the production of bromide, an inhibitor of the reaction, with a reaction rate depending on the local intensity of the illumination.[9,10] We show that various types of boundary layers may exist depending on the production rate of the inhibitor.

Experimental Method

The reaction mixture was prepared as described previously[11,12] from analytical grade chemicals (Waco Tech). The catalyst for the photosensitive reaction, $Ru(bpy)_3Cl_2$, was synthesized and purified as in refs 13 and 14. The solution composition was 1 mL of $NaBrO_3$ (1.5 M), 1 mL of H_2SO_4 (3.5 M), 2 mL of malonic acid (1 M), 1 mL of KBr (0.5 M), 0.6 mL of doubly distilled water, and 2.4 mL of $Ru(bpy)_3Cl_2$ (8.5 mM). Cel-

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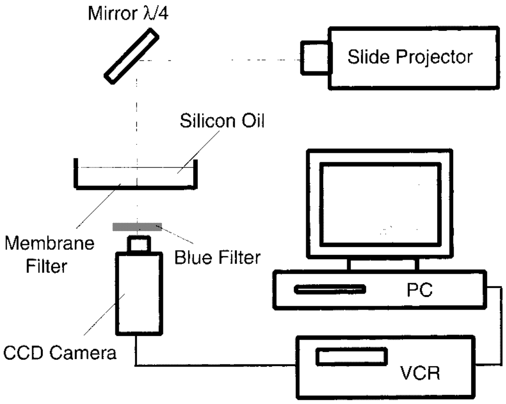

Figure 1. Scheme of the experimental setup.

lulose−nitrate membrane filters (A100A025A, 2.5 cm diameter, Advantec) with a pore size of 1 μm were rinsed in hot distilled water to remove hydrophobic materials from the surface and stored in distilled water. The solution was heated to 40−45 °C for ca. 1 min, and a pretreated membrane was soaked in the BZ solution for 15 min. The membrane was gently wiped with a Kimwipe to remove excess water and then placed in a Petri dish and immediately covered with silicon oil (Shin-Etsu Chemical Co.) to prevent it from drying and to protect from the influence of oxygen. The experiments were carried out at room temperature (ca. 20 °C) where the reaction medium showed no spontaneous excitation without any change in the behavior for approximately 1 h. Excitation waves were initiated by gently touching the surface of the membrane with a 1 mm thick silver wire.

The medium was illuminated from the top, as shown schematically in Figure 1. The halogen bulb (JCD100V-300W) of a slide projector (Cabin, Family II) was used as a light source, and the light intensity was varied by an external voltage controller. A black and white picture on a slide in the projector served as an illumination mask to create the appropriate boundary. The experiments were monitored with a CCD camera (Shimadzu CCD-S1) attached to a microscope (Nikon DIA-PHOT-TMD) from below, were recorded by a VCR (Panasonic NV-H200G), and were analyzed using standard imaging processing techniques. For image enhancement, a blue optical filter (AsahiTechnoGlass V-42) with a maximum transparency of 410 nm was applied. The light intensity through the different parts of the mask was determined by a self-assembled light sensor (Sharp BS520) calibrated using a light intensity meter (Minolta T-1H).

Experimental Results

In the experiments, spiral waves, as "natural" wave sources, were generated in the nonilluminated, i.e., excitable area. These excitation waves then traveled toward the illuminated, inhibitory region. (In the experiments, the effects of photochemical inhibition in the shadowed part were negligible, since the intensity of the monitoring light was 2 orders of magnitude less than that in the illuminated zone.) The wave propagation around the boundary separating the two fields was monitored microscopically. Figure 2 shows profiles of traveling waves for two different intensities of illumination, with arrows indicating the position of the wave defined as that of the maximum gradient in the profile. At low light intensity ($I = 2.9 \times 10^4$ Lx), the wave crosses the boundary and penetrates the illuminated area. While the amplitude of the wave gradually decreases, the wave propagates as far as 220 μm from the actual boundary into the inhibitory area, as shown in Figure 2a. When the light intensity is increased, the range of penetration decreases and the wave may collapse even before arriving at the border within the shadowed area (Figure 2b).

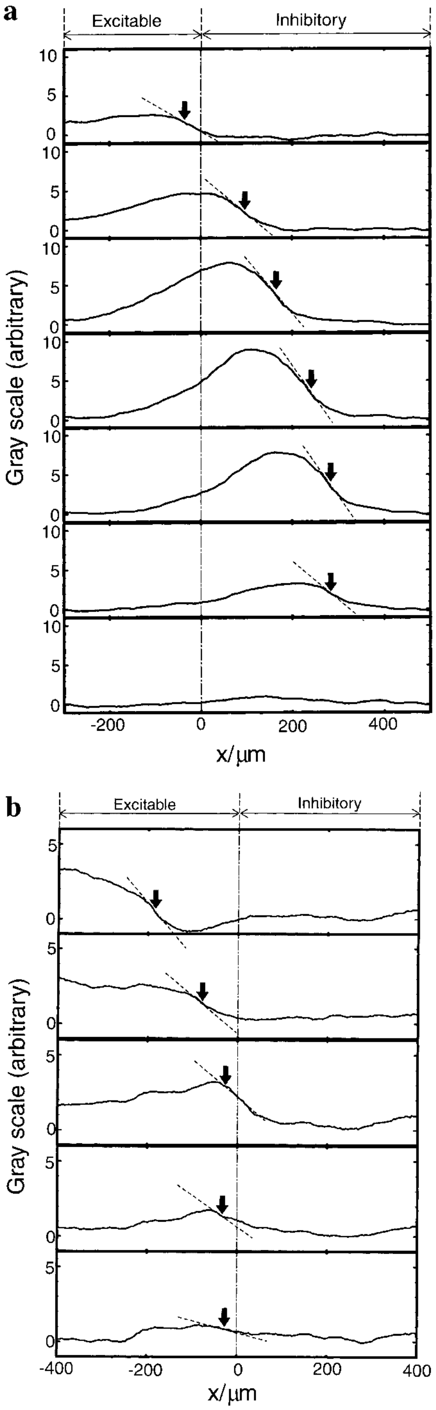

Figure 2. Experimental profiles of waves propagating near the boundary. For $x < 0$, the area is not illuminated, while for $x > 0$ the light intensity is (a) $I = 2.9 \times 10^4$ Lx and (b) $I = 5.4 \times 10^4$ Lx. Waves propagate from left to right; the time interval between the profiles is $\Delta t = 3.3$ s. The arrows indicate the position of the wave defined as the location with the maximum gradient.

To examine the shift of wave annihilation from the excitable region to the inhibitory one, we have determined the position of the disappearance of the wave, Δ, by systematically varying the intensity of illumination. In Figure 3 the positive values of Δ correspond to the penetration of the wave into the illuminated area, while the negative values to cases when the wave ceases

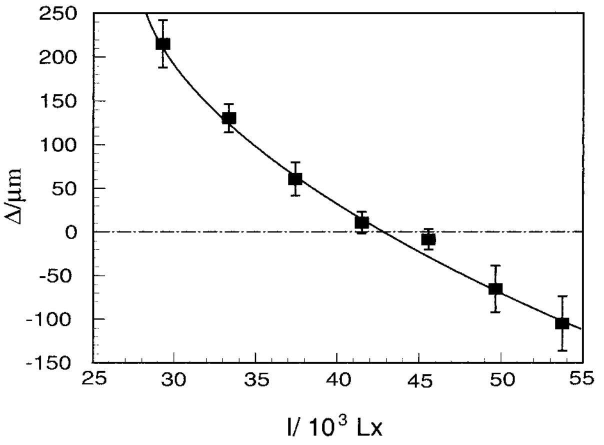

Figure 3. Position of wave collapse relative to the boundary, Δ, as a function of light intensity. Positive distances correspond to collapses in the illuminated inhibitory region, while negative values refer to those in the nonilluminated excitable region.

in the shadowed excitable area. The measured distances are the average of three independent measurements in at least five experiments.

The location of wave annihilation also depends on the incident angle of the wave with respect to the boundary. The results given in Figures 2 and 3 are for waves traveling perpendicular to the boundary. When the incident angle of the wave propagation is not parallel to the boundary, the wave collapse tends to shift toward the nonilluminated regime of the medium.

Computer Simulations

The dimensionless Oregonator model modified for the light-sensitive ruthenium-catalyzed BZ reaction was used in the simulations:[15]

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + \frac{1}{\epsilon_1}(u - u^2 + qw - uw)$$

$$\frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + u - v$$

$$\frac{\partial w}{\partial t} = \frac{\partial^2 w}{\partial x^2} + \frac{1}{\epsilon_2}(\phi - qw - uw + fv)$$

where the variables u, v, and w correspond to the dimensionless concentrations of $HBrO_2$, $Ru(bpy)_3{}^{3+}$, and Br^-, respectively. The term ϕ is proportional to the light intensity[16,17] and was varied between 0 and 0.02. The parameters of $f = 2.5$, $\epsilon_2 = 10^{-4}$, and $q = 10^{-4}$ were used throughout the calculations, while ϵ_1 was set to either 0.01 or 0.05.

The partial differential equations were converted to ordinary differential equations by discretizing the spatial dimension, and the ODEs were solved using the CVODE package[18] in one spatial dimension with no-flux boundary conditions at both ends. The calculations were carried out on 1001 points with a grid spacing of $h = 0.2$. The boundary separating a nonilluminated region ($\phi = 0$) from an illuminated one was placed in the middle. The stable steady states for a given light intensity on the two sides of the boundary were used as initial conditions. The integrations were then carried out until $t = 10$ to ensure a constant concentration profile. The position of the point corresponding to the critical bromide concentration was measured relative to the boundary. The critical bromide level was determined in separate sets of calculations where the bromide level w was increased until permanent wave propagation initiated by setting $u = 0.1$ in 25 points became impossible for $\phi = 0$.

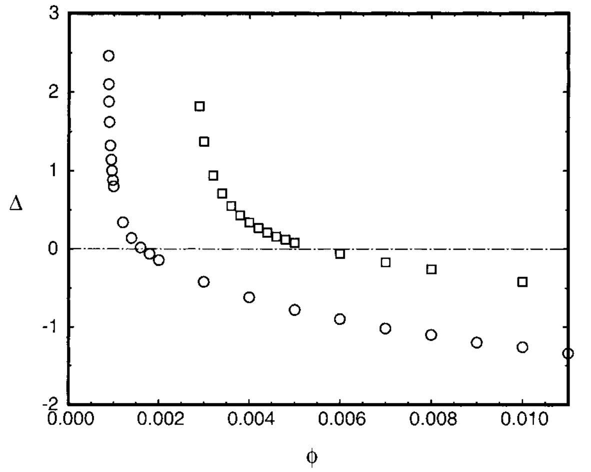

Figure 4. Position of wave annihilation, Δ, as a function of light intensity of the illuminated region for simulations with the Oregonator model. Circles correspond to $\epsilon_1 = 0.01$, and squares correspond to $\epsilon_1 = 0.05$.

Figure 4 shows the distance between the boundary and wave annihilation changes as a function of the intensity of the illumination. For small values of ϕ, i.e., low intensities of illumination, the curve asymptotically goes to infinity, which corresponds to the case of a "normal" wave propagation into an under-critically inhibited area. This bifurcation point separates waves with constant amplitudes and damped waves. The figure also illustrates that an increase in the excitability of the system results in a shift of the location of wave collapse toward the inhibited region of the medium.

Discussion

We have studied wave propagation through boundaries separating excitable and inhibited regions of an active medium. Because of molecular diffusion, a boundary layer is formed where the concentrations of the species are different from those far from the boundary. The actual position and size of the boundary layer depends on the production of the inhibitor and the diffusion of the ions. A simple mechanism illustrated in Figure 5 may explain the observed behavior. The left side of the medium is not illuminated and the bromide concentration far from the boundary can be determined from the basic mechanism of the BZ reaction.[19] Since the right side of the medium is continuously illuminated, the bromide concentration increases due to the photochemical reactions of the catalyst.[9,10] Waves can only propagate when the concentration of bromide is lower than a critical level. At low intensity of illumination, the critical bromide concentration is reached deep inside the illuminated area. An increase in the light intensity raises the bromide concentration, and hence the location of wave collapse shifts toward the boundary due to the free diffusion of bromide ions. For sufficiently intense light, the annihilation may occur at the boundary or even in the nonilluminated area. In principle, intrusion of waves into the illuminated area can be infinite, corresponding to the case of normal, nondamped propagation, as depicted in the computed curve in Figure 4. We could not observe such distinct behavior experimentally because the small neighborhood of the boundary was monitored to determine the exact location of wave collapse. Nonetheless, the measured curve exhibits the asymmetric characteristics with a distinct shift toward the illuminated region (Figure 3).

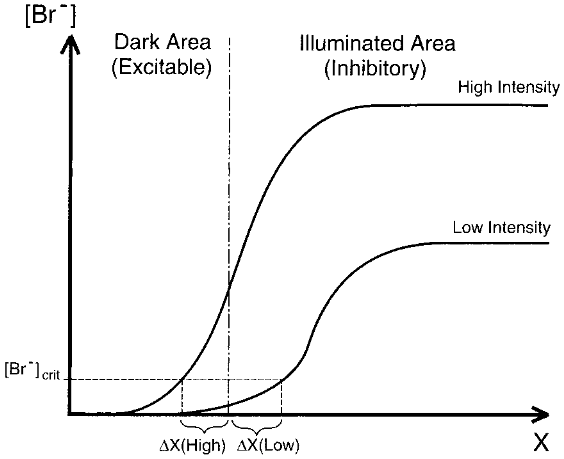

Figure 5. Schematic representation of the position of wave collapse at various rates of bromide production. The solid lines show the concentration profiles of the inhibitor, and the dashed−dotted line corresponds to the boundary. Depending on the intensity of the illuminated light, the annihilation point at the critical bromide concentration shifts markedly from one side of the boundary to the other.

The boundary layer may significantly change the effective size of the elements of the excitable medium. The knowledge regarding the actual size of the elements is very important when the active medium has a finite size,[20] particularly for estimating the minimal size of the elements in the BZ medium.

At first glance, the boundary between excitable and inhibited areas may seem to be similar to the sink-type boundary between active and passive parts of the medium. However, there are essential differences: for the sink-type boundary, the boundary layer is always excluded from the propagation area, resulting in some decrease in the excitable element. The layer adjacent to the boundary between inhibited and noninhibited regions of active media can either decrease or increase the effective size of the excitable element compared to its original geometry. In addition, the externally controlled inhibition allows the shift of the boundary layer in either direction which, we assume, will enable us to realign the switching of logic gates in excitable medium[21−23] without changing the actual geometry of the gates. As living organisms seem to perform different computations under the same neural network connections, a future study to examine the switching of the mode in logic computation on excitable field by changing the excitability may be of value.

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