

Critical conditions of chemical wave propagation in gel layers with an immobilized catalyst

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Autowaves spreading in a thin layer of the Belousov–Zhabotinsky reaction with ferroin catalyst immobilized in silica gel have been studied. It is found that there is a critical thickness of this layer such that autowaves could not propagate in thinner layers. The results of computer simulations in the two-variable Rovinsky model qualitatively fit the experimental data for the temperature range used.

1. Introduction

Recently some papers concerning autowaves in the immobilized catalyst Belousov–Zhabotinsky (BZ) reaction have appeared [1–4]. This system, in contrast to the liquid BZ reaction, is essentially heterogeneous: it consists of two layers – a solid gel layer containing an immobilized catalyst and a liquid one consisting of a mixture of the other reaction components, which can diffuse (because of small molecular diameters) in a gel. In such a system processes that occur on the boundary between the gel and the liquid layer must crucially affect the wave propagation.

Using the BZ reaction with a catalyst immobilized in silica gel [1, 4] of a wedge shape (fig. 1), we have observed that the propagation of waves was blocked in the thin part of the wedge, where the thickness of the gel was below the critical value (about 100 μm). In this case the loss of the autocatalytic reaction component HBrO_2 at the

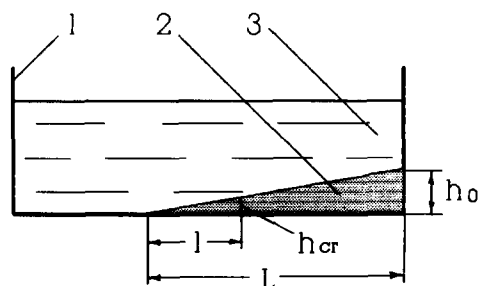


Fig. 1. Scheme of the experimental cell. A wedge-shaped layer with immobilized ferroin (2) was prepared in a petri dish (1). All ingredients of the BZ reaction had been added before the experiment began and formed a liquid layer (3).

gel layer boundary due to diffusion exceeded its reproduction in the BZ reaction.

Computer runs using the two-variable Rovinsky model [5–7] to test wave propagation in a gel layer of a fixed thickness, have given results close to the data observed in the BZ experiments.

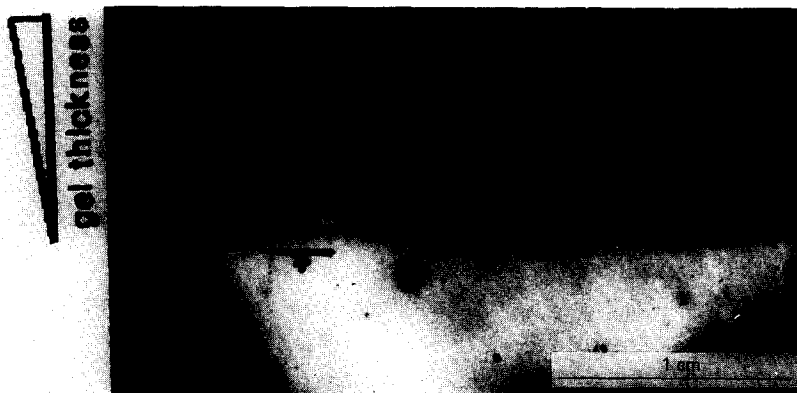


Fig. 2. Waves spreading in a thin layer of the BZ reaction. Autowaves spread in the wedge of the BZ reaction (schematically represented on the left part) but could not reach the corner of the wedge because of the small layer thickness at this place. Arrows mark the stripe near the corner into which waves propagation is impossible.

2. Experimental results

Experiments were performed in a petri dish, in which, according to the method described in ref. [1], a silica gel layer with immobilized ferrioin (concentration about 5 mM) was prepared (fig. 1). Before the experiments, all the essential BZ reaction ingredients were added in the following concentrations: sodium bromate 0.08 M, malonic acid 0.4 M, sulfuric acid 0.07 M. The thickness of the liquid layer thus formed was 8–10 mm, which prevented air oxygen from interfering with the development of the reaction. During the experiment the temperature of the layer was tuned and fixed by a thermostat with a precision better than 0.5°C.

A typical picture observed during waves propagation in the wedge shaped layer is presented in fig. 2. It is seen that waves propagate in the thicker wedge part (fig. 2, top), but are depressed in the region with a small thickness (narrow stripe in the center of fig. 2, marked by arrows). The maximum gel layer thickness, at which the propagation of waves was still possible, was taken to be a critical thickness, h_{cr} . This critical thickness was measured by the following procedure: after the gel was prepared, both the gel thickness near the wall h_0 (outside the capillary tension meniscus) and the wedge length L (see fig. 1) were mea-

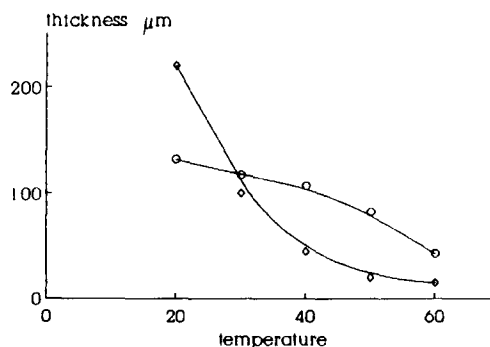


Fig. 3. Dependence of the ferrioin layer critical thickness on temperature. Circles denote experiments with the BZ reaction and diamonds computer runs.

sured with the aid of a scaled microscope. Then during the experiment h_{cr} was calculated as $h_{cr} = h_0 l / L$, where l is the width of the region in which waves could not penetrate while propagating (fig. 1):

The temperature dependence of the critical thickness h_{cr} is shown in fig. 3 (circles). One can see that as the temperature increases from 20 to 60°C, h_{cr} drops from 130 to 45 μm. In this figure there is also shown a curve (marked with diamonds) which describes wave propagation in the Rovinsky model of the BZ reaction [5–7]. Note that h_{cr} drops as the temperature increases in both the computer and natural experiments. Some quantitative discrepancies may be explained by

convective flows in the liquid layer depleting HBrO_2 . This process was not accounted for in the computer simulation because of its complexity.

3. Computer simulations

All the simulations have been performed with the two-variable Rovinsky model [5] (see appendix) in a two-dimensional medium (fig. 4) on a rectangular mesh (space step $\Delta x = 5$ to $50 \mu\text{m}$ and time step $\Delta t = 0.005$ to 0.02 s) using one explicit Euler method of integration.

The whole medium, which modeled a cross-section of the BZ system with the immobilized catalyst, was divided into two regions (separated by the dashed line in fig. 4), corresponded to the solid silica gel layer with immobilized catalyst (lower compartment) and the liquid layer of the other BZ ingredients (fig. 4, top) so that HBrO_2 could freely diffuse between these compartments.

In the lower compartment of thickness h_1 , the BZ reaction occurred according to the equations for ferroin and HBrO_2 evolution (see appendix and fig. 4). In the upper compartment of thickness h_2 , only the diffusion of HBrO_2 was

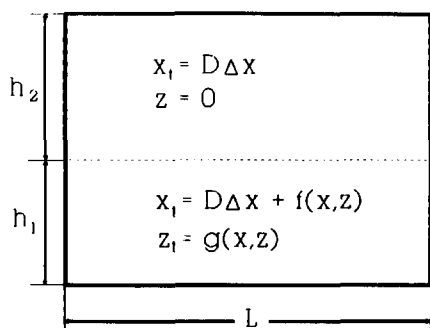


Fig. 4. A scheme of computer experiments of wave spreading in a thin layer of the BZ reaction. x and z denote the activator HBrO_2 and the inhibitor $\text{Fe}(\text{phen})_3^{3+}$ in the two-variable Rovinsky model, $f(x, z)$ and $g(x, z)$ are nonlinear terms of this model; D is the diffusivity of HBrO_2 , Δ is a two-dimensional Laplacian; h_1 and h_2 are the thicknesses of the immobilized ferroin layer and the liquid layer without ferroin ($z = 0$), respectively, L is the length of the computed region.

assumed to occur^{#1}. As a result, this species disappeared on the upper boundary (at this boundary the condition $[\text{HBrO}_2] = 0$ was set). At the other boundaries Neumann's (no flux) conditions were imposed.

A wave was initiated near one of the side walls by a short time 50-fold increase in the HBrO_2 concentration over the steady state value. Near the opposite wall the condition for the passage of a wave (a 10-fold increase in the HBrO_2 concentration over the steady state value) was checked during the experiment. So having a number of the experiments at different values of h_1 and fixing the fact of either passing or damping a wave, we could determine the critical thickness h_{cr} of the gel.

Fig. 5 depicts the wave propagation in the system where the value of the gel thickness h_1 was slightly greater than the critical one. In fig. 6 a damped pulse at $h_1 \approx h_{cr}$ is shown. Note that in fig. 6c the HBrO_2 pulse has dissipated because of diffusion, while the slower tail of ferroin (fig. 6c, lower) has not yet. Blocking of wave propagation at $h_1 < h_{cr}$ is shown in fig. 7. In this case the loss of HBrO_2 from the silica gel layer due to diffusion exceeds its reproduction in the BZ reaction.

4. Discussion

Autowave propagation has recently been studied in open flow membrane reactors [9, 10]. Along with all the advantages of such reactors, there is an evident shortcoming in comparison with homogeneous closed reactors: in open membrane reactors it is hardly possible to study processes having a characteristic time t less than the diffusion feed time required for the membrane of thickness d :

$$t \approx d^2/D.$$

Here D is the diffusion coefficient (in liquid,

^{#1}Allowance of the BZ reaction terms which involve HBrO_2 in the absence of ferroin gives rise to a negligible (less than 10%) growth of the critical thickness.

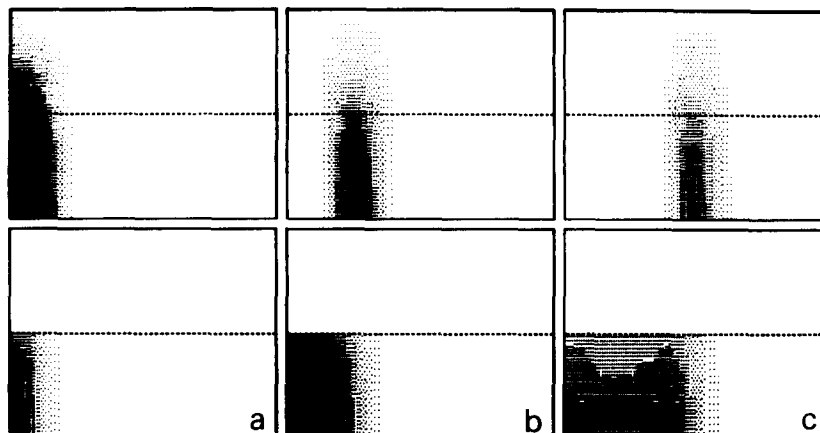


Fig. 5. Wave spreading in a thin layer ($100\ \mu\text{m}$ thickness) of the BZ reaction: computer simulation. The upper row depicts the HBrO_2 distribution and the lower row the $\text{Fe}(\text{phen})_3^{3+}$ distribution at successive time moments: (a) 30, (b) 90, (c) 180 s. $T = 30^\circ\text{C}$. Dark regions of the pulses correspond to higher concentration of the appropriate species.

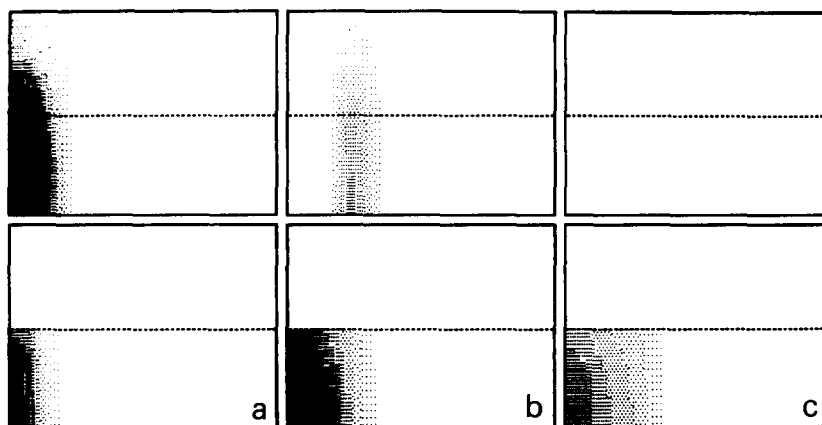


Fig. 6. Nonstationary pulse propagation in a thin layer ($95\ \mu\text{m}$ thickness) of the BZ reaction. All parameters are the same as in fig. 5. Note that at time 180 s (c) the fast variable HBrO_2 had already disappeared while the slower variable $\text{Fe}(\text{phen})_3^{3+}$ did not yet.

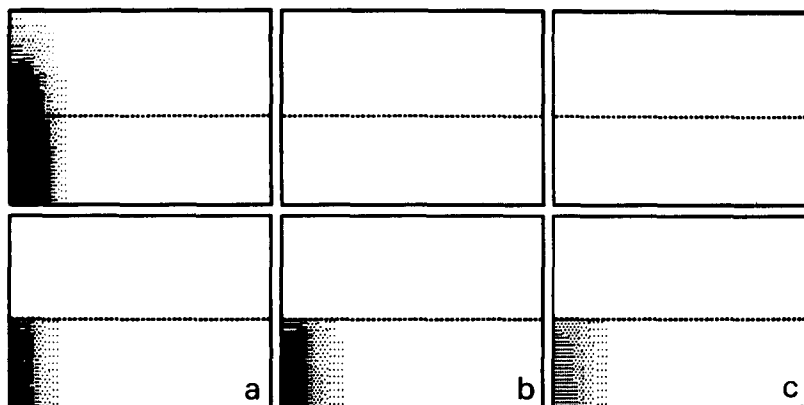


Fig. 7. Inhibition of conduction in a thin layer ($85\ \mu\text{m}$ thickness) of the BZ reaction. All parameters are the same as in fig. 5. Note that at time 90 and 180 s (b, c) there exist $\text{Fe}(\text{phen})_3^{3+}$ tails but no spreading of HBrO_2 is seen.

$D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), so for a membrane with $d = 0.1 \text{ cm}$, t is 16 min. For faster processes the system may not be regarded as a two-dimensional homogeneous one. These calculations are correct for the gel with an immobilized catalyst as well.

The present paper shows that the membrane thickness should not be too small (less than about 0.1 mm), because in this case the diffusion processes on the boundary between the membrane and the feeding liquid would significantly affect the reaction development inside the membrane (the same is of course, correct for gel reactors with the immobilized catalyst).

It should be noted that there are a few reasons for the divergence of computer simulations from experiments (fig. 3). First, we have used a two-variable model with roughly evaluated rate constants to simulate the complex BZ reaction. But we believe the second point to be of great importance: only the diffusion loss of reagent has been studied, whereas in real system there was also convection, which greatly amplified this loss on the boundary. Unfortunately, the precise calculation of this process is very difficult.

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Appendix. The model of the BZ reaction

We have used the two-variable Rovinsky model of the BZ reaction [5]:

$$\begin{aligned} x_\tau &= \frac{1}{\varepsilon} \left[x(1-x) - \left(2q\alpha \frac{z}{1-z} + \beta \right) \frac{x-\mu}{x+\mu} \right] \\ &\quad + D_x \Delta_p x, \\ z_\tau &= x - \alpha \frac{z}{1-z}, \end{aligned} \quad (1)$$

where

$$[\text{Fe}(\text{phen})_3^{2+}] \equiv Z = Cz,$$

$$[\text{HBrO}_2] \equiv X = \frac{k_1 A}{2k_4} x,$$

$$\varepsilon = \frac{k_1 A}{k_4 C},$$

$$\alpha = \frac{k_4 k_8 B}{(k_1 A h_0)^2},$$

$$\mu = \frac{2k_4 k_7}{k_1 k_5},$$

$$t = \frac{k_4 C}{(k_1 A)^2 h_0} \tau,$$

$$\beta = 2k_{13} B \frac{k_4 C}{(k_1 A)^2 h_0},$$

$$C = [\text{Fe}(\text{phen})_3^{2+}] + [\text{Fe}(\text{phen})_3^{3+}],$$

$$A = [\text{NaBrO}_3],$$

$$B = [\text{CH}_2(\text{COOH})_2],$$

$$\rho_i = r_i \left(\frac{k_1 A^2 h_0}{k_4 C} \right)^{1/2},$$

h_0 is the acidity function, q a stoichiometric factor, r_i and ρ_i are the usual and scaled spatial coordinates respectively; Δ_ρ is the Laplacian with respect to coordinates ρ ; $D_x = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The rate constants k_i were originally estimated for 40°C [5]. To make it possible to apply this model for different temperature we supposed that the rate constants depend on the temperature according to the Arrhenius law with the same activation energy [6, 7]. This relatively rough assumption resulted in a reasonable agreement between experimental and computed wave characteristics [6, 7]. Thus, the rate constants of the

model (1) rescaled to 20°C are

$$\begin{aligned}
 k_1 &= 10 \text{ M}^{-2} \text{ c}^{-1}, \\
 k_4 &= 1.7 \times 10^3 \text{ M}^{-1} \text{ c}^{-1}, \\
 k_5 &= 10^6 \text{ M}^{-2} \text{ c}^{-1}, \\
 k_7 &= 1.5 \text{ M}^{-2} \text{ c}^{-1}, \\
 k_8 &= 2 \times 10^{-6} \text{ M c}^{-1}, \\
 k_{13} &= 10^{-7} \text{ c}^{-1}, \\
 q &= 0.5.
 \end{aligned} \tag{2}$$

It should be noted that these values are close to the “Lo” set by Tyson [8] (accounting, of course, the difference in the numeration of the elementary BZ reaction stages in refs. [8] and [5]).

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