Chemical Diode

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A chemical active medium on the base of Belousov−Zhabotinsky (BZ) medium was used to design a "chemical diode". This system, similar to a semiconductor diode, shows unidirectional propagation of chemical pulses and may be possible to be used to construct a massively parallel computational medium. The system of two mesoporous glass plates with ferroin loaded at the surface was covered by BZ solution and maintained propagating excitation waves. The unidirectional propagation was observed when the plates were placed so that the corner of the one plate was close to the plane side of the other plate. The study shows that the important feature of the system is the geometrical arrangement of the plates and the gap distance between them. Computer simulations confirm the experimental results.

Introduction

Propagating chemical waves in the Belousov−Zhabotinsky (BZ) reaction attracted the attention of researchers as a convenient model for study of self-organization processes in excitable media.[1−3] Recent development of experimental techniques such as using different gels, immobilization of catalyst at chosen sites of the medium, etc., made possible not only to study but also to design "chemical-excitable" systems[4−10] with sophisticated geometry and features. On the other hand, chemical waves were found surprisingly suitable for some computational problems, especially for the algorithms applied for highly parallel computing systems.[11−15] In the present work we show that the chemical-excitable medium can also be made to function like a diode, the excitation waves can propagate through the system only in one direction and not in the opposite. This kind of unidirectional propagation of excitation is also well-known for a variety of biological systems, the most important example of which is synaptic transmission.

The conductivity of the diode is "unidirectional", the resistance in one direction is several orders of the magnitude higher than in the opposite one. In a nonstirred uniform homogeneous BZ medium, chemical waves propagate because of the diffusion coupling of the elementary volumes. In a normal aqueous solution, diffusive transfer of the species is an isotropic process, and it is impossible to induce "unidirectional propagation" by modifying the chemistry of the system. In a recent study it was found that not only chemical kinetics but also the geometrical shape and boundary conditions are very important for the development of wave patterns.[10,16,17] It is known that excitation waves can propagate distinctly anisotropically in a media with a special geometry, such as branching, narrow-wide paths junctions, involving curvature and front size dependent front propagation.[26,27] We observed the desired pattern by using an asymmetrical arrangement of two mesoporous glasses with bound catalyst.

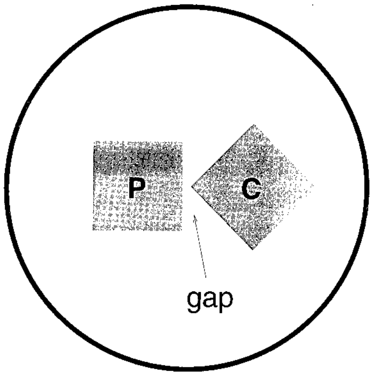

Figure 1. Scheme of the experiment. Two Vycor Corning glass plates (P−C arrangement) placed at the bottom of a 6-cm diameter Petri dish with the gap between them of 60 μm and covered by 17.5 mL of BZ solution: $NaBrO_3$ 0.17 M, H_2SO_4 0.11 M, $CH_2(COOH)_2$ 0.11 M, NaBr 0.03 M, all the concentrations are given before bromination, the temperature was kept at 25 °C. Vycor glasses were soaked for at least 1 h before the experiments started. The wave patterns were monitored with a SONY XC-77 CCD camera and recorded with a Mitsubishi HV-S11 VCR.

Results

We used mesoporous glasses with the ferroin (catalyst of the BZ reaction) bound at the their surface[9] and arranged them as shown in Figure 1. The glass plates of approximate size 10 mm × 10 mm × 1 mm were put closely together with a small gap between, so that one plate was oriented to the contact area by plane border (P side of the system), and the other glass plate was oriented by the corner (C side of the system). The glass plates were covered by the BZ solution ($NaBrO_3$ 0.17 M, H_2SO_4, 0.11 M, $CH_2(COOH)_2$ 0.11 M, NaBr 0.03 M; all the concentrations are given before bromination) for exception the catalyst, ferroin, which was available only in a thin layer (approximately 0.1 mm) at the surface of the glass plate. Thus, the wave propagation was possible only at the surface of the plate. The propagation of the wave from one plate to another was also possible, provided that the gap between plates did not exceed a critical value. Diffusive penetration of the wave through the nonreactive gaps was found in various gel and membrane systems,[17,18] where estimation of the critical value

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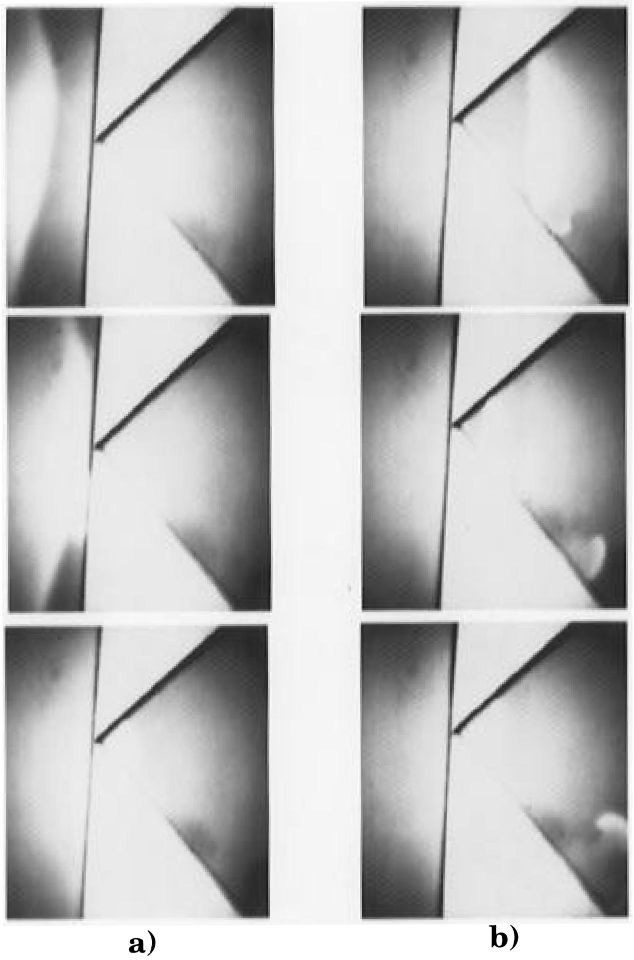

Figure 2. Unidirectional wave propagation in the P−C glass system: (a) the photos of wave propagation from P side (left plate), the wave approaches the gap between the glass plates and induces the wave at the C side (right plate), "jump" over the gap, time interval between frames is 60 s; (b) the wave approaches the gap from the C side (right plate) and disappears; no propagation at the P side (left plate); time interval between frames is 90 s.

of the gap, depending on chemical concentrations, was about 0.1−0.2 mm. In our experiments we observed the diffusive coupling of the surfaces of two glass plates if the distance between them did not exceed 60 μm. To eliminate effects of the wave propagation at the sides of the plate, also soaked with ferroin solution, the glass plate was carefully polished after the loading the ferroin, so that the ferroin containing part of the side of the glass plate was removed. Asymmetric P−C arrangement of glass plates made possible the unidirectional wave propagation, as shown in Figure 2, waves could penetrate through the gap from the P side of the system and could not from the C side.

Similar results on the wave propagation through a P−C system but in more detail were obtained by a computer simulation of the system. Numeric simulations were performed in a two-variable model of the ferroin-catalyzed BZ reaction developed by Rovinsky and Zhabotinsky[19] with rate constants estimated in ref 20. The model has been verified experimentally to adequately simulate spatio−temporal phenomena in the BZ reaction.[20−23] The computations were carried out in a two-dimensional array of 101 × 101 elements using the Euler explicit method of integration. The space and time steps, $hx = 0.1$ mm and $ht = 0.1$ s were chosen so that the system was calculated stably. A further decrease in hx and ht did not improve the accuracy of calculations markedly. For the simulations an essentially heterogeneous medium has been used: while simulating the mesoporous glass plates with loaded ferroin, it was accounted that the diffusion coefficient of bromous acid inside is reduced by a factor of 16 (see ref 9); while simulating the interplate space, the ordinary conditions for the liquid-phase BZ reaction were imposed.[20−23] Figure 3 shows the propagation of the waves from different sides of the system. The wave approaching from the P side successfully

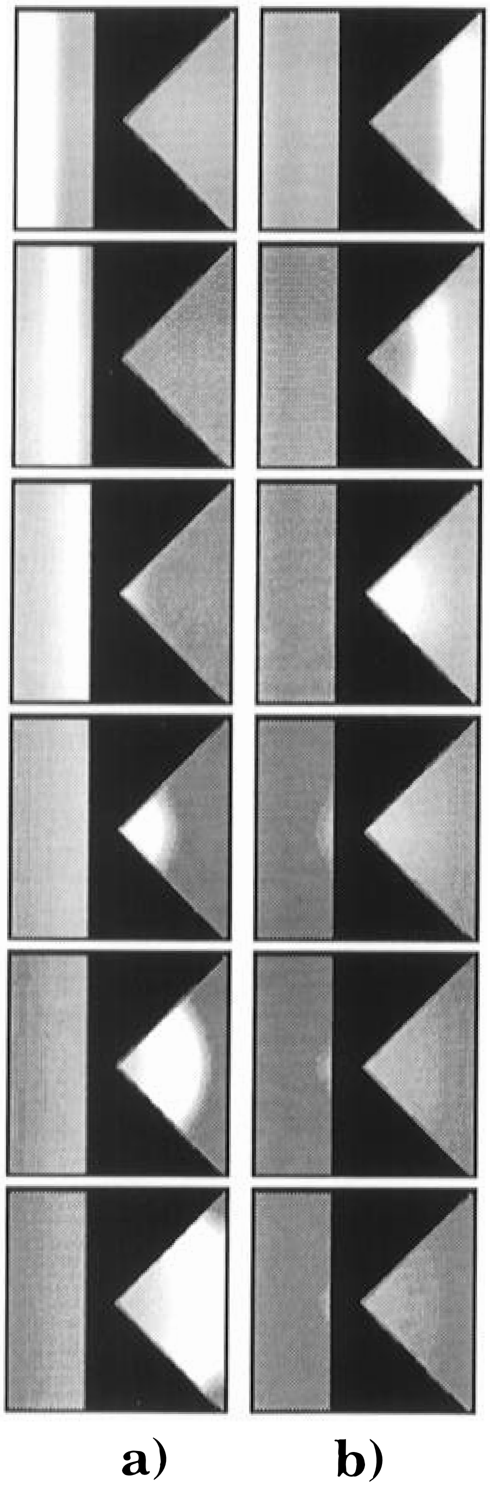

Figure 3. Unidirectional wave propagation in computer simulations. (a) Wave, propagation from the P side: successful "jump" over the gap. (b) Wave, propagating from the C side approaches the gap, frame 3, induces a tiny spot of excitation at the P side, frame 4 (which is not sufficient for the wave to start), and disappears. The pictures for both series (a) and (b) are taken at following consecutive moments of time starting from the beginning of computation: 31, 52.7, 74.4, 96.1, 117.8, 139.5 s.

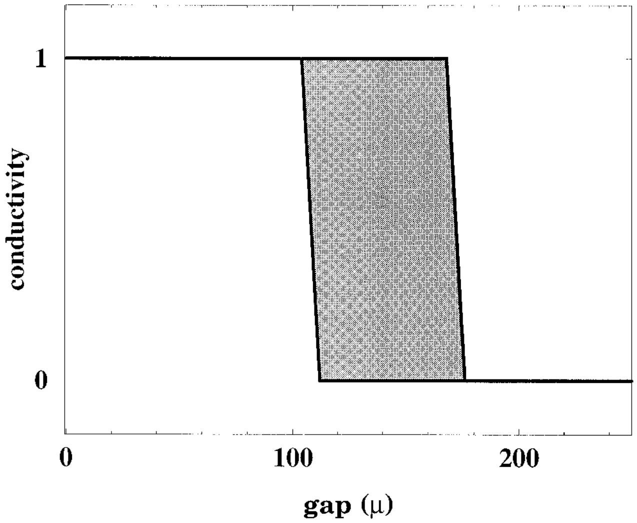

Figure 4. Diagram of the wave propagation versus size of the gap. Conductivity has values of 1 when wave can propagate from one glass plate to another or 0 when no propagation is observed. The painted area corresponds to the region of gap size where unidirectional propagation is observed.

"jumps" over the inactive gap, while the wave propagating from side C fails to overcome the gap.

Discussion

Asymmetric wave propagation results from the asymmetric geometry of the medium. A simple explanation involves the dependence of the wave propagation on the geometry and size of the wave front. It is known that there is the critical size of the propagating wave; wave fronts with the size less than the critical one cannot propagate.[24,25] It is easy to see that the wave propagating from the P side does not change its geometry or size in a course of the propagation, until it reaches the border of the P plate.

A different situation occurs for the wave propagating from the C side. Approaching the corner of the C glass plate, the wave front gradually shrinks, become close to the critical size when it reaches the distance, appropriate to induce the wave at the P plate.

The position of glass plates, however, is a necessary condition but not a sufficient one. The presence of the gap between the plates is also important; without a gap we had normal wave propagation from either the P side of the C side. By increasing the gap size, we could have unidirectional propagation. As shown in a diagram of the propagation versus gap size, obtained from computer simulations (Figure 4) the full contact between plates makes possible wave propagation in both directions. By increasing the gap width, we can obtain the desired unidirectional propagation, and a further increase resulted in the complete blockage for the chemical waves. We also can guess that the necessary gap width depends on the excitability of the medium, for a less excitable medium it should be apparently smaller. This consideration makes possible the next step: to control the propagation by external signal, decreasing or increasing the excitability of the system. For this purpose, for instance, it is possible to use light illumination, which controls the excitability of ruthenium version of BZ reaction.[4,11] And we hope to complete these experiments in a near future.

As far as we know, this is the first report of the experimental observation of unidirectional propagation of chemical waves. The important fact is that our P−C system can also be applied to a variety of excitable media, because the general effect is provided by geometry and boundary conditions and does not involve the particular chemistry of BZ waves.

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