Pattern Selection in the Belousov−Zhabotinsky Reaction with the Addition of an Activating Reactant

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Using the ferroin-catalyzed Belosov−Zhabotinsky (BZ) reaction with the addition of an activating reactant in a reaction−diffusion system, we experimentally studied the competition between target waves and spiral waves when the system was in an oscillatory state. We found that when the period of background oscillation is smaller than that of spiral waves, target waves automatically appear in the reaction medium despite of the presence of spiral waves. The target waves compete with spiral waves and eventually win over the spirals, driving them out of the reaction medium. We also carried out numerical simulations using a modified Oregonator model. Our simulation results qualitatively agree with the experimental observations.

Introduction

Spatiotemporal pattern formation has been extensively investigated both experimentally and theoretically in systems driven far from thermodynamic equilibrium. The two patterns mostly observed in reaction−diffusion systems are spiral waves and target waves. Rotating spiral waves are self-organized by a topological defect. Because of its wide existence and scientific importance, this pattern has been studied extensively in the context of various fields such as physical chemistry,[1] biology,[2] and cardiology.[3] Fruitful achievements yielded in recent years give us a deep understanding of spiral dynamics[4,5] as well as spiral instabilities[6−9] and spiral control.[10,11] Target waves are generated by a wave source, which sends concentric waves that radiate outward from the source center. In a reaction−diffusion system, the existence of target waves is often attributed to the presence of local inhomogeneities and perturbations, such as a grain of dust or other impurities.[12,13] Many systems support both spiral waves and target waves. A typical example is the Belosov−Zhabotinsky (BZ) reaction in a spatially extended system.[12−14] Dynamic process of entrainment between different types of waves and the resulting wave pattern selection are of great interests. There are many documents about the competition between spatial patterns, such as spiral−spiral,[15−18] and spiral−target.[19,20] In these systems, the final asymptotic states are in some cases dominated by spiral waves and in other cases by target waves. It is our interest to understand in general the underlying mechanism behind the wave pattern selection.

Compared with the study of spiral waves, however, the asymptotic state of target patterns has not been systematically investigated in experiments. There is a simple reason behind this situation: In BZ reaction systems or other chemical systems that have been experimentally studied, spiral waves always dominate when both types of waves are present. This happens because the frequencies of spiral waves are higher than those of target waves. As a result, target waves are suppressed by spirals. In this report, we study the competition between target and spiral patterns by adjusting the frequency of the oscillatory system. Our reasoning is the following: A spiral pattern can exist only when its oscillation frequency is higher than the frequency of background oscillation. When this situation is reversed, the spiral patterns may become unstable, leaving room for target patterns. Another scenario is also possible; it has been reported in refs 21 and 22 that when the frequency of the bulk oscillation of the system is higher than the asymptotic frequency of the spiral waves antispiral waves (spirals propagating inwardly instead of outwardly) will occur. Here, we conduct an experiment to test these two predictions.

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Experimental Setup

Our experiments were carried out in a quasi 2D spatial open reactor[23] using the ferroin catalyzed BZ reaction, except that we added methanol to the reaction system. It has been reported that methanol can strengthen the oscillations of a BZ system and increase the oscillation frequency.[24,25] The reaction medium is a thin, porous glass disk, 0.4 mm in thickness and 19.6 mm in diameter. The porous glass prevents convection in the reaction medium so that its reaction−diffusion feature is guaranteed. The opposite two sides of the porous glass disk are, respectively, in contact with two reactant compartments where the reactant concentrations are continuously refreshed and kept homogeneous. We arranged the chemicals in a way that one side (I) of the reaction medium is in the oxidized state and the other (II) is in the reduced state of the reaction system. The reactants from both sides diffuse into the glass and meet in the middle of the reaction medium, where reactions take place and sustained patterns occur. We chose the concentration of sulfuric acid in the oxidized side as the control parameter because our experiments showed that it can significantly influence the effect of methanol on spiral frequency. The concentrations of other reactants were kept fixed; $[NaBrO_3]^I = 0.8$ M, $[KBr]^I = 60$ mM, $[ferroin]^I = 1.0$ mM, $[CH_2(COOH)_2]^{II} = 0.8$ M, and $[CH_3OH]^{II} = 0.24$ M. The reaction temperature was 25 ± 0.5 °C. The initial condition was chosen so that there was only one spiral tip residing in the center of the reaction medium. Once a spiral was its asymptotic state, we studied it by changing the control parameter step by step while fixing all other conditions. Under each control parameter, we waited for at least 1 h so that the system could relax to its asymptotic state.

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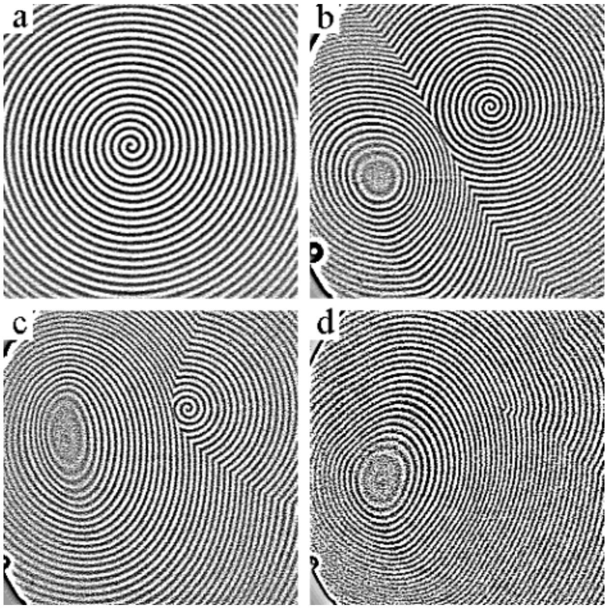

Figure 1. Observations of the change of the state of the system from a simple spiral (a) to emergence of target waves (b), then the shrinking of the spiral waves (c) and (d) as the concentration of sulfuric acid is increased. $[H_2SO_4]$: (a) 0.45, (b) 0.6, (c) and (d) 0.65 M.

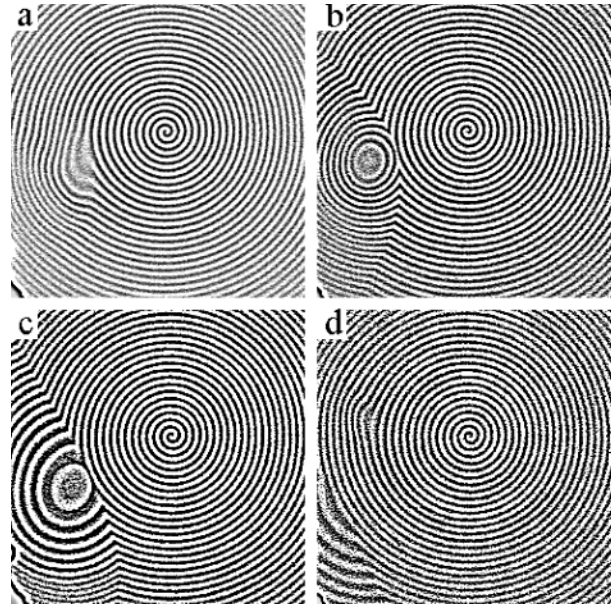

Figure 2. Images illustrating the automatic appearing and disappearing cycle of a target pattern when the control parameter is approaching the critical value ($[H_2SO_4] = 0.55$ M). The whole process lasts about 5 min. (a) $t = 0$ s, the onset of bubble up of the target waves; (b) $t = 110$ s, the target waves enlarge; (c) $t = 228$ s, the target waves shrink back; (d) $t = 290$ s, the target waves are suppressed by spiral waves.

Experimental Results

We first repeated our earlier experiments without methanol and recovered all of the observed phenomena. With the control parameter increased, the state of the system changed from meandering spirals (the trajectory of the spiral tip is a hypocycloid or an epicycloid) to simple spirals (the trajectory of the spiral tip is a small circle), and then to modulated waves (a convective velocity settles in). Finally, the system went through the long-wavelength instability to defect-mediated turbulence. This scenario has been reported in our earlier experiments.[6,8] However, when we set $[CH_3OH]^{II} = 0.24$ M, the system behaved differently. With the change of the control parameter, the system always remained in the state of simple spirals; neither meandering spirals nor modulated waves were found in the experiments. The simple spiral waves would never become unstable. Instead, they were driven out of the reaction medium by target waves when the control parameter passed a threshold value.

In the following, we focus our attention on the case where $[CH_3OH]^{II} = 0.24$ M. At low sulfuric acid concentrations, we observed a simple rotating spiral, where spiral waves travel out as the tip rotates around a small circle. Figure 1a gives an example where $[H_2SO_4]^{I}$ is 0.45 M. The high and low gray level in the picture represent, respectively, the oxidized and reduced states of the reaction. With the increase in the control parameter, the spiral stays simple, but the period and the wavelength of the spiral waves decrease. Under these conditions, although there must be perturbation existing in the reaction medium, the perturbation is not strong enough to lead to the emergence of the target waves because the bulk oscillations of the system are suppressed by spiral waves. The bulk oscillations of the system become more and more pronounced as the control parameter was increased. When $[H_2SO_4]^{I}$ reaches a critical value (about 0.6 M), target waves emerge automatically in the reaction medium. The center of the target pattern is away from the tip of the spiral waves, as shown in Figure 1b. The target pattern grows as time goes on and invades into the region of the spiral waves. These two types of patterns compete against each other; at the asymptotic state, they coexist in the reaction medium. If the control parameter is further increased so that the bulk oscillations are further enhanced, then the target pattern wins the competition. In this case, the target waves continuously invade the territory of spiral waves, as shown in Figure 1c. Soon, the whole reaction medium was occupied by target waves, as shown in Figure 1d.

The target source in Figure 1 differs from those observed in typical, excitable BZ systems, which can be considered to a point source. In our experiments, the observed target sources occupy a relatively large area and have elliptical or, more precisely, irregular shapes. There is a simple explanation behind this difference: In a gel or a Petri dish, impurities exist that induce the target patterns. Because the impurity is very small, it seems to be a point. In our system, the reaction medium is porous glass without impurities. In this case, the target pattern is generated by a small difference in dynamical behavior between different areas of the porous glass, for example, the thickness of the porous glass cannot be exactly the same. Because the system is in an oscillatory state, these small differences can generate target sources so that the source of the target pattern in our experiment is not a point but a large region. Later, in the simulation part of our paper, for simplicity, we introduce the target source in a small region, it does not affect the results.

Before the transition point ($[H_2SO_4]^{I} = 0.6$ M), target patterns are not favorable in the system. The pictures in Figure 2 were taken when the control parameter was 0.55 M, a little lower than the critical value. Under this condition, the bulk oscillations of the system were strong, but not strong enough to support target waves in the competition with spiral waves. We observed that once there was a large perturbation in the reaction medium, the target waves emerged (Figure 2a) and grew quickly (Figure 2b), but this was just a transient behavior. The spiral pattern rapidly recovered itself. The target waves died down (Figure 2c) and, at last, were suppressed by the spiral waves (Figure 2d). The system returned to the state of a single spiral. The course of target waves appearing and disappearing repeats randomly under this condition.

We measured the period of the spiral waves and that of the target waves independently, trying to get more information that might imply the mechanism of the above-described phenomenon. The measurements were conducted in our spatial open reactor with only a spiral or a target pattern present. The results are presented in Figure 3. We observde that the periods of both the spiral waves and the target waves decreased with the increase in the control parameter; however, the period of the target waves decreased faster than that of the spiral waves. Before the critical point, the period of target waves was larger. In this case, introducing a spiral in the medium of the target pattern destroyed the target waves, leaving a stable spiral in the medium. At the critical point where spiral waves and target waves coexist, the two periods were equal; beyond the critical point, the period of the target waves became smaller. In the last case, the spiral pattern disappeared, giving way to a target pattern. From these observations, we conclude that the result of competition between the two patterns is solely determined by their frequencies. When the two pattern coexist in the initial state, the pattern with higher frequency wins.

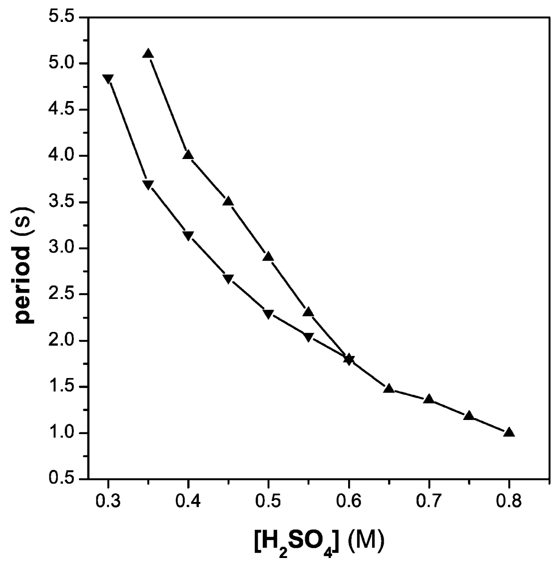

Figure 3. Measured periods of the target waves and the spiral waves vs the sulfuric acid concentration. (▲): Periods of the target waves. (▼): Periods of the spiral waves.

Simulation

To understand more clearly the dynamics underlying the phenomena presented above, we conducted computer simulations with partial differential equations. Previous studies showed that methanol acts as an activating agent. It reacts with sodium bromate and sulfuric acid, producing bromous acid, which is the activator of BZ reaction system. In the simulations, we use an Oregonator model[26] modified to contain the reaction of methanol with sodium bromate and sulfuric acid. It has been reported that the Oregonator model is not so accurate in the quantitative aspect, but it reflects main features of the excitable and oscillatory BZ systems.[27] The reaction−diffusion equations are presented as follows[25]

$$\frac{dU}{dt} = k_3AHU - 2k_4U^2 + 2k_mAHM - hk_5BV\frac{U - \frac{k_1AH}{k_2}}{U + \frac{k_1AH}{k_2}} + D_U\nabla^2U \quad (1)$$

$$\frac{dV}{dt} = 2k_3AHU - k_5BV + D_V\nabla^2V \quad (2)$$

where A, B, M, H, U, and V are, respectively, [$NaBrO_3$], [$CH_2(COOH)_2$], [CH_3OH], [H^+], [$HBrO_2$], and [oxidized catalyst]; k_i are rate constants of the chemical reactions; h is a suitable stoichiometric coefficient; and D_U and D_V are diffusion coefficients of U and V. The term $2k_mAHM$ represents the mechanism of the methanol−bromate−acid reaction, which produces bromous acid. This is an extra term added to the original Oregonator model. After rescaling, we obtain the following dimensionless form

$$\frac{du}{dt} = \frac{1}{\epsilon}\left(u - u^2 - fv\frac{u - q}{u + q}\right) + c + D_u\nabla^2u \quad (3)$$

$$\frac{dv}{dt} = u - v + D_v\nabla^2v \quad (4)$$

In eq 3, c comes from the additional term representing the methanol reaction with sodium bromate and sulfuric acid. The variables u and v represent the concentrations of the regents; ϵ and q are parameters, which are kept fixed in the program. As we can see from the original reaction−diffusion eq 1, there are two terms associated with sulfuric acid, k_3AHU and $2k_mAHM$. From experimental observations and theoretical analysis, we consider that the part of hydrogen ions that react with methanol plays a most important role in our research, so we chose c as the control parameter in our simulation work.

Equations 3 and 4 are integrated with the explicit Euler method on a large rectangular with grids of 400 × 400, imposing no-flux boundary conditions. The time and spatial steps are, respectively, 0.002 and 0.5. To obtain target waves, we chose a small area (3 × 3 grids) away from the spiral tip and kept the values of u and v constant ($u = 1.0$ and $v = 0.0$, the values of u and v were chosen so that they could act as pacemakers). This small area played the role of inhomogeneities in the region and served as a target source. For each simulation, eqs 3 and 4 were integrated for as long as 4000 time units so that the system would reach its asymptotic state. Typical simulation results are shown in Figure 4. Carefully setting the initial conditions, we started with a spiral pattern. When c is small, the bulk oscillation of the system is suppressed by spiral waves. In this case, despite the presence of the target wave source, a target pattern cannot bubble up; the spiral pattern occupies the whole region, as shown in Figure 4a. When the control parameter c was increased to 0.4, we observed the onset of the target waves, as shown in Figure 4b. When the control parameter arrives at the critical value ($c = 0.5$), the bulk oscillations are strong enough to sustain a stable target pattern. At this point, the target and the spiral pattern coexist in the system for the duration of our simulation time, as shown in Figure 4c. When c is increased further ($c = 0.6$), the target waves will drive the spiral waves to the boundary (Figure 4d); asymptotically, it dominates the whole system. These simulation results are consistent with our experimental observations.

We recorded the period of the spiral waves and the target waves with the variation of the control parameter c in the simulation. In the case of target waves, if a spiral pattern exists in the system, then target waves cannot grow before the critical value ($c = 0.5$). Because of this, we needed to remove spiral waves in the initial condition to obtain a target pattern. The same situation is also found in the experiment. The results, shown in Figure 5, are qualitatively in good accord with the

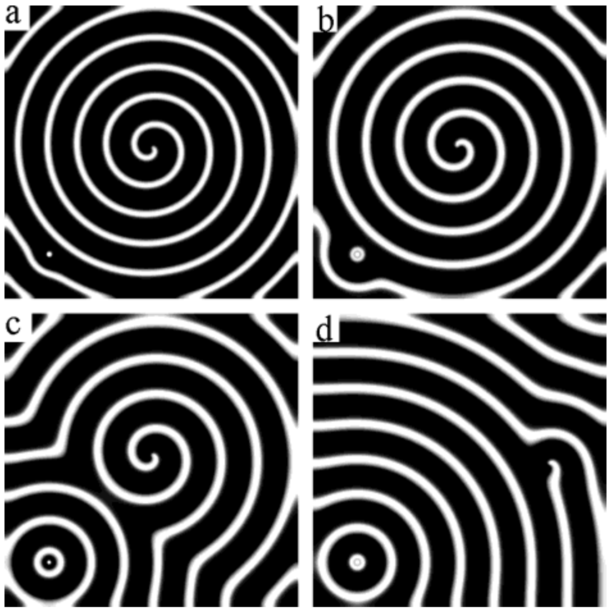

Figure 4. Simulation results with eqs 3 and 4. (a) $c = 0.3$, (b) $c = 0.4$, (c) $c = 0.5$, and (d) $c = 0.6$; other parameters are fixed at $f = 1.25$, $\epsilon = 0.1$, and $q = 0.002$.

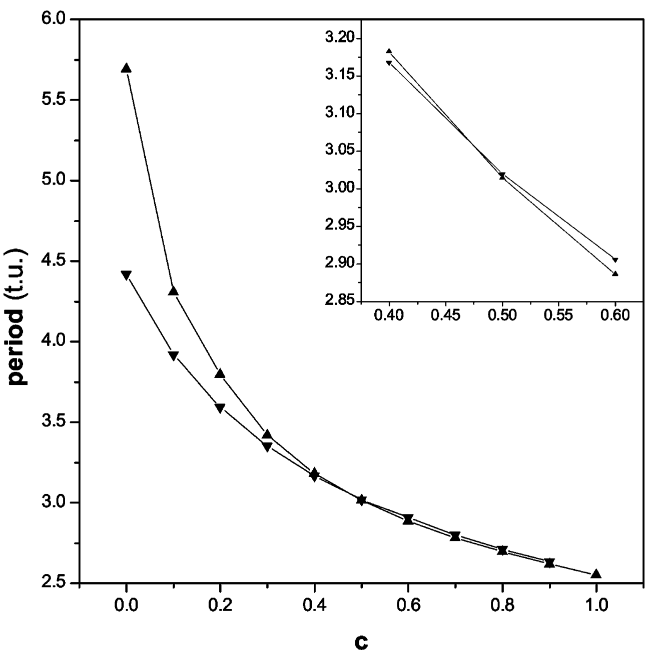

Figure 5. Simulation results. Periods of the target waves and the spiral waves as functions of the control parameter c. (▲): Target waves. (▼): Spiral waves. The inset is the local blowup of the region from $c = 0.375$ to 0.625. It shows that the two curves intersect in the vicinity of $c = 0.5$.

experimental results (Figure 3). The two curves of periods have the same tendencies with the increase in the control parameter. In the regime where a spiral wave dominates, its wave period is smaller than that of a target wave; in the regime where a target wave dominates, the spiral wave period is larger than that of a target wave. The two curves intersect in the vicinity of $c = 0.5$, where the exchange of stability between the two patterns occurs. The intersection can be seen clearly in the inset of Figure 5. The simulation result again verifies the importance of the wave period on pattern selection. Note that the difference between the two periods is very small, such a small difference is enough for one pattern to survive and eventually win in the competition with another pattern.

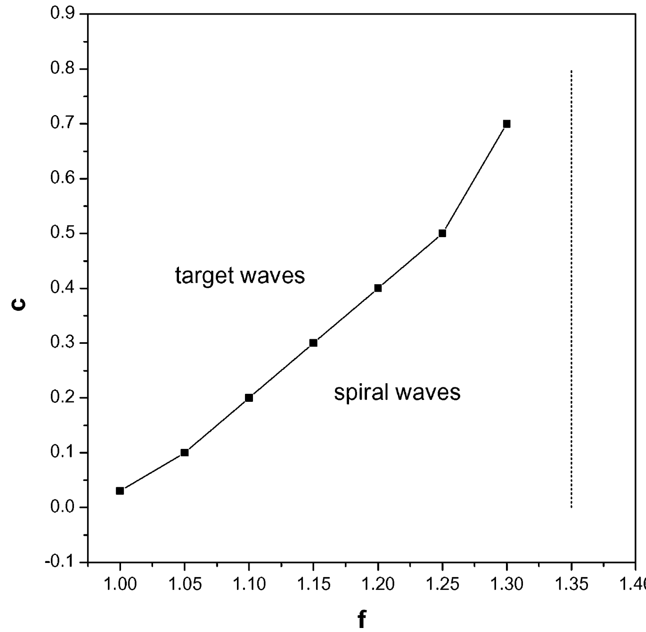

Figure 6. Phase diagram in the simulation. Other control parameters are $\epsilon = 0.1$ and $q = 0.002$. The dashed line indicates that for $f \geq 1.35$, there are no target waves appear, even though c is large enough.

In the simulation, we found that this phenomenon exists in a large range of parameter space. Figure 6 shows a phase diagram in the f−c space. The solid line in the plot is the critical line, representing the coexisting of spiral and target patterns where neither pattern can win over the other in the range of time we investigated. Below this line, the target pattern is suppressed in the presence of spiral waves. Across this line, target waves will grow and drive the spiral waves out to the boundary. We also found in the simulation that when f is greater than 1.35 target waves cannot appear, even when c is very large; the spiral pattern is always stable in this case. The dashed line in Figure 6 gives this boundary.

Conclusion

Our work provides a comprehensive description of the mechanism underlying pattern selection in the experiments. It is understandable that if there are two wave sources existing in a spatially extended system, then the waves with a relatively higher frequency will gradually drive the other away. Hence, if there is a pacemaker in the medium that happens to have a period smaller than the period of the spiral waves, it will eventually entrain spirals. The competition between spiral waves and target waves observed in this work shows this phenomenon. In the experiments, with the increase in the control parameter, the frequencies of spiral waves and target waves both increase. In the ordinary BZ chemical reaction with $[CH_3OH] = 0$ M, the frequency of target waves can never exceed that of spiral waves so that target waves have no chance to appear. However, when a proper amount of methanol is added to the reaction, the system provides a situation where the frequency of its bulk oscillation can be higher than the asymptotic frequency of the spiral waves. Under this condition, target waves emerge, and the phenomena described in this paper appear. It has been reported in ref 21 that when the frequency of the bulk oscillation of the system is higher than the asymptotic frequency of the spiral waves antispiral waves will occur; they give examples on the BZ system using Oregonator model in simulation. In this work, we find no antispiral waves in the control parameter that we searched, both in the experiments and the simulation.

We conclude that, in the BZ reaction, target waves rather than antispiral waves will appear when the bulk oscillation frequency is higher than that of spiral waves.

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