Self-Organization Induced by the Differential Flow of Activator and Inhibitor

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We have experimentally verified the prediction that a homogeneous steady state of an activator-inhibitor system can be destabilized by a differential flow of the key species, rather than by their differential diffusivity as for the Turing instability. Traveling waves are generated by a flow of Belousov-Zhabotinsky reactants through a tube containing ferroin immobilized on a cation exchanger. Without flow the system resides in a homogeneous steady state. This mechanism of spatiotemporal pattern formation avoids the restrictions of the Turing instability on the diffusion coefficients and can thus be expected to operate in a larger class of chemical, physical, and biological systems.

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The homogeneous steady state of a reactive system may lose its stability and form so-called Turing patterns [1, 2], provided two conditions are fulfilled: First, the kinetic system must contain an activator (e.g., autocatalytic) species and an inhibitor, whose function is to limit the autocatalytic growth. Second, the diffusion coefficient of the inhibitor must exceed that of the activator to an extent which allows the activator to grow locally while lateral inhibition prevents the spread of growth [3]. The primary role of diffusion in the instability is to spatially disengage the counteracting species. The mechanism is fundamental to biological morphogenesis [1,3] and it may operate also in a variety of physical systems [4].

We have recently suggested an alternative way of disengaging the key species by a differential bulk flow [5]. In this case the homogeneous steady state of the system may be destabilized by flows of activator and inhibitor at different flow rates, regardless of which one is faster. This makes the mechanism free of the Turing restrictions on the diffusion coefficients and thus much more general. We refer to the mechanism as the differential flow induced chemical instability (DIFICI).

Here we report the first experimental verification of the DIFICI and the resulting wave patterns in the ferroin catalyzed Belousov-Zhabotinsky (BZ) system in a quasi-one-dimensional flow tube. The ferroin ion is immobilized on a cation-exchange resin [6] that is packed in a vertical tubular reactor, while the remaining reactants flow through the tube, as in a chromatographic column. The experimental setup is shown schematically in Fig. 1.

We used Dowex 50X4-400 ion-exchange resin (in the form of beads of approximate size 40 μm) and Aldrich chemicals. The $2M$ stock solution of bromomalonic acid was prepared at 0 °C according to Ref. [7]. Before being loaded with ferroin, the ion exchanger was washed 5–7 times. Each time after the main part of the beads had settled, the translucent liquid fraction was decanted. Ultimately, the beads settled relatively quickly, leaving the supernatant liquid transparent. This suggests that the size distribution of the remaining beads was fairly narrow. Then the suspension of the ion exchanger in water was transferred into a measuring cylinder and when the beads had settled, the volume they occupied was determined. This volume was the reference value for the loading with ferroin instead of the weight of the beads used by other authors [6]. Normally, we loaded 10^{-4} moles of ferroin per liter of the ion-exchanger suspension. Assuming that the beads were identical spheres and that they packed densely one could estimate the free volume occupied by the flowing solution as 30% of the total volume. Accordingly, the ferroin concentration averaged over the reacting volume should be taken 3 times higher than that averaged over the total volume. Therefore, in our calculations we used $3\times10^{-4}M$ as the concentration of ferroin.

The loaded beads were then mixed with the solution of the other reactants and the larger part of the mixture was transferred to the tubular reactor (Fig. 1). The rest were poured into a Petri dish (depth of 1 mm beads, 10 mm liquid) for a reference experiment. As shown in Fig. 1, the beads filled the flow tube and part of the

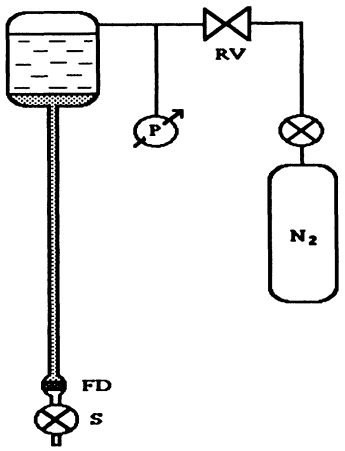

FIG. 1. Scheme of the experimental setup. The internal diameter of the glass tube is 3.2 mm, the length of the tube is approximately 25 cm, and the diameter of the reservoir is 25 mm. Designations: RV, regulating valve; FD, fritted disk; S, stopcock; P, pressure gauge.

reservoir. The latter portion of beads served as a second reference. A fritted glass disk prevented washout of the beads. The flow could be arrested by a stopcock. The flow rate was controlled by applying compressed nitrogen gas, and the flow was assumed proportional to pressure. To interpret our experiments unambiguously, efforts were made to avoid the regimes in which the system showed either oscillatory or pacemaker activity. Therefore, the experiment was discarded if this sort of activity was discovered either in the Petri dish or in the wide top of the column. We used mostly the sets of parameters $[H_2SO_4] = 0.02M, [Fe(phen)_3] = 1 \times 10^{-4}M$ (averaged over the total volume, as descibed above) and (a) $[NaBrO_3] = 0.8M, [BMA] = 0.4M$, and (b) $[NaBrO_3] = 1.5M, [BMA] = 0.5M$. Using malonic acid instead of BMA resulted in a poorer color contrast and reproducibility. Typically, one experiment lasted 0.5–2 h.

When pressure was applied, pale blue waves were observed that propagated along the tube in the direction of the flow. The waves were recorded on videotape, and the images were then processed on a computer to enhance contrast. Figure 2 is composed of five frames taken at 20 sec intervals at the relative time indicated. The length and velocity of the waves were measured as functions of applied pressure. The length was measured by applying a ruler to the tube. The velocity was determined by the time needed by a wave to pass the distance between two succesive distance markers (5 cm). The time interval was measured with a stopwatch. Both functions are linear [Figs. 3(a) and 3(b)]. The nonzero wavelength and velocity at zero excess pressure reflect a residual flow due to gravity filtration.

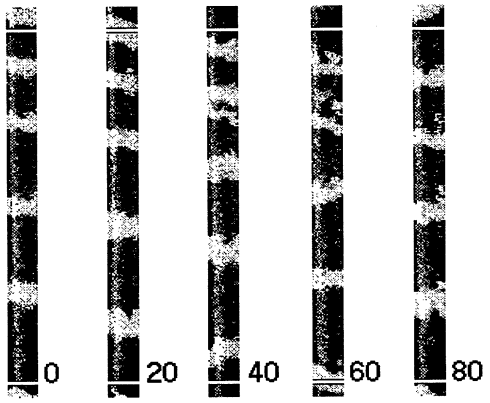

FIG. 2. The composition of the images of a part of the vertical tubular reactor showing propagation of the waves generated by the differential flow. Ferroin is immobilized on the ion-exchange resin that is packed in the tube. The flow of the other reactants is downwards. The light grey bands correspond to the areas where the ferroin is in its oxidized form (ferriin). The dark portions correspond to the reduced state. The horizontal black-and-white lines at the top and bottom are distance markers spaced 5 cm apart. The figures show the relative time in seconds for the succesive frames. The concentration set is (a) (see text).

A peculiarity of the BZ system is the evolution of gas. This evolution led to a slow buildup of internal pressure, normally small in comparison with the external pressure. However, it produced an interesting effect when the downstream stopcock was closed and the external pressure was released. In this case the internal pressure started to push the solution in the upper part of the tube upwards. Therefore one could see an initial fading of the waves, followed by the reappearance of waves that slowly moved upwards. By applying a small external pressure we could balance this effect and make the waves disappear again. Because of the dead volume between the filter plug and the stopcock, a small flow persisted even with the stopcock shut, when more pressure was applied. This additional pressure caused the waves to reappear and propagate downwards. When such a balance was achieved we could create and extinguish the waves and reverse their direction many times. The characteristic length of these slow waves was about 1 mm and they appeared and disappeared almost synchronously on a time scale of ca. 0.5 min on a ~ 10 cm segment.

The phenomenon is described [5] by the reaction-flow-diffusion equations

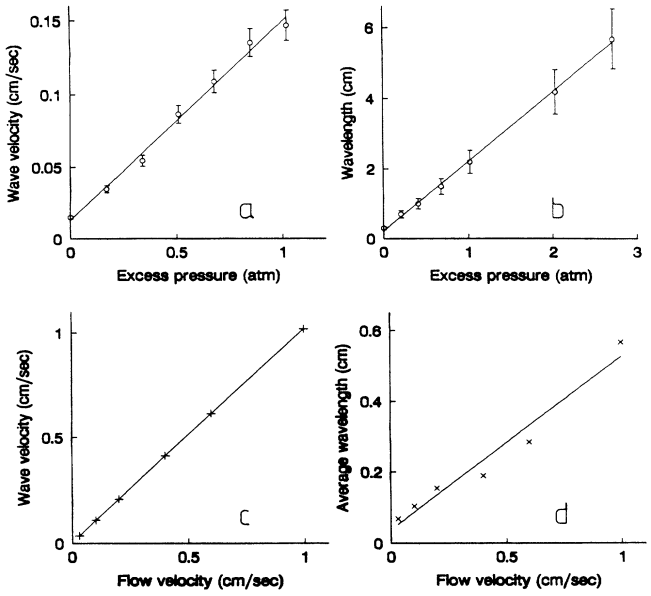

FIG. 3. (a) The velocity and (b) the length of the waves generated by DIFICI in the experiment; the concentrations are as in Fig. 2. Pressure of 1 atm corresponds approximately to 0.25 cm/sec of the flow velocity. (c) The velocity and (d) the length of the waves simulated by the numerical integration of the Puschinator model. The parameters are as in Fig. 2 except for $[Fe(phen)_3] = 3 \times 10^{-4}M$ (to account for packing density).

$$\dot{X} = f(X,Y) + v\frac{\partial X}{\partial r} + D\frac{\partial^2 X}{\partial r^2}\,,$$
$$\dot{Y} = g(X,Y)\,, \tag{1}$$

where the spatial coordinate axis lies in the direction of the flow. We assume that the chemical system has a stable steady state X_0, Y_0 [i.e., $f(X_0,Y_0) = g(X_0,Y_0) = 0$] when perfectly stirred. Consider further the Puschinator model of the ferroin catalyzed BZ reaction [8]

$$\frac{dX}{d\tau} = \frac{1}{\epsilon}\Big[X(1-X) - \Big(2q\alpha\frac{Y}{1-Y} + \beta\Big)\frac{X-\mu}{X+\mu}\Big]\,,$$
$$\frac{dY}{d\tau} = X - \alpha\frac{Y}{1-Y}\,, \tag{2}$$

where $[\mathrm{Fe(phen)}_3^{3+}] = CY$, $[\mathrm{HBrO_2}] = (k_1A/2k_4)X$, $\epsilon = k_1A/k_4C$, $\alpha = k_4K_8B/(k_1Ah_0)^2$, $\mu = 2k_4k_7/k_1k_5$, $t = [k_4C/(k_1A)^2h_0]\tau$, $\beta = 2k_4k_{13}B/(k_1A)^2h_0$, $C = [\mathrm{Fe(phen)}_3^{2+}] + [\mathrm{Fe(phen)}_3^{3+}]$, $A = [\mathrm{NaBrO_3}]$, $B = [\mathrm{CHBr(COOH)_2}]$, h_0 is the acidity function, q is the stoichiometric factor, and k_i are the rate constants [8]. (Here we use Y for $[\mathrm{Fe(phen)}_3^{3+}]$ instead of the traditional notation Z). Linear stability analysis [5] of Eq. (1) for the Puschinator model predicts dispersion relations shown in Fig. 4 for the eigenvalues of the homogeneous steady state (SS). The SS becomes unstable at flow rates exceeding a critical value. The resulting pattern was studied by numerical integration of the reaction-flow-diffusion equation (1) for model (2) in a circular reactor (periodic boundary conditions). The initial perturbation of the SS (a sum of all possible cosine harmonics with equal amplitude, 2.5×10^{-5} of the SS value) developed into wave trains traveling with the flow. The calculated velocity and wavelength are plotted in Figs. 3(c) and 3(d). Since we modeled a circular reactor, the wavelength could only change by a finite value in response to a parameter change. Obviously this is the reason for the deviation of the calculated values from a smooth line.

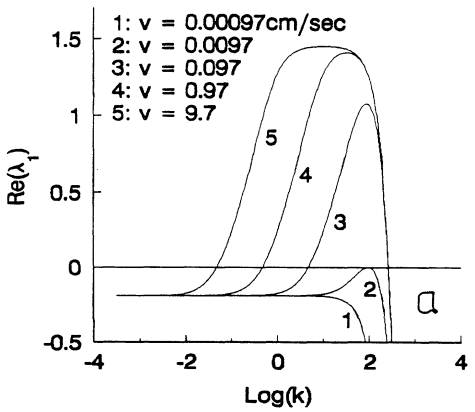

FIG. 4. The real part of the eigenvalue as a function of wave number for the DIFICI in the Puschinator model. The parameters are as in Figs. 3(c) and 3(d).

Experimentally, the velocity of the flow through the packed tube could not be measured precisely, since the packing density was unknown; therefore, the experimental [Figs. 3(a) and 3(b)] and calculated [Figs. 3(c) and 3(d)] graphs cannot be superimposed directly. We made a rough evaluation of the flow velocity by measuring the volumetric flow rate through the tube and assuming that the spherical beads are closely packed. The resulting upper limit estimate of the flow velocity is 0.25 cm/sec at 1 atm of excess pressure. This means that the semiquantitative agreement between the experimental and calculated plots is already good and that the quantitative agreement could be expected to be even better if the actual flow velocity could be measured.

As in Turing structures, the wavelength is an intrinsic property of the system and is not determined by an external pacemaker as in trigger waves. Another difference is that the waves induced by DIFICI develop simultaneously over the entire reactor and they are asymmetric, propagating only in the direction of the flow. Trigger waves, on the other hand, are excited locally and emitted with radial symmetry [9]. This difference is illustrated by comparison with a previous experiment [10] where a similar setup was used to study the effect of a differential flow on externally initiated trigger waves. The latter propagated in both directions from the pacemaker, they persisted at zero flow, and they disappeared above a critical flow rate. For the DIFICI, on the other hand, theory predicts [5] a lower limit of the flow rate but no upper limit. Although we could not measure this lower limit (because the mentioned gravity filtration and gas evolution made the small velocities hard to control), the above observations are clear evidence for its existence. There was no evidence for the existence of an upper limit.

While the occurrence of the Turing instability depends crucially on the ratio of diffusion coefficients $\delta = D_{\mathrm{inh}}/D_{\mathrm{act}}$, the flow-induced instability is determined merely by the magnitude $|v|$ of the easily controllable relative flow velocity (or rather by the ratio $|v|/\sqrt{D}$ when diffusion is included). Thus it is immaterial which of the two control species is immobilized: As the previous analysis [5] and present experiment show, fixing the inhibitor promotes the DIFICI, while this would prevent the Turing instability from occurring.

This paper presents the first experimental verification (using a chemical example, by convention and convenience) of a rather general principle (referred to as DIFICI) by which a dynamical system characterized by activation-inhibition kinetics is caused to self-organize in response to a differential bulk flow of the key species. The class of systems fulfilling the first, kinetic, requirement (i.e., including the activator and inhibitor subsystems) is very broad. Examples can be found in chemistry, plasmas, semiconductors, lasers, heterogeneous catalysis, biological development, physiology, and population dy-

namics. The second, or differential transport, condition restricts the pattern formation to a smaller subclass. The differential bulk flow condition for the DIFICI is less restrictive, and hence covers a larger subclass than does Turing's condition of differential diffusivity. Diffusivity is a molecular property and therefore is not easily controllable. There are many ways, however, by which differential bulk flows can be realized and controlled: In our paper we present one example, and electrolytes, plasmas, and semiconductors in external fields form another class, while biological cells and organs that are bathed in streams of fluids form a third class. Turing patterns are widely recognized as important vehicles for biological and physical self-organization. Our emphasis on the more general notion of differential bulk flow expands the conceptual basis of Turing's original idea, and, thus, also expands its field of applicability.

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