Reports

Ferroin-Collodion Membranes: Dynamic Concentration Patterns in Planar Membranes

Abstract. *Patterns and waves of the Belousov-Zhabotinskii reaction are produced in membranes in which one reactant is immobilized. Convection is eliminated, the generation and deformation of wave forms are studied, and patterns are permanently fixed. Wave shape, frequency, length, and phase velocity are explained theoretically by the interactions of diffusion with reaction.*

By adapting the methods of Carr and Sollner (*1*) and Gregor and Sollner (*2*), we have cast membranes of hydrated collodion matrix containing substantial amounts of immobilized tris(1,10-phenanthroline) ferrous complex (ferroin). As a result we are able to study concentration wave phenomena associated with the Belousov-Zhabotinskii reaction (*3, 4*) directly in membranes. The Belousov-Zhabotinskii reaction is one of the few documented examples of a liquid-phase system which can exhibit homogeneous chemical oscillations (*4*). The overall process consists of the oxidation of malonic acid by acidic bromate solutions and is catalyzed by certain complex ions such as ferroin. In well-stirred vessels, the reaction system under some conditions exhibits uniform temporal oscillations characterized by the relative amounts of oxidized and reduced metal ion complex. If the reactants are placed in long tubes or shallow dishes without continuous stirring, concentration bands or waves consisting of alternate regions of oxidized and reduced metal ion complex can arise under certain conditions (*4–6*). This is the first report of such patterns in membranes.

Pattern formation is virtually free of the degrading influences of convection; we have found it possible to swirl the membranes during an experiment without disturbing the pattern. One of our purposes is to demonstrate that the dynamic patterns originate in interaction of chemical reaction and diffusion, both processes playing essential roles, and to show that hydrodynamic flow plays no such role, especially in the case of spiral wave initiation (*6*). By casting membranes as planes, cylinders, spheres, and so forth, the effects of surface topology on parameters such as wave propagation rate, wavelength or pattern size, and wave shape can be investigated.

Planar membranes, approximately 0.025 ± 0.001 cm thick and containing reduced immobilized ferroin, which is bright red, are submerged in a petri dish containing $0.05M$ $KBrO_3$, $0.07M$ $CH_2(COOH)_2$, and $1.25M$ H_2SO_4. As reaction proceeds the system evidently approaches a state of redox instability: transitory perturbing influences cause spots of blue, oxidized ferroin, to appear at locations chaotically spaced over the membrane edge as well as the interior. The blue spots become circular fronts that rapidly enlarge and engulf the entire membrane. The blue color everywhere changes smoothly to pale red as ferroin is reduced again. It does not return to its original, fully reduced state. This sequence may be repeated one or more times (in nearly the same locations), the oxidation fronts moving less rapidly in each successive episode. When the rate of frontal growth drops into the range of 0.1 to 0.5 cm/min the reduction step is proceeding in a band immediately behind the advancing front, and consequently there may be a succession of sharp red → blue fronts and more diffuse blue → red transitions marching concentrically outward. Thus, the field in which the reaction and diffusion are taking place develops nests of outgoing circular concentration waves. When the red → blue front is highly curved, as around an oxidation center which has just appeared, its shape is unstable; this is because the greater its curvature, the less rapidly the front advances, evidently because of local alteration of the diffusion flux fields. Thus, a blue spot may become unstable in form, a slight ellipticity warping into a bilaterally symmetric kidney shape, the reentrant portion of which halts owing to the local balance between reaction and diffusion of reactants and intermediates. The shape becomes increasingly bowed, the ends bending around toward each other, each end becoming the inner nose of one of a pair of oppositely winding spirals; the reaction-diffusion field develops tightly wound, spiral concentration waves. When fronts begin propagating from points near the membrane edge, either a sector of circular waves or an interrupted, single spiral wave develops, depending on whether the blue oxidation center in its early stages suffers shape instability. Figure 1 shows the growth of a single spiral concentration wave from a center near the membrane edge.

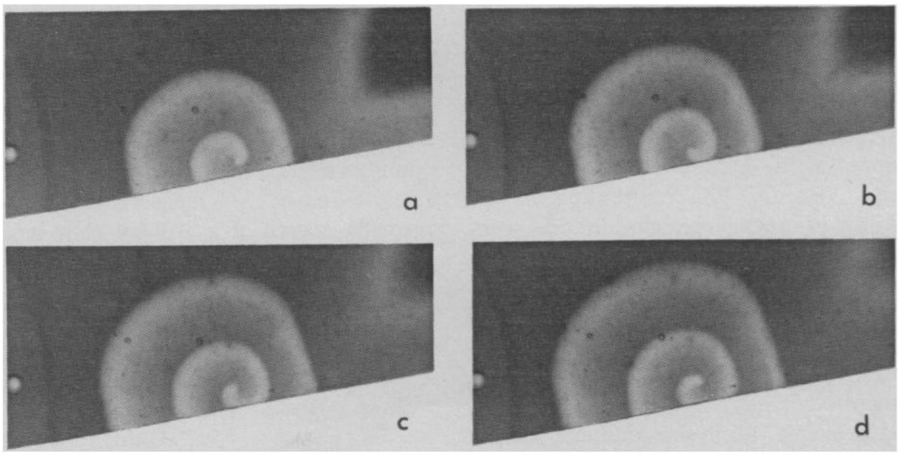

Fig. 1. A single spiral wave of immobilized ferroin which developed from a center near the membrane edge. The period of rotation close to the center is about 28 seconds and the rate of advancement of the nearly circular arms is about 3.6 mm/min.

The concentration waves observed in these and earlier studies (*4–6*) indicate the existence of wavelike solutions to

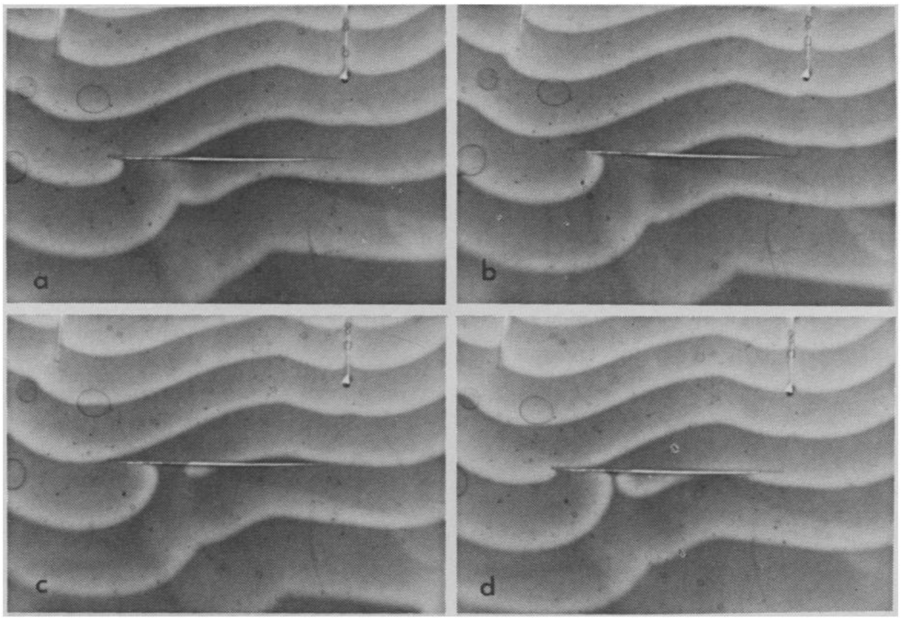

Fig. 2. Interaction of waves with slits in the membrane. The slits contain reservoir reagents but are devoid of ferroin. For sufficiently narrow slits communication by diffusion across a slit is effective. Slit width, 0.06 mm.

sets of reaction-diffusion equations. If the participating chemical species diffuse and react in the simplest ways, these equations take the linear form,

$$\partial c_j/\partial t = D_j\nabla^2 c_j + a_{j0} + \sum_k a_{jk}c_k \qquad (1)$$

Here c_j is the concentration and D_j the diffusion coefficient of molecular species j; a_{j0} is a zeroth-order reaction rate, the a_{jk} are first-order reaction rate constants (*7*), and t is time. Concentration waves must depend on diffusion—without the diffusion of at least one species there would be no means of spatial ordering—and on reaction kinetics, as well as on the configuration of the system and the nature of the boundary conditions. Gmitro and Scriven (*8*) have shown that in general the behavior of a reaction-diffusion system depends not so much on specific values of reaction and diffusion parameters as on certain combinations of them (*9*). The wave velocity need not be limited by the diffusion velocity of any component—a fact borne out by observation of the oxidation waves of immobilized ferroin in our experiments.

To illustrate wave solutions we consider the case of two reactive species, one of which is not diffusible; that is, $D_1 = 0$ and $D_2 > 0$. By standard methods we find that Eq. 1 is satisfied by harmonic, plane waves propagating unattenuated in the x-direction. Such waves are represented by (*10*) $c_1 - c_1^0 = A_1\cos(2\pi x/\lambda \pm \omega t)$ and $c_2 - c_2^0 = A_2\cos(2\pi x/\lambda \pm \omega t - \phi)$, provided the wavelength λ and circular frequency ω are related to the invariants of the reaction and diffusion matrices (*8*) by

$$\lambda = 2\pi\,[D_2/(a_{11} + a_{22})]^{1/2},\ a_{11} + a_{22} > 0 \qquad (2)$$

$$\omega^2 = a_{11}a_{22} - a_{12}a_{21} - a_{11}(a_{11} + a_{22}),$$
$$a_{12}a_{21} < -a_{11}^2 \qquad (3)$$

In this case, propagating waves, whether unattenuated or not, require autocatalytic production of at least one of the species. Equation 3 shows that a degree of asymmetry in the reaction kinetics is needed (*11*). If a system described by Eq. 1 is in a state to propagate harmonic plane waves without attenuation, it is also in a state of marginal oscillatory instability (*8*). Nonlinear effects not accounted for in Eq. 1 may favor waves over general instability; then the wave speed can be expected to be very nearly $v = \omega\lambda/2\pi$.

Two wave patterns usually seen on our membranes are concentric circles and singly wound spirals. Equation 1 admits propagating waves of both forms and the (as yet unobserved) multiply wound spiral. By standard methods we find that when $D_1 = 0$, Eq. 1 is satisfied by (*10*)

$$(c_1 - c_1^0)/M_m(kr) = A_1\cos[\alpha \pm (\omega t - m\theta)]$$
$$(c_2 - c_2^0)/M_m(kr) =$$
$$A_2\cos[\alpha \pm (\omega t - m\theta) - \phi] \qquad (4)$$

where r and θ are polar coordinates; $M_m(kr) \equiv [J_m^2(kr) + Y_m^2(kr)]^{1/2}$; $\alpha(r) \equiv \tan^{-1}[Y_m(kr)/J_m(kr)]$; and J_m and Y_m are Bessel functions of the first and second kind, of integral order m. If the wave number $k \equiv 2\pi/\lambda$ is given by Eq. 2 and the circular frequency ω is given by Eq. 3, then the waves are unattenuated by reaction or diffusion, although in propagating outward they are attenuated by the purely geometric effect of spreading. When $m = 0$, Eq. 4 represents circular waves, for as $r \rightarrow \infty$, $M_m(kr) \rightarrow (2/\pi kr)^{1/2}$ and $\alpha(r) \rightarrow k(r - r_0)$, where $r_0 \sim (2m + 1)\pi/4k$. Asymptotically, the curves of constant phase are $r - r_0 = \pm vt + 2\pi p/k$ ($p = 0, 1, \ldots$), which represent large circles propagating radially inward or outward at speed $v = \omega/k$ and spacing $\lambda = 2\pi/k$, the speed and spacing at which plane waves propagate. Unlike true plane waves, the phase curves have a geometric attenuation factor which varies asymptotically as $1/r^{1/2}$. Wave fronts at smaller distances from the center of curvature propagate more slowly than plane waves. The phase velocity of circular waves is $v_n = \pm v(\pi/2)krM_0^2(kr)$, the ambiguous sign representing converging and diverging waves. The wave speed diminishes as the radius of a circular wave diminishes, and thus as its curvature increases.

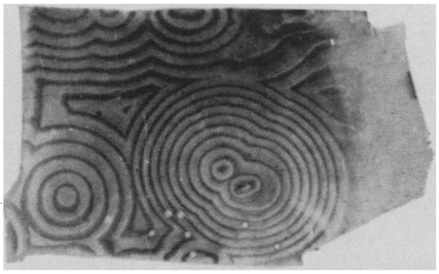

Fig. 3. A pattern fixed by first treating the membrane with AgBr. The record captures two neighboring spots at initiation resembling isopotentials of an electric dipole. One of these centers is slightly distorted from circular symmetry, but evidently not sufficiently to cause spiral formation. Also shown are another internal initial center and several edge initiation points.

When $m \neq 0$, Eq. 4 represents spiral waves, asymptotically given by $r - r_0 = \pm(m/k)[\pm(\omega t/m) - \theta + (2\pi p/m)]$ ($p = 0, 1, \ldots, m - 1$), which represents m Archimedean spirals of pitch m/k wound on a circle of radius r_0 and spaced at intervals of $2\pi/m$ radians (*12*). Of the ambiguous signs, plus-plus represents clockwise expanding spirals; plus-minus, clockwise contracting spirals; minus-minus, counterclockwise expanding spirals, and so forth. The phase speed of the spiral wave is $v_n = (\omega r/m)[1 + 4/\pi^2 m^2 M_m^4(kr)]^{-1/2}$. In the limit as $r \rightarrow \infty$, $v_n \rightarrow \omega/k = v$ and is radial: wave propagation at large radii resembles that of plane waves. But as $r \rightarrow 0$, $v_n \rightarrow \omega r/m$ and is azimuthal around the center: the spiral "noses" at small radii rotate at an angular velocity v_n/r which is submultiple m of the natural chemical frequency ω. Moreover, the entire spiral pattern appears to turn as a solid at angular velocity $(\partial\theta/\partial t)_{r,c} = \omega/m$, as is evident from Eq. 4. Here too is indication that the more highly curved a chemical wave, the lower its normal velocity.

This case of only two reactive species, one immobilized, which obey linear reaction kinetics and diffusion laws is no doubt too simple to describe accurately the Belousov-Zhabotinskii reaction in membranes or in shallow dishes [we performed experiments resembling those of Winfree (*6*) in shallow dishes]. Nevertheless, the oversimplified model indicates what is possible with only diffusion and chemical reaction in more complicated, multicomponent systems that lack oscillating chemical sources or "pacemakers." What waves appear in a system hovering on instability depends on chance nonuniformities and transitory perturbations. The model shows that the wave speed decreases when the wave-front curvature increases. The experimental observations suggest that this is responsible for the shape instability leading to spontaneous growth of spiral waves from an isolated perturbation or fluctuation in a homogeneous system. The model shows that the involute of a circle is not the only wave shape in which rotation and time translation are interchangeable (*13*) and makes plain that the pitch and velocity of a spiral chemical wave, like the wavelength and speed of plane, harmonic chemical waves, are completely dependent on chemical kinetics and diffusivities.

Membranes can be washed and reused. New wave patterns appear randomly; there is no evidence of "pacemaker centers" (*6*). The interaction of wave dynamics and membrane structure can be studied (*14*). Figure 2 shows propagation across slits; the propagation is from top to bottom. When the wave velocity and slit length coincide in direction (as at the slit shown in the upper right in each photograph), waves propagate in phase along the slit. When a wave impinges on a slit obliquely the front divides and propagates out of phase along the edges. At the horizontal slit in Fig. 2, the branch propagating along the lower edge is also moving away from the slit, creating an arc of high curvature that advances more slowly than the upper branch. Figure 2c shows a wave reappearing on the lower edge, as though the wave on the upper side has bridged the ferroin-free gap. The most probable mechanism is diffusion of mobile species; the estimated diffusion time for a slit 0.006 cm wide and for $D = 10^{-6}$ to 10^{-5} cm²/sec is 3 to 30 seconds, in agreement with the observations.

The dynamic state of a developing pattern can be halted and recorded permanently by using a membrane precoated with silver bromide. As dynamic patterns develop, the areas occupied by oxidized ferroin blacken with precipitate. In water the darkened regions remain and record the state of the pattern at the time of washing; see Fig. 3. Fixation yields examples of static patterns whose origins lie in the interaction of several dynamic processes. Pattern generation by interfering diffusion and chemical reaction underlies the theory of biological morphogenesis first suggested by Turing (*15*).

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7. The parameters a_{i0} and a_{jk} can be managed to account for interchange between reservoir and membrane, which can be described by $H_i(c_i' - c_i)$; see Gmitro and Scriven (*8*).
8. J. I. Gmitro and L. E. Scriven, in *Intracellular Transport*, K. B. Warren, Ed. (Academic Press, New York, 1966), p. 221.
9. In the case of systems described by linear equations of the form of Eq. 1, the behavior depends on the independent invariants of a matrix of reaction rate constants, a matrix of diffusion coefficients, and the products of those two matrices (*8*).
10. The constants c_1^0 and c_2^0 are chosen to eliminate the terms a_{10} and a_{20} from the reaction-diffusion equations, that is,
$$c_1^0 = \frac{a_{20}a_{12} - a_{10}a_{22}}{a_{11}a_{22} - a_{12}a_{21}},\quad c_2^0 = \frac{a_{10}a_{21} - a_{20}a_{11}}{a_{11}a_{22} - a_{12}a_{21}}$$
We restrict c_1^0 and c_2^0 to positive values; A_1 and A_2 are amplitudes and are arbitrary except that they may not be greater than c_1^0 and c_2^0, respectively; ϕ is the phase angle by which the concentration wave of species 2 lags that of species 1.
11. J. Higgins, *Ind. Eng. Chem.* **59** (No. 5), 18 (1967).
12. H. M. Cundy and A. P. Rollett, *Mathematical Models* (Oxford, London, ed. 2, 1961), p. 73.
13. Winfree (*6*) assumed that the magnitude of the phase velocity is independent of position on the wave. This leads to involutes of circles as solutions. The spiral solutions admitted by a reaction-diffusion analysis indicate that v_n varies and in general decreases as the curvature increases.
14. Ferroin-collodion membranes appear to offer a means by which the Belousov-Zhabotinskii reaction may be coupled to transmembrane electric current in diffusion cell studies. Transport and conductance measurements across membranes with variable charge density may be useful models for active transport in biomembranes.

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Crystal Growth of Silicon and Germanium in Metal Films

Abstract. *Amorphous silicon in contact with silver films and amorphous germanium in contact with aluminum films form crystalline precipitates when heated to temperatures well below those at which any liquid phase is present. Crystallization occurs by an initial dissolution of the semiconductor into the metal film solvent followed by the growth of crystals out of the solvent.*

Crystal growth can occur from any nutrient medium: vapor, liquid, gel, or even solid (*1*). As an example of crystal growth in a solid, we find that solid metal films can provide a medium for the growth of semiconductors such as Si and Ge at temperatures well below those at which any liquid phase is present (that is, eutectic temperatures). For example, we have observed the crystal growth of Ge in Al films at temperatures as low as 100°C. In this case, the metal dissolves the semiconductor at one interface, transports it, and permits it to grow into crystals at another location, with all processes occurring some 300°C below the eutectic temperature.

In addition to the surprisingly rapid kinetics just noted, we find in evaporated films a naturally occurring and convenient driving force for the above reactions. In our earlier investigations (*2*) we have relied on a temperature cycle to obtain supersaturation of a solid metal solvent with Ge or Si and hence crystal growth; this is the familiar metallurgical process of saturating