Cross-membrane coupling of chemical spatiotemporal patterns

David Winston, Mukesh Arora, Jerzy Maselko, Vilmos Gáspár & Kenneth Showalter*

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045, USA
* To whom correspondence should be addressed

CHEMICAL systems may communicate by exchange of common species through mass transport, and such coupling may give rise to dynamical complexity beyond that possible in the independent systems[1–5]. We report here on dynamical behaviour arising from the diffusive coupling of chemical spatiotemporal patterns across a membrane. Chemical waves appear on Nafion membranes that are loaded with ferroin catalyst and bathed in a mixture of the reagents of the Belousov–Zhabotinsky oscillatory reaction. The waves on each side of the membrane couple by diffusive transport through the membrane. The coupling initially gives rise to the spontaneous appearance of spiral waves, and subsequent behaviour reveals several distinct phases of evolution, ultimately leading to complete spatiotemporal entrainment.

Figure 1*a* shows an image of regular wave behaviour on the ferroin-loaded Nafion membrane; the three horizontal lines correspond to grey-level profiles depicted in Fig. 2. Arcs defined by the intersection of these lines with a particular wave allow

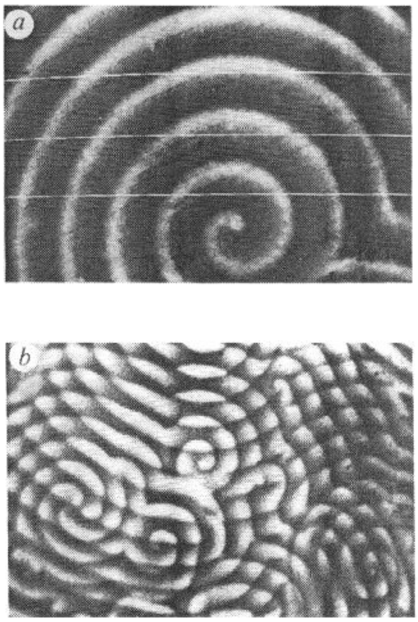

FIG. 1 Chemical waves propagating on the surface of a ferroin-loaded Nafion membrane suspended in a continuous-flow stirred-tank reactor (CSTR) (stirring rate 300 r.p.m.) pumped with Belousov–Zhabotinsky reaction mixture. These digital images[11,16] show the intensity of light (wavelength 500 nm) transmitted through a membrane 0.18 mm in thickness; field of view is 6.2 × 4.7 mm. The three horizontal lines correspond to the grey-level profiles in Fig. 2. Reactant concentrations in CSTR: $[NaBrO_3] = 0.19$ M, $[H_2SO_4] = 0.24$ M, [malonic acid] $= 1.9 \times 10^{-2}$ M, [ferroin] $= 5.8 \times 10^{-5}$ M, and [KBr] $= 8.7 \times 10^{-2}$ M; reactor residence time is 56.93 min; temperature maintained at 25.0 ± 0.2 °C. *a*, Nafion membrane loaded with ferroin to 16.7% capacity, giving strong coupling. The image was obtained 4.0 h after the reaction was initiated. *b*, Nafion loaded to 38.7% capacity, giving weak coupling. Image obtained 4.5 h after initiating the reaction. Note that the left-most spiral source is a spontaneous three-armed vortex.

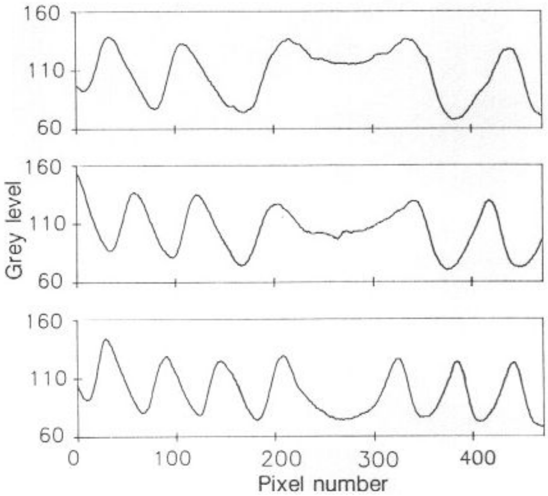

FIG. 2 Grey level as a function of distance for profiles corresponding to the three horizontal lines in Fig. 1*a*. Each pixel represents 12.1 μm.

calculation of the velocity normal to the front. Plots of wavefront position as a function of time are highly linear (a normal velocity of 0.163 ± 0.001 mm min^{-1} was calculated from Fig. 2 and subsequent profiles). These waves are much like those exhibited in thin films of Belousov-Zhabotinsky (BZ) solutions[6-8], but with shorter wavelengths and smaller propagation velocities.

The image in Fig. 1*b* shows a very different type of wave behaviour. Although successive images seem to suggest that the overall behaviour results from two sets of wave patterns evolving relatively independently, closer inspection shows that the two patterns are not independent. Their interaction is sufficiently weak, however, for the features to remain much the same for many hours.

The behaviour in Fig. 1*b* can be understood by considering the characteristics of Nafion, a perfluorosulphonic acid ionomer[9,10]. Partial ionization of covalently bound sulphonic acid groups gives rise to an overall net negative charge on the membrane, and negative ions do not significantly penetrate the resin matrix. The chemical-wave activity is therefore confined to the membrane surface because the anion BrO_3^- is an essential reactant. Studies of BZ chemical waves on polystyrene cation-exchange beads have clearly demonstrated that wave activity occurs on the surface of the resin matrix[11]. These considerations indicate that the waves in Fig. 1*a* also occur on both sides of the membrane; here, however, it is apparent that the wave activity is synchronized. The different behaviour in Fig. 1*a* and *b* results from strong coupling across the membrane in *a* and weak coupling in *b*.

The best candidate for the messenger species that mediates the coupling is bromous acid, the essential autocatalyst of the BZ reaction[8]. Bromous acid is a neutral molecule in the acidic reaction mixture and can diffuse readily through the membrane. A critical factor in the effectiveness of the messenger is the extent of ferroin loading: the entrained waves in Fig. 1*a* occur on a membrane in which 16.7% of the cation-exchange sites are occupied by ferroin; the relatively uncoupled waves in Fig. 1*b* occur on a membrane loaded to 38.7%. Higher loading apparently results in the interception of $HBrO_2$ in an oxidation-reduction reaction with ferroin[12], although other oxybromine species, such as BrO_2, might also serve as messengers and be similarly intercepted. Alternatively, it is possible that the diffusive transport of the messenger species is simply impeded by the bulky ferroin complex ions in the channels of the membrane.

The images in Fig. 3 show a system in which the wave behaviour is coupled over the course of many hours. Near the beginning of the experiment (Fig. 3*a*), faint semicircular patterns appear on each side of the membrane. The effects of cross-membrane coupling are clearly evident: spiral waves are spontaneously initiated at crossing points of the superimposed waves. The complex pattern of strongly coupled waves in Fig. 3*b* appears 1.0 h later. The pattern evolves to that shown in Fig. 3*c* 4.5 h later, with entrained but irregular behaviour displacing the cross-hatched patterns. The image in Fig. 3*d* shows complete entrainment and regular behaviour 31 h after initiation of the reaction.

These results can be viewed as the spatiotemporal analogue of coupled chemical oscillators[4,5]. In the strongly coupled system (Fig. 1*a*), the waves on each side of the membrane are entrained throughout. With weaker coupling (Fig. 1*b*), the patterns develop differently on each side of the membrane and seem at first to be independent, but become gradually entrained over long timescales (Fig. 3). Insights into the mechanism of entrainment may be obtained using a four-variable model based on two diffusively coupled two-dimensional chemical-wave systems. We use a computationally efficient scheme for excitable

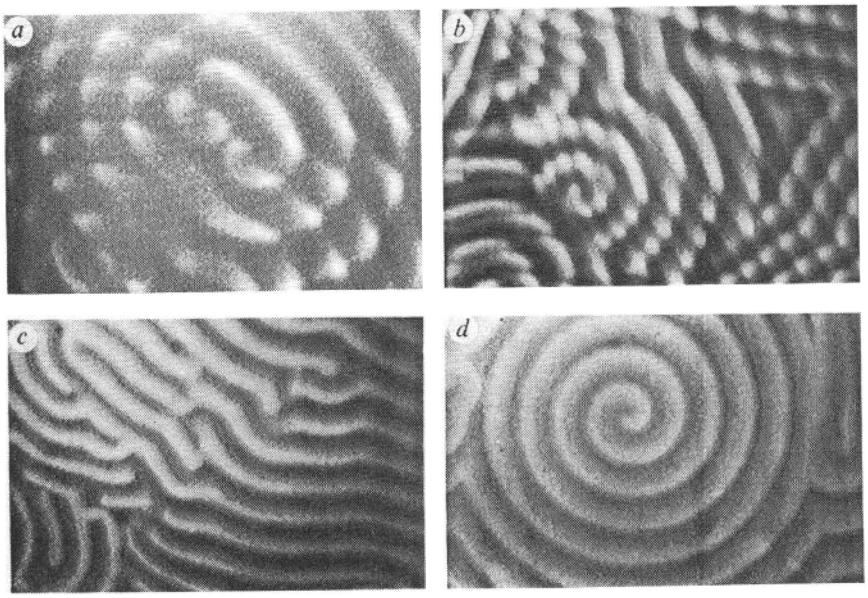

FIG. 3 Transition of spatiotemporal patterns from uncoupled to entrained; conditions are the same as in Fig. 1*b*. *a*, Behaviour after 5.5 h; *b*, 6.5 h; *c*, 11.0 h; *d*, 31.1 h. (The image of the spiral source in *d* was taken at a location near to that of the earlier images.)

media[13], which mimics the fast-slow dynamics of the Belousov-Zhabotinsky reaction[14]. Figure 4 shows one spiral on each side of the model membrane, evolving from uncoupled in **a** to fully entrained, although somewhat irregular, behaviour in *c*. An identical calculation with slightly higher coupling strength yields the more ordered behaviour in *d*, dominated by a single entrained spiral. Intermediate behaviour in *b* demonstrates the importance of relative wave orientation in the coupling, with ray-like domains of relatively uncoupled behaviour, and of partial and complete entrainment. The initially uncoupled spirals exhibit slightly different rotational periods (in a ratio of 11:12), and the higher-frequency spiral dominates throughout the evolution. The period of the entrained spiral in Fig. 4*d* lies between that of the initial spirals, reflecting the characteristics of both systems. These results indicate that the patterns observed in the experimental case result from spirals with slightly different frequencies on each side of the membrane. Other calculations for rotational periods in the ratio 1:2 show phase locking with

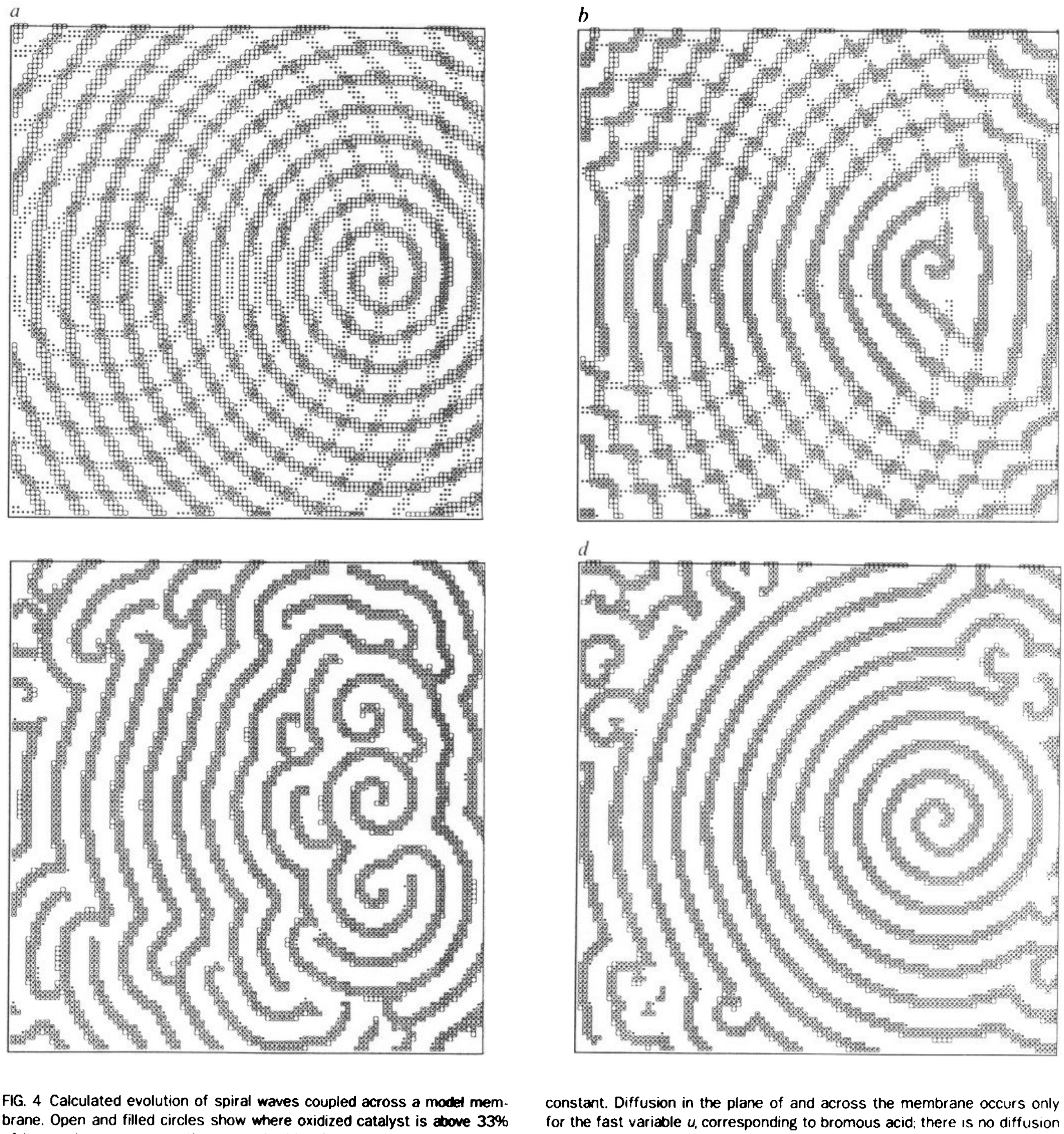

FIG. 4 Calculated evolution of spiral waves coupled across a model membrane. Open and filled circles show where oxidized catalyst is above 33% of its maximum concentration on each side of the membrane. The model for two coupled two-dimensional chemical-wave systems is based on a generic scheme for excitable media[13]: $\partial u/\partial t = f(u, v) + \nabla^2 u$, $\partial v/\partial t = g(u, v)$, where $f(u, v) = \varepsilon^{-1} u(1-u)(u - u_{th}(v))$, $g(u, v) = u - v$, and $u_{th} = (v+b)/a$. The two schemes are diffusively coupled by $\alpha(u_2 - u_1)$ and $\alpha(u_1 - u_2)$ terms for sides 1 and 2, respectively of the membrane, where α is transverse coupling constant. Diffusion in the plane of and across the membrane occurs only for the fast variable *u*, corresponding to bromous acid; there is no diffusion of the slow variable *v*, corresponding to the fixed catalyst. *a*, Initially uncoupled spirals. *b*, Interacting waves after 2,000 iterations. *c*, Entrained waves after 16,000 iterations. *d*, With stronger coupling: regular entrained spiral after 16,000 iterations. The transverse coupling constant $\alpha = 0.35$ in *a*–*c* and 0.45 in *d*. Parameter values: $a = 0.55$, $\varepsilon = 0.02$ and $b = 0.010$ and 0.016 for higher- and lower-frequency spirals. Grid: 200×200.

1 : 2 oscillations interspersed with 1 : 1 behaviour and, at a slightly different coupling strength, phase death[4], where the wave patterns on one side of the membrane are completely extinguished by those on the other side.

Cross-membrane coupling of spatiotemporal patterns provides a new configuration for investigating communication between chemical systems. Transverse gradients of messenger species give rise to the spontaneous formation of spiral waves, which govern the subsequent evolution of entrainment (which includes the possibility of phase locking). Further studies of such cross-membrane coupling may provide insights into intercellular communication and coupling of excitable media in biological systems[15]. □

Received 22 February; accepted 25 March 1991.

1. Bar-Eli, K. *J. phys. Chem.* **88**, 3616–3622 (1984).
2. Györgyi, L. & Field, R. J. *J. phys. Chem.* **92**, 7079–7088 (1988).
3. Aronson, D. G., Doedel, E. J. & Othmer, H. G. *Physica* D **25**, 20–104 (1987).
4. Crowley, M. F. & Epstein, I. R. *J. chem. Phys.* **93**, 2496–2502 (1989).
5. Bar-Eli, K. *J. phys. Chem.* **94**, 2368–2374 (1990).
6. Zaikin, A. N. & Zhabotinsky, A. M. *Nature* **225**, 535–537 (1970).
7. Winfree, A. T. *Science* **181**, 937–939 (1973).
8. Field, R. J. & Noyes, R. M. *J. Am. chem. Soc.* **96**, 2001–2006 (1974).
9. Eisenberg, A. & Yeager, H. L. (eds) *Perfluorinated Ionomer Membranes; Am. chem. Soc. Symp. Ser.* **180** (American Chemical Society, Washington, DC, 1982).
10. Larter, R. *Chem. Rev.* **90**, 355–381 (1990).
11. Maselko, J. & Showalter, K. *Nature* **339**, 609–611 (1989).
12. Yatsimirskii, K. B., Tikhonova, L. P., Kovalenko, A. S. & Moshkovich, F. S. *J. phys. Chem.* **93**, 2848–2852 (1989).
13. Barkley, D., Kness, M. & Tuckerman, S. *Phys. Rev.* A **42**, 2489–2492 (1990).
14. Tyson, J. J. & Fife, P. C. *J. chem. Phys.* **73**, 2224–2237 (1980).
15. Winfree, A. T. *When Time Breaks Down* (Princeton Univ. Press, 1987).
16. Maselko, J. & Showalter, K. *J. phys. Chem.* **93**, 2774–2780 (1988).

ACKNOWLEDGEMENTS. We thank the US NSF and NATO (Scientific Affairs Division) for financial support of this work. K.S. thanks Z. Noszticzius for recommending that KBr be added to the reactant stream.

