

Spatial patterns in a uniformly fed membrane reactor

G. Kshirsagar¹, Z. Noszticzius², W.D. McCormick and Harry L. Swinney³

Center for Nonlinear Dynamics and Department of Physics, The University of Texas, Austin, TX 78712, USA

A novel reactor, consisting of a thin membrane with each side exposed to fluid from a well-stirred flow reservoir, has been developed for the study of sustained chemical spatial patterns. This reactor bears some similarity to another continuously fed unstirred reactor with a uniform feed, the disk-shaped reactor developed by Tam et al. [J. Chem. Phys. 88 (1988) 3395], but the present reactor differs in two important aspects: (1) The effective residence time, which is determined by the thickness of the gel, can be very short (of the order of seconds). (2) The feed is from two reservoirs rather than one; this opens up new regions of chemical composition for study. Examples are presented of patterns obtained for the Belousov–Zhabotinsky reaction in the membrane reactor.

1. Introduction

Two decades ago Zhabotinsky [1], Winfree [2], and others conducted pioneering studies on the formation of spatial patterns in chemical systems. Those experiments have been followed by many others that have examined the patterns that form, usually in thin fluid layers, as a function of the initial chemical concentrations, temperature, and light intensity. Those studies have always concerned *transient* patterns—the patterns emerge, evolve continuously, and finally decay as the system approaches thermodynamic equilibrium. Recently a new generation of reactors has been developed that makes it possible to study *sustained* patterns: the chemical system is maintained in a well-defined nonequilibrium state by a chemical flux, just as in a CSTR (continuous flow stirred tank reactor), but in these new types of reactors there is no stirring in the region in which patterns can form. To emphasize the analogy and the contrast with stirred tank reactors, these new

types of reactors are sometimes called CFURs (continuous flow *unstirred* reactors). With these reactors it is now possible to study *bifurcations* in spatiotemporal patterns formed by reaction–diffusion systems. Control parameters can be increased and decreased through a particular transition to determine whether or not it is subcritical (hysteretic) or supercritical (nonhysteretic). Long-time series data can be obtained for a well-defined asymptotic state of the system and analyzed by the techniques of dynamical systems to obtain, for example, the generalized dimensions D_q , the spectrum of Lyapunov exponents, and the metric entropy [3]. The spatiotemporal character of a pattern can be deduced from space–time correlation functions and from the flow of information [4].

Two basic types of CFURs have been developed thus far. One type has an imposed chemical gradient, as in the two-dimensional ring-shaped reactor of Noszticzius et al. [5] and Kreisberg et al. [6], and in the effectively one-dimensional Couette reactor developed in Austin [7] and Bordeaux [8]. A second type of reactor has a uniform diffusive feed orthogonal to the line or plane in which a pattern forms. An example of this type of apparatus is the disk-shaped reactor of Tam et al. [9] and Skinner and Swinney [10]; the patterns form in a thin inert gel layer that is

¹Present address: Puritan-Bennett Corporation, 10800 Pflumm Road, Lenexa, KS 66215, USA.

²Permanent address: Institute of Physics, Technical University of Budapest, 1251 Budapest, Hungary.

³To whom correspondence should be addressed. e-mail: swinney@chaos.utexas.edu

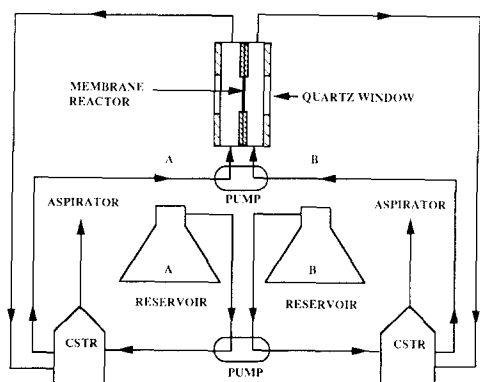


Fig. 1. Chemical patterns form in a thin gel-impregnated membrane placed between two compartments containing rapidly flowing reagents. In the present experiments reagents A and B are respectively the oxidant (KBrO_3 with or without H_2SO_4) and reductant of the BZ reaction (malonic acid and ferroin with or without H_2SO_4). The reactor body is constructed of plexiglas (polymethylmethacrylate). Circulating water from a thermostat maintains the temperature at $25.0 \pm 0.1^\circ\text{C}$.

in diffusive contact with a CSTR through a thin capillary array.

This paper describes a new type of reactor of the second type: patterns form in a thin gel layer placed between *two* compartments that may respectively contain, for example, the oxidant and reductant of a reaction. This design offers considerable flexibility for studies of sustained patterns under a wide range of chemical compositions. We have examined the versatility of this reactor using the Belousov–Zhabotinsky (BZ) reaction.

2. Experimental system

Fig. 1 is a schematic diagram of the system. The reaction occurs in a polyacrylamide-impregnated PVC membrane, 0.75 mm thick by 25 mm in diameter. The two sides of the membrane are identical compartments (each 1.9 ml in volume) fed with chemicals from two external CSTRs (each 4.0 ml in volume), which in turn are fed from reservoirs A and B, respectively; see the diagram in fig. 2. The feeds are maintained with peristaltic pumps.

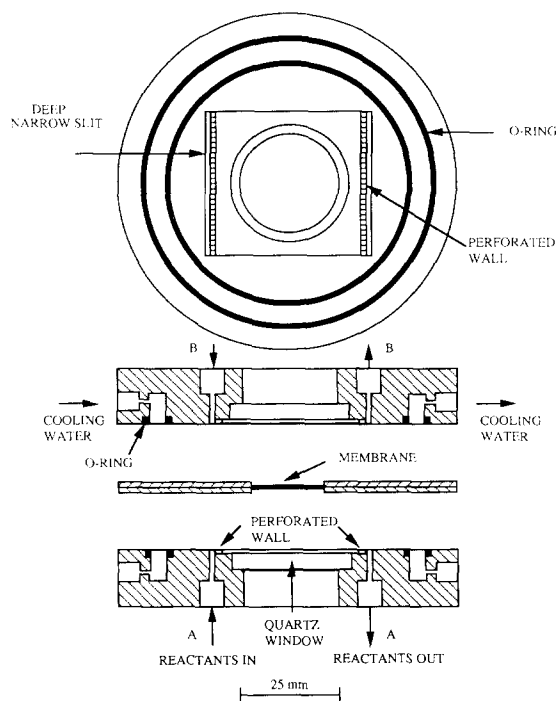


Fig. 2. Top view and exploded side view of the uniformly fed membrane reactor. The top view shows only the principal features while the side view gives more details. The circular membrane is held between two thin circular plexiglas plates that are compressed between the larger reactor components that contain the feed chemicals and have quartz windows for viewing the patterns. The perforated wall ensures uniform feed parallel to the membrane. The chemicals pass from the deep narrow slits through perforated walls into compartments (1 mm deep) in contact with the membrane.

The effective residence time of the reagents in the membrane reactor is $\sim d^2/\pi^2 D$, where D is the diffusion coefficient and d is the membrane thickness; this time is ~ 1 min for our membranes. The residence time of the reagents in the compartments in contact with the membrane must be short to insure uniform feed to the entire membrane. A compartment residence time of 18 s was found to yield reproducible patterns, but significantly longer residence times gave patterns that were clearly affected by nonuniformity of the feed. In the experiments the residence times of the two external CSTRs were varied in concert in the range from 17 to 68 min.

Most of our experiments were conducted with a PolySil^{#1} membrane with a pore size of 0.5 μm and a porosity of 70–80%; the membrane is made by incorporating silica in a PVC matrix. To decrease the porosity we impregnated the membrane with a polyacrylamide gel, which was made from the following solutions: A, 20% acrylamide; B, 4% piperazine diacrylamide (this cross-linking agent, from Bio-Rad Laboratories, is superior for our purposes to the usual N,N'-methylene bisacrylamide); C, 30% triethanol amine; and D, 20% ammonium persulfate. The PolySil membrane was first soaked under vacuum (to remove air trapped in membrane pores) in a solution containing 5 ml of A, 25 drops of B, and 6 drops of C (1 drop equals about 0.03 ml). Then 3 drops of D, the initiator for gel formation, was added to the solution containing the membrane, and the solution was stirred rapidly. The membrane and solution were then placed for 30 min in a mold between plexiglas plates separated by a 0.65 mm spacer, after which the membrane was rinsed to wash out any unreacted gel solution. The gel was then placed in water overnight and it would swell to a thickness of about 0.75 mm.

Reservoir solutions for the BZ reaction were made using reagent grade chemicals as supplied, except for KBrO_3 , which was doubly recrystallized before use. The solutions were passed through cellulose nitrate filters (0.45 μm pore size) and degassed before use. The control parameters in the experiments were KBrO_3 concentration in the reservoir and the residence time in the external CSTRs.

Patterns were viewed from the side of the membrane in contact with the compartment containing bromate, while the compartment on the other side of the membrane contained malonic acid and ferroin. Some experiments were conducted with the sulfuric acid on the bromate side,

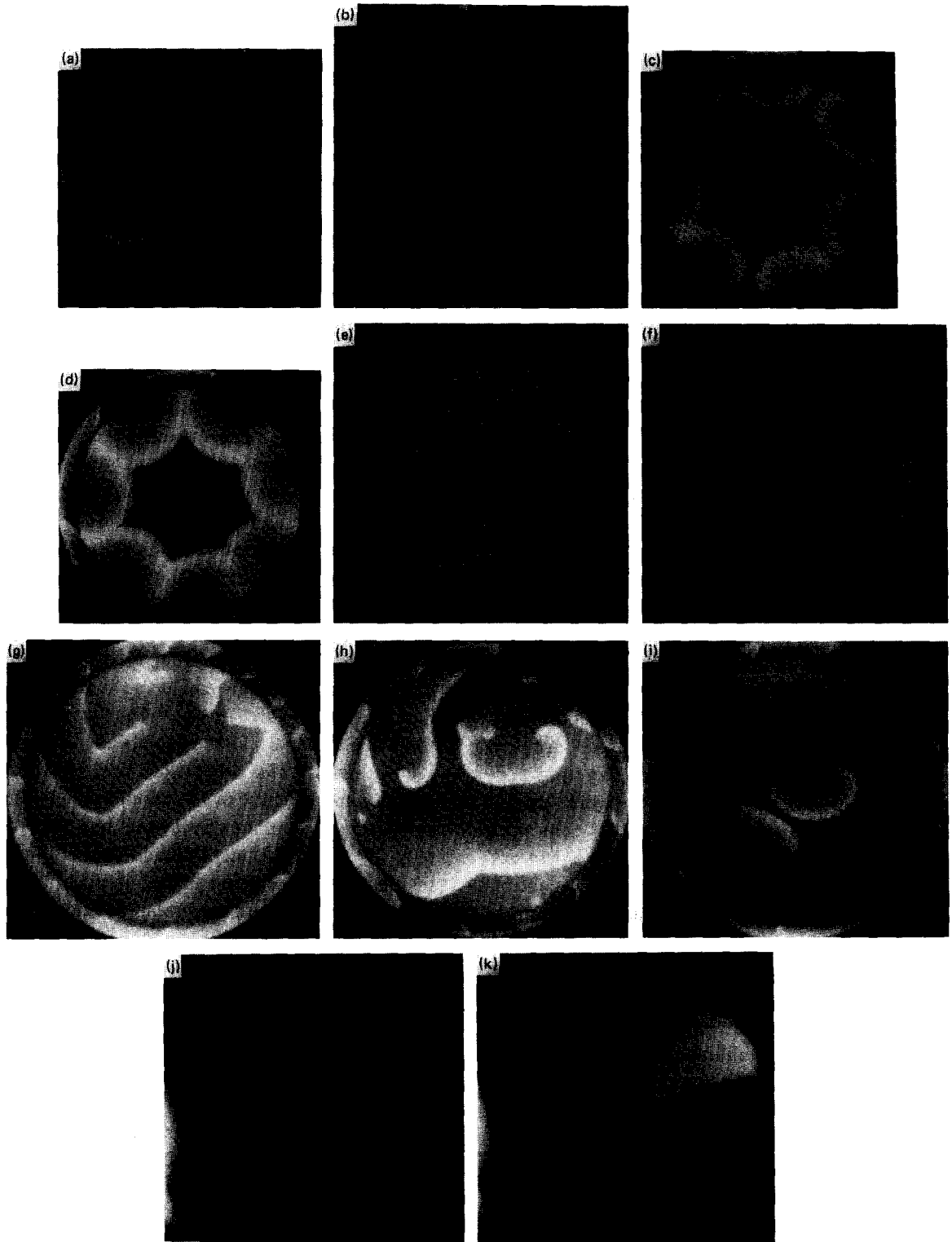
but for most the acid solution was on the ferroin side. The ferroin concentration was observed to depend on the sulfuric acid concentration in the reservoir; therefore, we examined the stability and equilibrium composition of the ferroin as a function of acid concentration, as described in the appendix.

3. Results

We have varied the bromate concentration and the residence time of the two external CSTRs while other parameters were held fixed. Waves have been observed to originate only in the rim of the membrane. No pacemakers occur in the central region, probably because of the short residence time. Waves can be created in the central region, however, by perturbation with UV light. Pacemakers and sustained rotating waves (*pinwheels* [5, 6]) can form spontaneously in the rim of the membrane, where the residence time is long because the plexiglas plates that support the membrane prevent the direct feed of reagent to that region. Pinwheels can be seen in the rim in figs. 3a–3i. A wave in the bulk that originated from a pacemaker in the membrane rim can be seen in fig. 3a. The pacemakers and pinwheels in the membrane rim can be completely eliminated by blocking the entry of reagents into this region (e.g., by filling the membrane rim with plexiglas dissolved in chloroform before it is impregnated with gel). In this case waves can be triggered with UV light, as in fig. 3j–3k.

We conducted experiments with UV light as a perturbation, using a ring-shaped lamp with peak output at 350 nm and a half-width of 50 nm. When the medium had partially recovered from a previous wave, then only the edge of the membrane in contact with the waves of the pinwheel was excitable, as shown for example in fig. 3c. When the medium was excitable and had completely recovered from a previous perturbation, the whole membrane could be excited, as shown in fig. 3e. The clear 7-fold symmetry of figs. 3c

^{#1}PolySil, a registered trademark of Polysciences, Inc., is a polyvinylchloride-silica-based membrane that is used for thin-layer chromatography. The silica in the membrane provides natural wetting characteristics, and it has greater thickness and mechanical strength than nitrocellulose membranes.



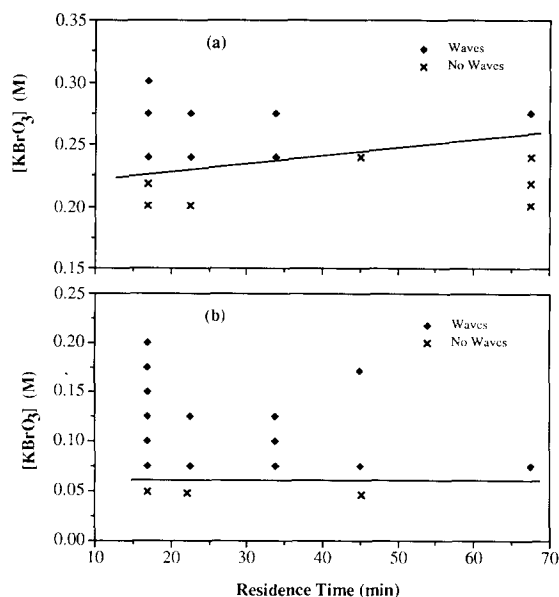


Fig. 4. Threshold for excitability determined with sulfuric acid (0.2 M) contained in the (a) ferriin-malonic acid reservoir and (b) bromate reservoir. The threshold for excitability is lower in (b) than in (a). Malonic acid concentration was 0.1 M; ferriin concentration was 0.00478 M in (a), 0.00600 M in (b).

and 3d, derived from the 7-wave pinwheel, and the rotational symmetry of figs. 3e and 3f attest to the uniformity of our reactor; thus this reactor should be ideal for studying the stability and lifetime of patterns imposed by exposure to light [11].

Fig. 4a is a phase diagram showing the threshold for excitability as a function of bromate concentration. Above the threshold waves spontaneously form in the unfed perimeter of the membrane where it is clamped between plexiglas plates. These waves propagate into the central portion of the membrane, as illustrated in fig. 3a. The wave front is sharp and the waves are thin when the sulfuric acid is fed with the malonic acid and ferriin, as in the experiments illustrated in figs. 3a–3i and the phase diagram in fig. 4a. The waves are thicker and the width increases with increasing bromate concentration when the sulfuric acid is fed with the bromate, as in figs. 3j–3k and in the phase diagram in fig. 4b. A similar effect was observed by Nagy-Ungvarai et al. [12] in experiments and simulations for the cerium-catalyzed BZ batch reaction. At a bromate concentration of 0.2 M or larger, three-dimensional effects and the effect of the finite size of the container become apparent. Simulations by Vasquez et al. [13] of a two-dimensional reaction-diffusion system with Oregonator kinetics support the observation that the width of the front increases with increasing bromate. Qualitatively, this is due to the higher bromate concentration, which leads both to a higher wave speed and to a longer time for the bromide concentration to build up and suppress the oxidation of ferriin.

◀ Fig. 3. Photographs of patterns formed in the membrane reactor: (a) A wave excited by a pacemaker in the rim of the gel. A spontaneously formed pinwheel exists in the rim, where the membrane holder blocks the direct feed of the reagents. (b) Quiescent state following the passage of the wave in (a); the system is in the refractory phase. (c) Effect of illumination with UV light for 5 min when the medium is in the refractory state after the passage of a wave; the 7-armed pinwheel generates a pattern with 7-fold symmetry. (d) Evolution of the system from (c) after the removal of the perturbation. (e) Effect of illumination with UV light for 2 min after the medium has sufficiently recovered from an excitation and is again fully excitable. (f) Evolution of the system from (e) after the removal of the perturbation. (g) At higher bromate concentration, 0.275 M rather than 0.240 M as in (a)–(f), the pinwheel excites waves that have different speeds in the rim and bulk, and this type of pattern forms. (h) Long-time evolution of the system in (g) to spirals (for same bromate concentration as in (g)). (i) Pattern formed from (h) after the residence time was reduced from 68 to 22 min (for same bromate concentration as in (g)). In (a)–(i), the sulfuric acid was contained in the ferriin-malonic acid reservoir. In the last two photographs, (j)–(k), the sulfuric acid was contained in the bromate reservoir, which results in thicker wave fronts: (j) Wave at 0.125 M bromate concentration. (k) A somewhat thicker wave obtains when the bromate concentration is increased to 0.175 M. Residence times: (a)–(f) 22 min, (g)–(h) 68 min, (i) 22 min, (j)–(k) 17 min. In all cases malonic acid concentration was 0.1 M and sulfuric acid concentration was 0.2 M; ferriin concentration was 0.00478 M in (a)–(i) and 0.00600 M in (j)–(k).

We also observe that leaching silica from the PolySil membrane (using 15% NaOH) leads to thicker waves. For the same chemistry the waves are considerably thicker if the gel-filled PolySil membrane is replaced by a gel that is supported by an Anopore filter^{#2}.

4. Discussion

The experiments described here successfully test and demonstrate the usefulness of the membrane reactor. Since the residence time for the reaction in the membrane is determined by the membrane thickness rather than by the residence time of the reagents in external CSTRs, the residence time for the membrane reactor can easily be made much shorter than in previous continuously fed unstirred reactors. Experiments can be conducted for a wide range of excitable and nonexcitable media with a flexibility in reagent composition that is not possible with other reactors developed for studying sustained two-dimensional patterns. For example, studies of chaotic spatiotemporal dynamics including phase turbulence [14, 15] and amplitude turbulence [14, 16] have been proposed for several years but have not been conducted in reaction–diffusion systems for lack of a suitable laboratory tool. The membrane reactor now provides such a tool.

Some measurements were made with membranes both thicker and thinner than the 0.75 mm thick membranes used for most of our study. In the thinnest membrane studied (0.2 mm thick), the patterns had a short wavelength (~ 0.2 mm) and poor contrast. The wave patterns appeared sharp and two-dimensional for membranes less than about 1 mm thick, but, of course, there are concentration gradients in the direction perpen-

dicular to the membrane, making all patterns in fact three-dimensional. Three-dimensional effects became apparent for thick membranes or high bromate concentration, and the visibility of the observed two-dimensional projection of the pattern rapidly decreased; no pattern was discernable for a 4 mm thick membrane, even for chemical compositions favoring excitability.

We have examined several other chemical compositions of the BZ reaction in addition to those described here. Most of the experiments were conducted with the sulfuric acid in the malonic acid and ferroin feed rather than the bromate feed because this leads to long gel life (~ 2 weeks) and to few CO₂ and CO bubbles. A malonic acid concentration of 0.1 M was found to be high enough to give good contrast but not so high that it led to significant bubble formation. Similarly, a ferroin concentration of 0.006 M was high enough to give good contrast but low enough so that bubble formation was not a problem. We have also obtained patterns with acetyl acetone rather than malonic acid as the organic substrate, a chemistry which has been shown to be nearly bubble free [17].

The membrane reactor should be particularly amenable to studies of dynamical behavior following a perturbation because the short residence times in the membrane lead to very rapid recovery. Future studies with this reactor should examine pattern formation for a range of chemical compositions and boundary conditions, particularly in inorganic oscillating reactions [18–20], which can have simpler mechanisms than the BZ system. Thus it should be possible to make quantitative comparisons of patterns observed in such experiments with the results of numerical simulations of reaction–diffusion model systems.

Acknowledgements

We thank Qi Ouyang and Mary Noszticzius for helpful discussions. This work is supported by BP Venture Research.

^{#2}Anopore is a registered trademark for an inorganic membrane that is a high purity matrix with an extremely well-defined capillary structure. It is also available as Anodisk, a membrane filter disk.

Appendix. Stability of ferroin under strongly acidic conditions

The concentration of ferroin obtained after mixing phenanthroline and ferrous ammonium sulfate decreases with increasing acid concentration. An excess of Fe(II) or phenanthroline can shift the complex equilibrium [21] and thereby stabilize ferroin at a higher concentration than that would be obtained from the stoichiometric ratio. For the typical acidic conditions of experiments on patterns in the BZ reaction there is essentially no free phenanthroline. Most of it is in the form of the 1:3 complex $\text{Fe}(\text{phen})_3^{2+}$ (ferroin) or the 1:1 complex; the 1:2 complex is highly unstable and has a negligibly small concentration at equilibrium. There is also a relatively small amount of protonated phenanthroline present.

At low pH (2–5) the ferroin concentration can be computed within experimental accuracy from the stoichiometric amounts of phenanthroline and ferrous ammonium sulfate. Under the strongly acidic conditions of our experiments, however, the full set of chemical equilibria need to be considered in order to compute the ferroin concentration accurately. Ferroin concentrations determined independently from optical absorption measurements at 488 nm (extinction coefficient = $10090 \pm 285 \text{ M}^{-1} \text{ cm}^{-1}$ [22]) agree within 5% with those computed numerically from the equations for the complex equilibrium [21]. At acid concentrations greater than 0.2 M, a difference between experimental and calculated values arises mainly due to activity coefficient corrections, which then must be taken into account.

The calculated ratio of ferroin to monophenanthroline complex decreases from 118 to 31 in the range $0.005 < [\text{H}^+] < 0.5 \text{ M}$, which is the typical acidity range for experiments on patterns in the BZ reaction. At $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$ ($[\text{H}^+] = 0.261 \text{ M}$ [23]), the effect of 50% excess iron is the same as 7.5% excess phenanthroline; however, for 50% excess iron there is significant amount of free Fe(II) and monophenanthroline complex (the ra-

tio of tris to mono complex is 21, compared to 62 for 7.5% excess phenanthroline).

When ferroin and malonic acid are together in a reservoir, the acidity is low (for malonic acid, $\text{p}K_1 = 2.86$, $\text{p}K_2 = 5.7$ [24]) and within the accuracy of the measurement (about 3%) the stoichiometric amount of ferroin is obtained; acidity prevents air oxidation of Fe(II) and the solutions remain stable. When ferroin, malonic acid, and sulfuric acid are in the same reservoir, the ferroin concentration is determined by the effective concentration of $[\text{H}^+]$, which is mainly due to the sulfuric acid alone since the dissociation constant of malonic acid is very low. At high acidity the solutions become less dark and the contrast of the patterns decreases. It is not clear that the mono complex of Fe(II) plays the same role in the BZ reaction as ferroin. Our experiments confirm the validity of the equilibrium data [21] at the acid concentrations we have used, and suggest that to increase the ratio of the tris to the mono complex of phenanthroline, an excess of phenanthroline rather than Fe(II) is preferred.

References

- [1] A.M. Zhabotinsky, in: *Oscillating Processes in Biological and Chemical Systems*, ed. G.M. Frank (Science Publ., Moscow, 1967) p. 149;
- [2] A.N. Zaikin and A.M. Zhabotinsky, *Nature* 225 (1970) 535.
- [3] A.T. Winfree, *Science* 175 (1972) 634.
- [4] J.P. Eckmann and D. Ruelle, *Rev. Mod. Phys.* 57 (1985) 617.
- [5] K. Kaneko, *Physica D* 37 (1989) 60;
- [6] J.A. Vastano and H.L. Swinney, *Phys. Rev. Lett.* 60 (1988) 1773.
- [7] Z. Noszticzius, W. Horsthemke, W.D. McCormick, H.L. Swinney and W.Y. Tam, *Nature* 329 (1987) 619.
- [8] N. Kreisberg, W.D. McCormick and H.L. Swinney, *J. Chem. Phys.* 91 (1989) 6532.
- [9] W.Y. Tam, J.A. Vastano, H.L. Swinney and W. Horsthemke, *Phys. Rev. Lett.* 61 (1988) 2163;
- [10] W.Y. Tam and H.L. Swinney, *Physica D* 46 (1990) 10;
- [11] J.A. Vastano, T. Russo and H.L. Swinney, *Physica D* 46 (1990) 23.
- [12] Q. Ouyang, J. Boissonade, J.C. Roux and P. De Kepper, *Phys. Lett. A* 134 (1989) 287;
- [13] P. De Kepper, Q. Ouyang, J. Boissonade, J.C. Roux,

- Reaction Kinet. Catal. Lett. 42 (1990) 275;
Q. Ouyang, V. Castets, J. Boissonade, J.C. Roux, P. De Kepper and H.L. Swinney, *J. Chem. Phys.*, submitted for publication.
- [9] W.Y. Tam, W. Horsthemke, Z. Noszticzius and H.L. Swinney, *J. Chem. Phys.* 88 (1988) 3395.
- [10] G. Skinner and H.L. Swinney, *Physica D* 48 (1991) 1.
- [11] L. Kuhnert, K.I. Agladze and V.I. Krinsky, *Nature* 337 (1989) 244.
- [12] Zs. Nagy-Ungvarai, S.C. Müller, J.J. Tyson and B. Hess, *J. Phys. Chem.* 93 (1989) 2760.
- [13] D. Vasquez, W.D. McCormick, W. Horsthemke and Z. Noszticzius, *Reaction Kinet. Catal. Lett.* 42 (1990) 253.
- [14] Y. Kuramoto, *Prog. Theor. Phys.* 71 (1984) 1182.
- [15] Y. Pomeau, A. Pumir and P. Pelce, *J. Stat. Phys.* 37 (1984) 39.
- [16] H.R. Brand, P.S. Lomdahl and A.C. Newell, *Physica D* 23 (1986) 345.
- [17] Q. Ouyang, W.Y. Tam, P. De Kepper, W.D. McCormick, Z. Noszticzius and H.L. Swinney, *J. Phys. Chem.* 91 (1987) 2181.
- [18] P. De Kepper, I.R. Epstein, K. Kustin and M. Orban, *J. Phys. Chem.* 86 (1982) 170.
- [19] D.M. Weitz and I.R. Epstein, *J. Phys. Chem.* 88 (1984) 5300.
- [20] I. Lengyel, G. Rabai and I.R. Epstein, *J. Am. Chem. Soc.* 112 (1990) 4660.
- [21] W.W. Brandt, F.P. Dwyer and E.C. Gyarfás, *Chem. Rev.* 54 (1954) 959.
- [22] P.M. Wood and J. Ross, *J. Chem. Phys.* 82 (1985) 1924.
- [23] E.B. Robertson and H.B. Dunford, *J. Am. Chem. Soc.* 86 (1964) 5080.
- [24] J.A. Dean, ed., *Lange's Handbook of Chemistry*, 12th Ed. (McGraw-Hill, New York, 1979) pp. 5–32.