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COMMUNICATIONS

Sustained spiral waves in a continuously fed unstirred chemical reactor

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Many experiments on spatial self-organization in chemical systems have yielded spiral waves and concentric ring patterns.[1–15] Those experiments were conducted in closed reactors; hence the systems evolved irreversibly and uncontrollably towards thermodynamic equilibrium. The transient nature of the spatial patterns and the lack of a well-defined control parameter complicates the interpretation of those experiments—existing theories concern the asymptotic (long time) states.[16,17]

About a decade ago the CSTR (continuous flow stirred tank reactor) replaced closed reactors in experiments on well-mixed oscillating chemical reactions. Subsequently, a wide variety of new dynamical phenomena were discovered.[18]

Here we introduce a continuously fed unstirred reactor (CFUR), which can serve as a tool for systematic studies of spatial pattern formation in the same way that the CSTR has served in studies of homogeneous reations. The CFUR, diagrammed in Fig. 1(a), can be maintained indefinitely at a fixed distance away from equilibrium by the continuous feed of reagents.[19] The feed is uniform and in a direction perpendicular to the plane in which patterns can form.

The disk-shaped reaction region in which patterns can form contains a gel that prevents the convective motion that has plagued some previous studies of chemical pattern formation. The gel allows mass transport through diffusion, yet it is inert to the chemicals of the reaction. (The reaction studied in the present experiments was the Belousov–Zhabotinskii reaction.) A crucial feature of the reactor is a glass capillary array that connects the reactor to a CSTR. The array ensures that only *vertical* mass transport occurs between the gel and the CSTR. If horizontal diffusion were not suppressed, spatial pattern formation could occur already in the capillary array.

Spiral patterns such as those shown in Fig. 1(b) form when the $NaBrO_3$ concentration exceeds a value of about 0.018 M. The spirals form quickly after the start of an experiment for $NaBrO_3$ concentrations just beyond 0.018 M, but for concentrations above about 0.025 M, irregular wave fronts form first, followed many hours later by the appearance of one or more spirals. The formation of spirals from the irregular wave fronts can be initiated by a perturbation. For example, stopping the stirrer for a short time creates a spatial inhomogeneity in the CSTR, and hence in the feed to the gel; this perturbation breaks up a wave front into two disconnected fronts, the interior tips of which then evolve into spiral cores. The right-hand photograph in Fig. 1(b) shows spiral waves generated by such a perturbation.

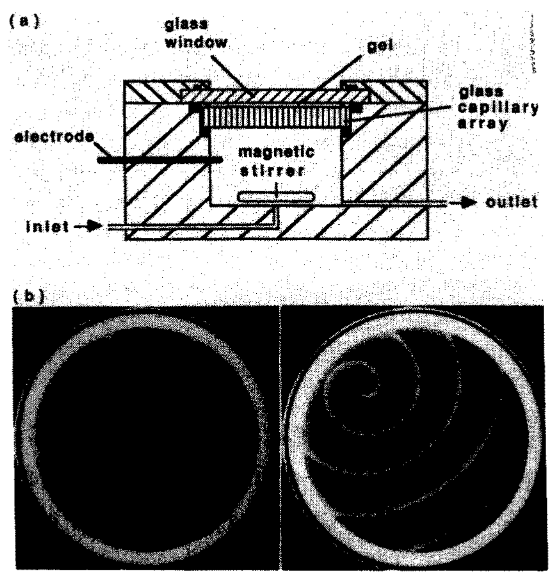

FIG. 1. (a) A CFUR consisting of a 0.076 cm thick polyacrylamide gel, sandwiched between a glass window and a glass capillary array (2.54 cm diameter, 0.1 cm thick) that has evenly spaced 10 μm diameter capillaries (a Galileo Electro-Optics capillary array). The CFUR communicates through the capillary array with a CSTR [volume, 5.3 cm^3; pressure, 10 atm (to prevent bubble formation); stirring rate, 1900 rpm; temperature, 23 °C]. A filter membrane (0.2 μm pore size) between the gel and the array provides a white background for pattern visualization. The four feeds, combined into a single line before entering the CSTR, were: (1) H_2SO_4 (0.2 M), (2) malonic acid (0.05 M) and ferroin (0.0025 M), (3) $NaBrO_3$, and (4) water; the concentrations are the values in the reactor. The flow rates for (1) and (2) were 10 ml/h, while the flow rates for (3) and (4) were varied to change the $NaBrO_3$ concentration over the range 0.01–0.05 M; the total flow rate was 30 ml/h. (b) Spiral waves observed at $NaBrO_3$ concentrations of 0.0195 M (left) and 0.0500 M (right).

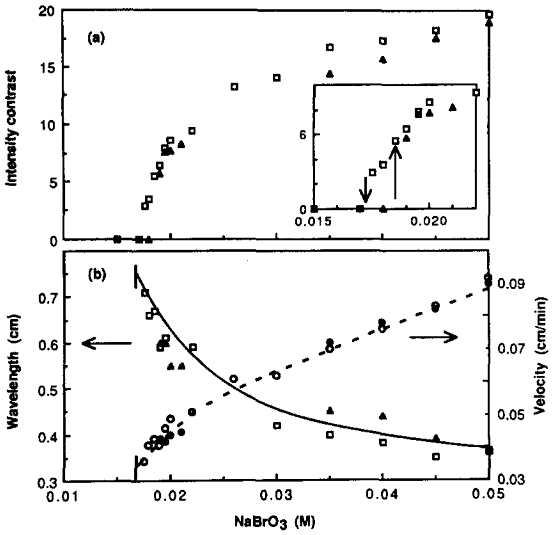

FIG. 2. (a) The intensity contrast, which is the difference between the maximum intensity of a spiral wave front (the oxidized state) and the minimum intensity (the reduced state), is shown as a function of $NaBrO_3$ concentration (□, decreasing concentration; ▲, increasing concentration). The appearance (disappearance) of the spiral waves with increasing (decreasing) concentration is indicated by ↑ (↓) in the inset. (b) The wavelength and the velocity of the spiral waves are shown as a function of $NaBrO_3$ concentration. The wavelength (velocity) is denoted by the solid (dashed) line and the symbols □ and ▲ (○ and ●); open symbols indicate measurements for decreasing concentration, solid symbols, increasing concentration. The reaction in the CSTR reservoir was oscillating in the range 0.02 M $< [NaBrO_3] <$ 0.04 M and time independent outside this range.

The transition to spirals with increasing $NaBrO_3$ concentration is illustrated in Fig. 2. A small amount of hysteresis in the spiral transition was observed, as the inset in Fig. 2(a) illustrates. The location and size of the hysteresis loop were reproducible within a few percent in runs with different gels. The measured values of the wave velocity and wavelength, shown in Fig. 2(b), were also reproducible in different runs.

In summary, the CFUR makes it possible now to study the *stability* of chemical patterns and the *transitions* between well-defined states with different patterns.

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High-pressure NMR study of the dynamical solvent effects on the rotation of coordinated ethylene in $(\pi\text{-}C_5H_5)Rh(C_2H_4)_2$

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The dynamical solvent effects on the unimolecular isomerization dynamics have recently received considerable theoretical and experimental attention.[1–4] The theoretical models based on an early model developed by Kramers[5] predict a bell-shaped dependence of the barrier crossing rate upon the solvent friction. At low friction, in the so-called inertial regime, the barrier-crossing rate increases with the solvent friction. In the high-friction (diffusive) regime, however, the barrier crossing rate decreases with the solvent friction. This turnover behavior has been observed in the chair-boat inversion of cyclohexane in CS_2,[3] and Hochstrasser *et al.*[6] have recently reported the Kramers turnover region in the isomerization of *trans*-stilbene using high-pressure gaseous ethane. In addition, Troe[7] has implied such behavior for stilbene isomerization by combining experiments both in the liquid and in gases at high pressure. Nevertheless, most of the studied systems in condensed media fall into the intermediate- to high-friction regime. Hynes *et al.*[1,8] argue that the low-friction regime is essentially a problem in internal vibrational relaxation and activation. However, re-

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