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Pattern Formation in Reaction−Diffusion Systems: Cellular Acidity Fronts

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Propagating fronts with cellular structure may emerge in an initially homogeneously distributed acid-catalyzed reaction mixture where the hydrogen ions are partially immobilized with a complexing agent. The evolution of this spatial structure is a further type of spontaneous diffusion-driven spatiotemporal pattern formation in a chemical system.

An autocatalytic reaction in a thin layer of unstirred solution can yield a reaction−diffusion front.[1−3] A planar front produced by the addition of a small amount of autocatalyst propagates into the homogeneous reactant zone and retains its planar configuration under normal conditions. In systems exhibiting cubic autocatalytic kinetics and in which the reactants diffuse faster than the autocatalyst, the planar front may lose stability resulting in the formation of a cellular structure accompanied by loss of symmetry[4,5] similarly to thermodiffusive fronts in premixed flames.[6,7] The iodate−arsenous acid reaction provided the first experimental evidence to this type of instability by exhibiting small deviations from the planar front in good agreement with modeling calculations.[5]

The acid-catalyzed reaction between chlorite and tetrathionate ions[8]

$$2S_4O_6^{2-} + 7ClO_2^- + 6H_2O \rightarrow 8SO_4^{2-} + 7Cl^- + 12H^+$$
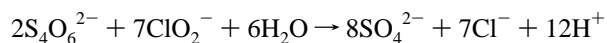
satisfies the kinetic requirement for the onset of instability as the determined empirical rate law of the reaction shows second-order kinetics with respect to the autocatalyst hydrogen ion.[9] In aqueous solutions the hydrogen ions diffuse approximately a magnitude faster than other small hydrated ions with the exception of hydroxide ion. The instability of planar symmetry

resulting in the formation of cells in a reaction−diffusion front, however, requires an autocatalyst with low diffusivity compared to the reactants. Experimentally this can be achieved by introducing an immobile complexing agent[10] which reversibly binds hydrogen ions without interfering with the chlorite−tetrathionate reaction.

Throughout the experiments reagent-grade chemicals were used, except NaClO$_2$, which was recrystallized[9] to achieve a purity higher than 99.5%. Thin hydrogel made of cross-linked polyacrylamide was utilized as a two-dimensional reaction medium.[11] Toward small hydrated ions it acts as an aqueous solution allowing free diffusion; at the same time it eliminates any hydrodynamic effects that would appear in the presence of convection. It further allows the incorporation of carboxylate groups into the carbon chain during polymerization with the addition of an appropriate amount of sodium methacrylate to the monomer solution. The immobilized carboxylate groups reversibly bind hydrogen ions resulting in an effective diffusion coefficient for hydrogen ions much smaller than that for the reactants. After polymerization the hydrogel was soaked in the reactant mixture prepared with doubly distilled water. Congo red indicator was added to the solution to make the reaction front visible as a result of color change. A chemical front was initiated along the edge of the rectangular gel by bringing another strip of gel containing product mixture with excess autocatalyst into contact with the reactant medium. The propagating reaction−diffusion front was monitored using a
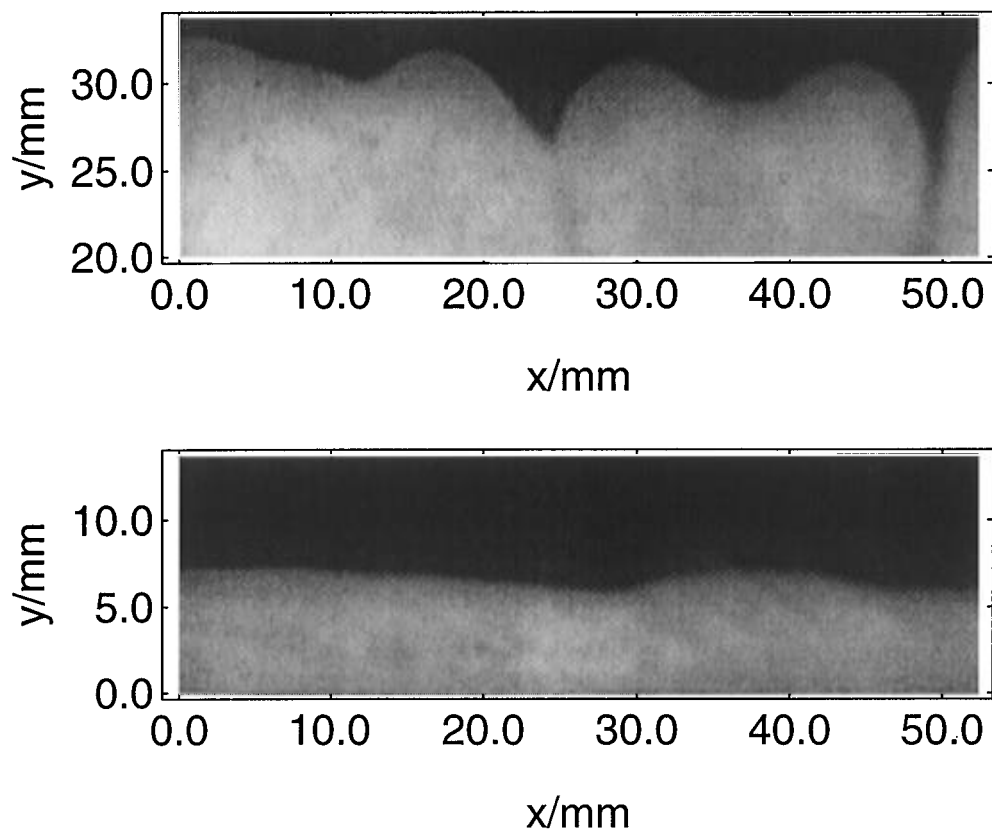

Figure 1. Evolution of a slightly perturbed planar front (bottom) leading to a cellular structure (top). Dark regions correspond to the unreacted solution ahead of, and light ones to the product mixture behind the front. Bottom: front at $t = 1$ h after initiation resembles the initial geometry. Top: front at $t = 19$ h exhibits definite cell formation. The reagent concentrations are $[K_2S_4O_6] = 5.0 \times 10^{-3}$ M, $[NaClO_2] = 0.02M$, $[NaOH] = 10^{-3}$ M, $[congo\ red] = 0.04\%$. The concentration of sodium methacrylate in the gel is 0.0225 M (0.800% methacrylate in the copolymer). The temperature of the solution is 23 ± 1 °C.

video camera, and the acquired images were digitally stored for further processing.

The initial front geometry simply reflects the shape of the interface between the two gels. With planar initiation in methacrylate-free hydrogel the structure remains stable as the front propagates into the fresh reactant zone. In polymer containing carboxylate groups, however, the planar front geometry loses stability; microscopic perturbations due to random noise are amplified leading to a nonplanar, cellular structure in the front as shown in Figure 1. The cells are characterized by smooth leading edge and joined in sharp cusps pointing opposite to the direction of propagation. The size of the individual cells is an intrinsic property of the system and independent of the initiation.

The evolution of front from a translationally perturbed initial geometry is illustrated in Figures 2 and 3. In the former case the reaction is run in methacrylate-free gel allowing free diffusion of the autocatalyst hydrogen ions. The initial sharp corners are smoothed out as the geometry is transforming into the stable planar form. In the latter the hydrogen ions are immobilized in the gel containing methacrylate, resulting in the destabilization of the planar front. The cellular structure evolved is not simply a reflection of the initial geometry; cusps connecting adjacent cells may appear from originally invisible perturbations due to random noise present in experimental systems as shown in Figure 3.

We can rationalize the existence of these cells by considering the diffusive fluxes of the reactants and the autocatalyst in a slightly perturbed nonplanar front profile compared to that in a planar one.[4,7] In the leading segments of the front there is an additional flux of the reactants due to the curvature in the front profile resulting in an increase in the reaction rate and hence in
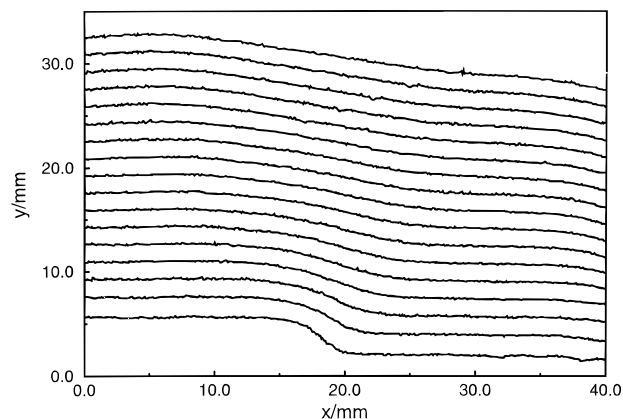

Figure 2. Front profiles showing the propagation of a translationally perturbed front in methacrylate-free hydrogel at $\Delta t = 6$ min intervals. The initial perturbation is decreased with the front profile evolving toward the stable planar geometry. Conditions and reactant concentrations are the same as in Figure 1.

the propagation velocity. In the trailing segments, however, there is less reactant available leading to a decrease in the velocity. Therefore the diffusion of the reactants tends to increase the curvature in the front. The opposite case arises for the diffusion of the autocatalyst; the curvature decreases stabilizing the planar structure. The outcome of these two competing transport processes is determined by the relative magnitude of the diffusion coefficients for the reactants and the autocatalyst, which—in our experiments—may be controlled with the amount of methacrylate in the hydrogel. With the hydrogen ions diffusing faster than the reactant chlorite and tetrathionate ions in methacrylate-free gel, the diffusion of the
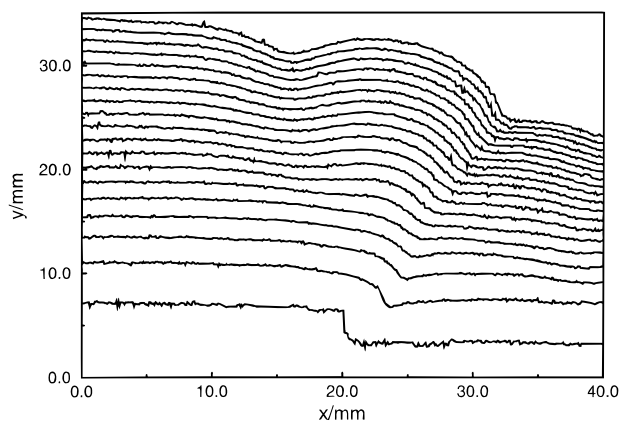
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Figure 3. Front profiles showing the propagation of a translationally perturbed front in hydrogel containing 0.0225 M methacrylate at $\Delta t = 1$ h intervals. Three cells are formed with one cusp originating from the initial perturbation and the other from inherent noise. Conditions and reactant concentrations are the same as in Figure 1.

autocatalyst ensures the stability of the planar symmetry (Figure 2). When the hydrogen ions are partially immobilized with carboxylate groups in the gel, the diffusion of the reactants will dominate leading to the amplification of the initial experimental noise; the planar front loses stability and a cellular front structure develops, as Figures 1 and 3 illustrate. The introduction of methacrylate in the hydrogel does not break the homogeneity of the medium, which was tested in a separate experiment using an excitable Belousov−Zhabotinsky solution. The obtained spiral waves and target patterns showed no irregularity that would otherwise appear in a heterogeneous medium.[12]

The evolution of cellular front structure accompanied by loss of symmetry is presented in a simple chemical system. Similarly to other diffusion-driven spatiotemporal pattern formation,[13−15] the unequal diffusivities of species give rise to the instability of the homogeneous state. These spontaneous patterns have been typically associated with complex chemical[13−15] and biological[16,17] processes. Our experiments, however, demonstrate that even a single autocatalytic reaction may yield patterned front structure.

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