Pattern Formation at Liquid Interfaces

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Although many examples of pattern formation resulting from chemical reactions at liquid interfaces are known, few have been studied in detail. We report a quantitative study of patterns formed by the photoproduction of Fe^{2+} and its subsequent reaction to form Turnbull's Blue. The experiment leads to the postulation of a mechanism in which autocatalysis is enhanced by double diffusion. The phase diagram contains a line of phase transitions whose critical behavior is discussed.

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Patterns can be formed when chemical reactions occur at interfaces of unstirred liquids. The phenomenon has been observed[1,2] for a large variety of reactions that yield colored products. In some cases one of the reactants is a gas that is in contact with the surface, while in others a reactant is allowed to diffuse to the surface through a membrane; patterns also can be formed by photochemical reactions that are driven by irradiation of the interface. After an initial stage during which the spatial distribution of the products remains uniform, concentration inhomogeneities with a characteristic wavelength develop in the surface layer.

The fact that such patterns are found in a wide variety of reactions suggests that there may be a general mechanism for their formation, i.e., one in which the chemical reaction triggers a physical instability. Several mechanisms have been postulated for the origin of the instabilities.[2,3] There is enough information to reject some of the mechanisms, but the experiments have generally not been sufficiently quantitative to distinguish between others. We describe here the results of a detailed study of pattern formation in one reaction and provide evidence for a specific type of physico-chemical instability. The mechanism predicts the existence of a "phase transition" point at which the wavelength of the pattern and its onset time diverge according to power laws.

We have focused our attention on the photoreduction of Fe^{3+} to Fe^{2+} in the presence of oxalic acid. A colored product is formed when the Fe^{2+} reacts with ferricyanide ions. The reactions can be written

$$4Fe^{3+} + (COOH)_2 \xrightarrow{uv} 4Fe^{2+} + 4H^+ + 2CO_2, \qquad (1)$$

$$Fe^{2+} + Fe(CN)_6^{3-} \rightarrow Fe^{II}Fe^{III}(CN)_6^-, \qquad (2)$$

although the mechanism is more complex. The blue product is $KFe^{II}Fe^{III}(CN)_6$ (Turnbull's Blue), which is insoluble in water but which forms a colloidal suspension in the presence of oxalic acid. The CO_2 remains in solution. This reaction has previously been studied by Avnir and co-workers,[2] but our experiments are more extensive and are not completely in accord with theirs.

We present a brief account of the experimental details here; a full description will be given later.[4] The solutions were illuminated from above with a 100-W mercury arc. A lens and circular apertures were used to produce a 20-mm-diam beam of nearly uniform profile. To reduce the infrared component, the beam was reflected from a "cold mirror" that has its maximum reflectivity at about 325 nm. The area in which the pattern formed was defined by smaller apertures cut in transparent adhesive tape. The tape transmits the residual ir radiation but attenuates the uv. Thus the full circular spot on the surface is heated uniformly but only a portion is illuminated by uv. The patterns produced in this way are remarkably more regular and stable than those obtained by previous investigators.[2]

For most of the experiments the cells were made from two microscopic slides separated by rubber-band spacers, but studies were also performed on free interfaces. The development of the pattern was monitored with a television camera and recorded. Measurements were usually carried out at room temperature.

A typical pattern is shown in Fig. 1. A homogeneous blue layer of product first develops at the upper interface (either liquid-gas or liquid-air). After several minutes the concentration of the product, i.e., the intensity of the blue color, increases at the vertices and edges of the illuminated square. At the same time, weaker lines of higher concentration also begin to appear inside the square. The density of blue product at their intersections

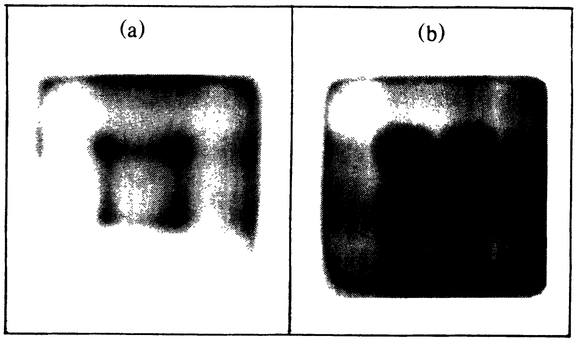

FIG. 1. Product concentration pattern, with $c_F=0.004M$, $c_O=0.60M$, and $c_C=0.020M$, viewed from above after (a) $t=360$ s and (b) $t=450$ s. The pattern in (a) is not associated with flow, while in (b) droplets have descended and spread out over the lower interface.

is nearly as intense as that of the edges. Droplets then form at each vertex and along the edges. The concentrations at the intersections within the square continue to increase and droplets begin to fall from each of these "dots." Once the droplets reach the bottom they spread and merge. Experiments with square apertures of different dimensions and with circular apertures demonstrate that L, the characteristic length scale of the pattern, does not depend on the size or shape of the aperture. This length scale is also independent of h, the height of the fluid, as long as $h>0.6L$. For $h<0.6L$, L decreases linearly with h until at a thickness of about 0.1 mm the product layer remains homogeneous.

The dependence on the concentrations of the reactants was studied in experiments in which the illuminated area was a 5.2-mm square and the fluid depth was 1 mm. In one set of studies the molar ratio of oxalic acid to $FeCl_3$ was held constant and the concentrations of $FeCl_3$ (c_F) and of $K_3Fe(CN)_6$ (c_C) were varied. Experiments were also carried out in which the oxalic acid concentration (c_O) was fixed and c_F was varied along a path of constant c_O. Figure 2 shows the number of spots in the irradiated area as a function of c_F and c_C with $c_O=15c_F$. The diagram reveals two different regimes: At low c_C the number of spots increases strongly with increasing c_F; at high c_C, a pattern of four spots (2×2) is always observed, independent of both reactant concentrations. The border between these two regimes is roughly along the line $c_C/c_F=5$, indicated in Fig. 2. The intensity of the pattern increases with increasing c_F and decreases with increasing c_C. For very low c_C ($\leq 0.0003M$) a blue homogeneous layer is formed, but no pattern formation occurs. Near the border line, L is commensurate with the size d of the aperture, i.e., $L=\frac{1}{3}d$ or $\frac{1}{4}d$ (see Fig. 2). This suggests that there could be many more commensurate "phases" but with smaller stability intervals.

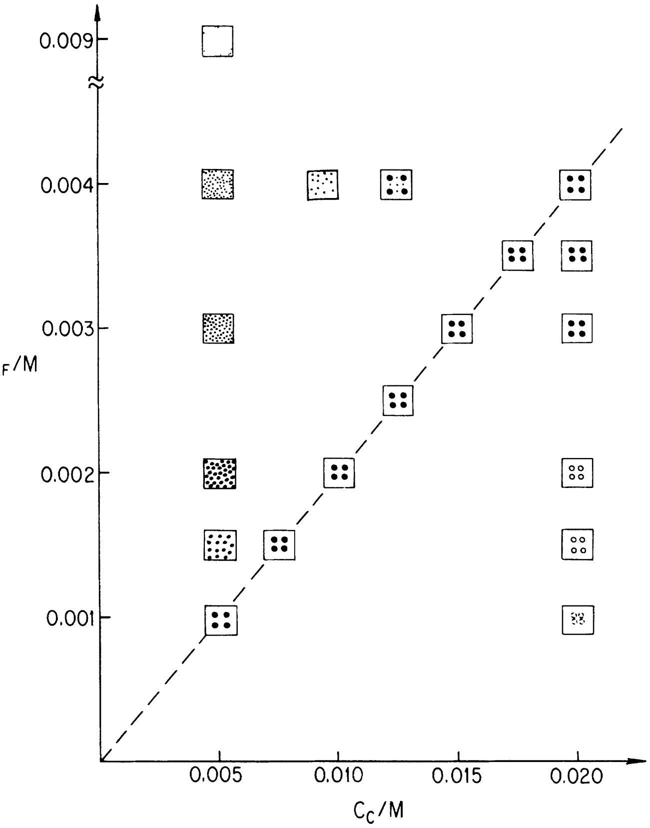

FIG. 2. Phase diagram. The pattern is shown as a function of the $K_3Fe(CN)_6$ concentration (c_C) and the $FeCl_3$ concentration (c_F). The dashed line is the locus points c_{Fc} where the length scale L becomes comparable to the illuminated area.

For experiments in which c_O was varied at constant c_F/c_C, it was found that L increases (i.e., the number of spots decreases) with decreasing c_O. We have never observed L values greater than 1.7 mm. Another characteristic of the pattern formation is the onset time t_0, the time after the start of irradiation at which the instability appears. At constant c_O the onset time varies linearly with L.

It is well established[5] that patterns at fluid interfaces can be caused by convection. Since the product layer formed in our experiments is denser than the surrounding solution, a convection mechanism might be thought to be applicable. However, despite the fact that droplets fall to the bottom of the cell during the *second* stage of pattern formation, neither we nor Avnir and co-workers[2] have observed flows during the initial stage. To test for convective effects, we changed the viscosity η by using glycerol-water mixtures as solvents and observed that L *decreases* strongly with increasing η, in disagreement with any flow-based mechanism. Furthermore, at very low c_C ($<3\times10^4M$) the pattern remains homogeneous despite the formation of the denser layer at the surface. Thus, the underlying mechanism must be due solely to the coupled reaction-diffusion system. Linear reaction-diffusion systems do not show pattern formation and indeed the rate of reaction (2) markedly increases on consumption of ferricyanide for $c_C \gtrsim 0.005M$, an autocatalytic effect. Since we observe that pattern formation continues after termination of radiation, the pattern formation is, in fact, associated with the second step.

We will not be concerned here with the chemistry of the autocatalytic mechanism itself, but we will discuss only the consequences for pattern formation. The second step of the reaction can be represented by the following reaction-diffusion system:

$$dR/dt = J - k(P)R + D_R\nabla^2 R, \tag{3}$$

$$dP/dt = k(P)R + D_P\nabla^2 P. \tag{4}$$

Here J is the photoproduction rate of reactant R, in this case Fe^{2+}; P is the concentration of the product, Turnbull's Blue; $k(P)$ is the product-dependent reaction rate[4] or order 1 min^{-1}; and D_R and D_P are the diffusion constants of the reactant and product, respectively. We take $D_R \gg D_P$, in accord with the literature[6] values: 2.5×10^{-7} $cm^2\,s^{-1}$ for Turnbull's Blue and 1.1×10^{-5} $cm^2\,s^{-1}$ for $FeCl_3$. Note that Eqs. (3) and (4) imply a conservation law for $R(t)+P(t)-Jt$.

The proposed mechanism is really the chemical analog of the double-diffusion instability.[7] Imagine a small local increase in P that, because of the nonlinearity, leads to a small corresponding increase in the reaction rate and thus to a decrease in R. Since R diffuses rapidly and P slowly, the decrease in R is replenished while the excess P is retained. The initial concentration fluctuation thus keeps growing and growing. The difference in diffusion constants "magnifies" the nonlinearity.

The analysis will be published elsewhere,[8] but the main predictions are as follows. Assume that we start with the homogeneous solution ($R_0 = J/k$ and $P_0 = Jt$). It is easy to show that this solution becomes unstable once R_0 (or J) exceeds a critical concentration $R_c = (D_P/D_R)k[dk/dP]_{P=P_0}^{-1}$. Note that if $D_P \ll D_R$ even a very *weak* concentration dependence of k leads to an instability. After the homogeneous solution has destabilized, the reactant concentration R in Eq. (3) indeed develops into a lattice of spots with high reactant concentration. If we linearize $k(P)$ around P_0 then the length scale L depends on R_0 as

$$L/\xi \approx \begin{cases} 2/[(R_0/R_c)-1]^{1/2}, & R_0 \approx R_c, \\ 2.7, & R_0 \gg R_c, \end{cases} \tag{5}$$

where $\xi = (D_R/k)^{1/2}$ (≈ 0.1 mm) is the characteristic length of the problem. The instability initially grows exponentially with a time constant $\tau \approx L^2/D_R$ so that at the phase transition point ($R = R_c$), both L and τ diverge with critical exponents $\frac{1}{2}$ and 1, respectively. This is actually a band of unstable wave vectors with L the wavelength with the largest growth rate. The band extends down to zero wave vector, which places the instability in the Hohenberg-Cross[9] category II. This should have been expected in view of the conservation law implied by Eqs. (3) and (4).

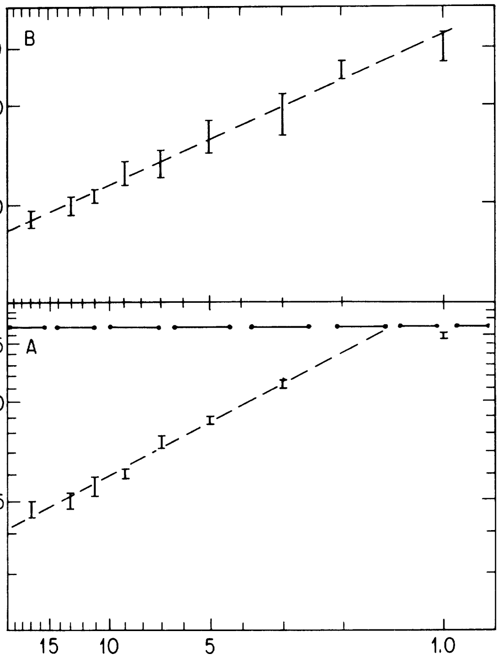

FIG. 3. Dependence of (a) the pattern length scale L and (b) the onset time t_0 on the concentration $\Delta c = (c_F - c_{Fc})/c_{Fc}$ for $c_{Fc} \cong 0.0005M$; $c_O = 0.15M$ and $c_C = 0.005M$. The length L does not exceed 1.67 mm, indicated in (a) by a dash-dotted line.

The essential result is the prediction of a phase transition where the translational invariance is broken and both the characteristic length scale and time scale diverge. The experiments show (Fig. 2) that a lowering of c_F leads to a steady increase in L until it becomes comparable to the dimensions of the exposed area, after which it saturates (at about 1.7 mm). For smaller c_F, the pattern begins to disappear. We interpret this as the phase transition, thereby defining the dashed line in Fig. 2 as our critical concentration c_{Fc}. The concentration dependence of L is shown in Fig. 3(a) and it corresponds to a power law $(c_F - c_{Fc})^{-\alpha}$ with an exponent $\alpha = 0.46 \pm 0.09$, in agreement with Eq. (5). However, although there is also critical slowing down near c_{Fc}, the formation time diverges roughly as L, not L^2 as predicted [Fig. 3(b)] for τ, and so we cannot equate t_0 with τ.

A second test concerns the viscosity dependence of L. According to Eq. (5), L should be proportional to $D_R^{1/2}$, and so, with use of Stokes' law, proportional to $1/\eta^{1/2}$. For glycerol-water mixtures we saw an approximate power law $L(\eta) \sim 1/\eta^{\beta}$ with $\beta = 0.51 \pm 0.12$, which is strong evidence for a diffusive mechanism for the instability. Finally, for very low c_C ($\lesssim 0.003M$) there is no dependence of k on c_C and indeed no pattern formation is observed.

These observations all provide support for the existence of a phase transition driven by a combination of autocatalysis and diffusion. The static critical behavior appears to be in approximate agreement with the proposed mechanism, although the observed critical slowing down cannot be explained.

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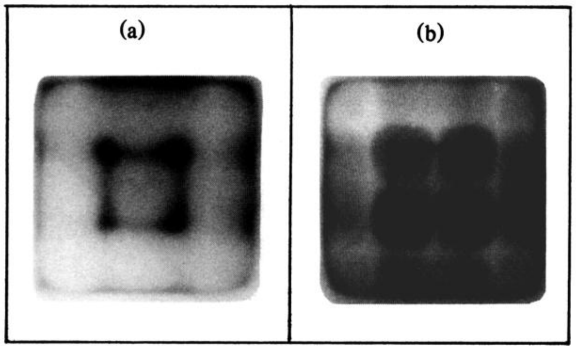

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