Research Letter

Spatial Heterogeneity and Imperfect Mixing in Chemical Reactions: Visualization of Density-Driven Pattern Formation

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Imperfect mixing is a concern in industrial processes, everyday processes (mixing paint, bread machines), and in understanding salt water-fresh water mixing in ecosystems. The effects of imperfect mixing become evident in the unstirred ferroin-catalyzed Belousov-Zhabotinsky reaction, the prototype for chemical pattern formation. Over time, waves of oxidation (high ferriin concentration, blue) propagate into a background of low ferriin concentration (red); their structure reflects in part the history of mixing in the reaction vessel. However, it may be difficult to separate mixing effects from reaction effects. We describe a simpler model system for visualizing density-driven pattern formation in an essentially unmixed chemical system: the reaction of pale yellow Fe^{3+} with colorless SCN^- to form the blood-red $\text{Fe}(\text{SCN})^{2+}$ complex ion in aqueous solution. Careful addition of one drop of $\text{Fe}(\text{NO}_3)_3$ to KSCN yields striped patterns after several minutes. The patterns appear reminiscent of Rayleigh-Taylor instabilities and convection rolls, arguing that pattern formation is caused by density-driven mixing.

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1. Introduction

Good mixing is a major challenge in many areas of chemistry and chemical engineering, ranging from continuously stirred tank reactors (CSTRs) [1] to industrial level processes [2], where imperfect mixing can adversely affect product quality and yield. Many of us are familiar with mixing problems in making bread, stirring paint, mixing gasoline and air in internal combustion engines, and mixing driven by density differences (salt water-fresh water convection) but even mixing of ordinary liquids can pose challenges. (The density of pure water is 1000 kg/m^3 . Ocean water is more dense because of the salt in it. Density of ocean water at the sea surface is about 1027 kg/m^3 . There are two main factors that make ocean water more or less dense than about 1027 kg/m^3 . From <http://www.csgnetwork.com/h2odenscalc.html> we derived Table 1 (accessed 1/2009)).

The effects of imperfect mixing are perhaps most dramatically evident in excitable chemical systems [1, 3] such as the BZ reaction [4–9] and the chlorite-iodide reaction [10–12]. An excitable chemical reaction is a reaction in

which suitable small perturbations from steady state generate large excursions (excitations) before the system returns to steady state. Many excitable reactions display auto-oscillatory behavior in which sustained oscillations about an unstable steady state are observed. The effects of imperfect mixing can be seen readily in the unstirred, ferroin-catalyzed Belousov-Zhabotinsky (BZ) reaction in a Petri disk, a quasi-two-dimensional (2D) system [3–8]. The catalyst in this reaction, ferroin/ferriin, also serves as an indicator; blue/oxidized at high [ferriin] and red/reduced at low [ferriin]. After an induction period of several minutes, one sees the “spontaneous” formation of target patterns of blue/oxidized rings moving outward from oscillatory (red/blue) centers into a red/reduced background.

Menzinger and Dutt [1] first described the effects of imperfect mixing upon reactions involving excitable media. We have explicitly demonstrated nonrandom spatiotemporal order in target formation in the unstirred BZ reaction, with targets preferentially occurring in excitable regions near existing targets, but too far from pre-existing targets to be generated by wave propagation or chemical diffusion [3].

FIGURE 1: (a) Excitable BZ reaction medium, stirred after initial pattern formation, 2.1 mm depth. From [9, Figure 2c]. Scale bar: alternating 2.1 mm lines and spaces. (b) Chemical model: Fe^{3+} and SCN^- , 2 mm depth. Scale bar: alternating 2 mm lines and spaces. Striped patterns formed outside the visible droplet boundary (lower left of figure). The color corresponds to the concentration of FeSCN^{2+} . Resolution $\sim 30 \mu\text{m}$ in photos (b) through (f). Time: about two minutes after addition of one drop of Fe^{3+} solution. (c), (d) Evolution of panel (b). Same experimental run, 45 and 30 second earlier. Note pattern initiation 2 mm behind visible wavefront (of diffusion wave) and effect of diffusion in blurring visible boundaries as concentration gradients are reduced. (e) Same model, but 3 mm depth, early stage of pattern formation. Note visible droplet boundary in center of figure, and larger scale that corresponds to greater depth as in (b) through (d). (f) Same model, 1 mm depth, early stage of pattern formation. Scale bar: 1 mm. Note fine structure ($\ll 1 \text{ mm}$) transverse to a spatial filament of the reaction, and initial excitation of 1 mm scale.

We explained the observed spatiotemporal order in terms of mixing heterogeneities in preparing the 2D reaction medium likely because of the sensitivity of the dynamics to very small perturbations at the onset of oscillation [13, 14]. In conditions of almost complete mixing, striped patterns reminiscent of convection rolls with spacing approximately equal to the depth of the medium were often observed (Figure 1, panel (a)). Here we describe an even simpler model system which displays analogous pattern formation driven by density differences, c.f. [15–17].

2. Pattern Visualization with $\text{Fe}(\text{SCN})^{2+}$

The present experiment arose from trying to understand how slight density differences might drive this pattern formation. Since BZ dynamics are relatively complex, we sought a simpler, minimal example to better visualize and understand the effects of mixing heterogeneity. We used a simple chemical reaction, in which two nearly colorless solutions, one containing Fe^{3+} (pale yellow) and the second containing SCN^- (clear), are mixed, producing a deep reddish color

TABLE 1: Densities of salt water and pure water at various temperatures

Temp ($^{\circ}\text{C}$)	Ionic strength	Calc. density (g/cm^3)
23	3500	1.000215
	0	0.997568
26	0	0.996814
20	0	0.998234
30	0	0.995678

where Fe^{3+} and SCN^- combine to form the complex ion FeSCN^{2+} in an essentially irreversible reaction. We made a simple modification—instead of mixing the two solutions, we added a small drop ($< 1 \mu\text{L}$) of 0.1 M Fe^{3+} (as $\text{Fe}(\text{NO}_3)_3$) to a 1–4 mm deep solution of 0.02 M SCN^- (as KSCN) optionally containing a very small amount of surfactant (which had no apparent effect). The deep reddish color where Fe^{3+} and SCN^- combine to form FeSCN^{2+} clearly labels interfaces between Fe^{3+} -dominated and SCN^- -dominated regions. We found patterns reminiscent of convective rolls

with spacing equal to the depth of the corresponding reaction medium (Figure 1, panels (b)–(e), below, similar to patterns seen under conditions of almost complete mixing in the BZ reaction, panel (a)). Note that the $\text{Fe}(\text{NO}_3)_3$ solution is denser than the KSCN solution: 1.010(4) versus 1.001(2) g/mL.

The resulting patterns demonstrate behavior expected in the Rayleigh-Taylor instability [18, 19], which occurs when a heavier fluid (here the $\text{Fe}(\text{NO}_3)_3$ solution) is placed on top of a lighter fluid (here the KSCN solution). Gravitational forces drive the heavier solution downward through the lighter solution in an unstable, turbulent manner, until concentration (and thus density) differences are destroyed by diffusion. In our model system, one sees initial small scale instabilities (panel (f)) which are gradually destroyed by diffusion as longer length scales are excited, with one added twist—selection of a length scale corresponding to the depth of the reaction medium after a time delay a few multiples of the time it takes a drop to fall the depth of the solution. From Stokes law, the net force on a small drop depends upon its volume, velocity, and density difference ($\rho_1 - \rho_2$). In our model a drop of radius $50\text{ }\mu\text{m}$ rapidly reaches terminal velocity of $\sim 50\text{ }\mu\text{m/s}$, making the natural time scale (time to fall 2 mm) $\sim 2\text{ mm}/(50\text{ }\mu\text{m/s}) = 40\text{ second}$, consistent with the formation of relatively stable patterns over $\sim 3\text{ minutes}$ (~ 4 times this natural time scale).

3. Conclusion

This simple minimal model, in a nonexcitable system, demonstrates excitation of the most unstable mode (the only one that survives over minutes). It visually demonstrates the persistence of spatial heterogeneities in liquids. The problem of mixing is important in real-world situations often encountered by chemical engineers (industrial chemical reactions), process/flow engineers, and even fields such as hydrology and geoscience—temperature and salinity differences can cause density differences in water similar in magnitude to the density differences in this experimental model. This simple model provides a mechanism to experimentally visualize and study the patterns formed by density differences.

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