PLUME AND FINGER REGIMES DRIVEN BY AN EXOTHERMIC INTERFACIAL REACTION

Alexander Grahn and Kerstin Eckert

1. Introduction

Studies of convection in fluids, like Rayleigh-Bénard- [1] or Bénard-Marangoni convection [2] have strongly influenced our understanding of pattern formation and turbulence. In these systems energy is supplied by an external temperature difference applied across a given vertical length scale. However, this situation is not representative for a variety of systems occurring in nature. Here, the dynamics is driven by internal sources of energy and the selected length scale is a part of the solution of the problem. The study of such systems is interesting from both a fundamental point of view and with respect to potential applications of basic research. Promising candidates for such studies are systems involving chemical reactions. Consumption of educts and the release of reaction enthalpy are sources of solutal and thermal gradients. Hydrodynamic instabilities, driven by these gradients, can drastically alter the chemical reaction rate [3]. We demonstrate that a rather simple interfacial neutralization reaction can develop an unexpected coupling of different hydrodynamic instabilities (for details we refer to [4]).

2. Experimental set-up and chemistry

The experiments were performed in a two-layer system, placed in a Hele-Shaw-cell (Fig. 1). The gap width was \( d = 0.1 \) cm. Visualization of the patterns was done by means of a shadowgraph technique. The two-layer-system inside the cell consisted of a lower aqueous layer (water and base) and an upper organic layer (isobutyl-alcohol and carboxylic acid). The viscosity of the organic solvent is four times higher than that of water. Since water and isobutyl-alcohol have a certain solubility (12 % at \( T = 25 \) °C) saturated solutions were prepared before filling. Saturation was to prevent interfacial turbulence arising from counterdiffusion of the solvents into each other. The respective densities are 0.987 g/cm\(^3\) (upper layer) and 1.016 g/cm\(^3\) (lower layer, including the base concentration). The density of both phases increases with increasing acid concentration. While the concentration of the base B in the water was fixed to \( c_B = 1 \) mol/l, different concentrations \( c_{HA} \) of the acids have been used (\( c_{HA} = 0.04 \) to 0.08 g/l or equivalently 0.5 to 2 mol/l).

Fig. 1: The two-layer system in the Hele-Shaw cell. The given densities refer to the saturated phases.

---

1 Institute for Thermofluid Dynamics, TU Dresden, Germany
The basic reaction is the neutralization of carboxylic acid by a base, sodium hydroxide, close to the interface. Precondition of this reaction is the dissociation of both species, i.e.,

\[ \text{HA} + \text{H}_2\text{O} \rightarrow \text{A}^- + \text{H}_3\text{O}^+ \quad (1) \]

\[ \text{B} + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad (2) \]

sodium hydroxide as a strong base is completely dissociated, the dissociation degree of the weak organic acids is smaller than 1%. If a hydronium ion \( \text{H}_3\text{O}^+ \), formed by dissociation, encounters a \( \text{OH}^- \) ion, neutralization takes place, i.e.,

\[ \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2 \text{H}_2\text{O} \quad (3) \]

The enthalpy released by this reaction amounts to -57 kJ/mol.

### 3. Observations

The system displays three basic regimes (Fig. 2). The initial one (Fig. 2a) is dominated by rising *plumes* in the upper organic layer. The plumes are emitted from an unstable boundary layer (b.l.) above the interface. We assume that they consist of warmer fluid with lower acid concentration. The intensity of the plume regime is most distinct in the formic-acid system and decreases with increasing chain length. The duration is of the order of minutes.

![Fig. 2: The three basic regimes. (a) Rising plumes, (b) plumes and irregular fingers, (c): nearly regular fingers in the lower.](image)

The intermediate regime (Fig. 2b) is characterized by plumes in the upper layer and by an irregular formation of fingers in the lower layer. The onset of the fingers starts the earlier the longer the acid chain length is. The duration of this second regime is of the order of 1 hour. In its course the upper layer plume regime becomes increasingly disorderd till it fades away.

In the final regime (Fig. 2c) the system displays an array of regularly spaced *fingers*. In the fingers warmer fluid, rich in acid/acetate ions, moves downwards. In between the fingers colder fluid, which should have a higher hydroxide concentration, moves in the opposite direction towards the interface. This is a double diffusive instability arising from the different diffusivities of heat and mass. Since heat diffuses 100 times faster than mass, the convective motion is driven by the horizontal concentration difference between the rising and falling fluid columns. Next we analyse the upper-layer motions by studying the advancing of the Plumes with time (Fig. 3). This is done by tracing the head positions of the plumes in the
digitized shadowgraph images and averaging over the plume ensemble. Usually approx. 10 plumes are taken into account. We find that the velocity of the upper layer plume ensemble decreases with increasing chain length of the carboxylic acid.

To determine the wavenumber as the characteristic horizontal length scale of the finger structure we apply the one-dimensional Fourier transformation to lines parallel to the interface. The corresponding power spectra are shown in Fig. 4. At equal molar concentrations all three systems display nearly the same wave numbers \( k \). After 90 min we find \( k = (3.9 \pm 0.3) \text{ mm}^{-1} \). We could not detect a significant dependence on the gap width (0.5, 1.0 and 2.0 mm).

4. Discussion

The engine of the dynamics is the diffusion of acid from the upper into the lower layer. The acid diffusion leads to an unstable density stratification at both sides of the interface since heavier fluid lies above lighter fluid. Convection in the form of plumes, emitted from the concentration boundary layer, sets in (Fig. 1a). The neutralization reaction provides a local heating and an additional decrease of the density of regions close to the interface. Consequently, the effective Rayleigh number, governing the stability of the boundary layer of the upper phase, is higher. Solutal plumes move faster due to additional thermal buoyancy in the systems with reactive mass transfer.

However, the temperature gradient has a stabilizing effect on the boundary layer below the interface. The destabilizing concentration gradient is superimposed by the stabilizing temperature gradient. This configuration leads to double-diffusive instability which is known from thermohaline convection in oceans, responsible for the exchange of salt and heat between surface and deeper water layers. The nature manages both effects by switching to the finger instability to provide a very efficient mixing. Both plume and finger instability are responsible for the self-sustained dynamics observed in the experiment for more than 2 hours. We expect that numerous interfacial reactions are accompanied by the formation of fingers and plumes. Since both instabilities lead to an efficient mixing they can strongly accelerate diffusion-controlled interfacial reactions. Thus, the understanding of the hydrodynamics offers a possibility to control this reaction type.
5. References