Convective instability
in the chlorite-tetrathionate system

Thesis of the PhD dissertation

Tamás Bánsági

Supervisors: Dr. Ágota Tóth and Dr. Dezső Horváth

University of Szeged

Szeged, 2004

1 Introduction

In a non-stirred homogeneous medium of an autocatalytic reaction, an interface between the solutions of reactants and products moving at constant speed develops. A planar reaction diffusion front may lose stability due to the effect of gravitational field. Under isothermal conditions, if the density change is positive, i. e., the solution of products is denser, the upward propagating planar front remains planar because the system is hydrodynamically stable. In the opposite case the planar front becomes unstable and fingers develop resulting in a cellular structure. In addition, under non-isothermal conditions the density change generated by heat evolution is negative in all known reaction fronts. Thus, generally both the solutal and thermal density change can affect the stability of fronts: simple convection appears if both density changes are negative or if they have opposite signs but the density change in the chemical composition dominates. Multicomponent convection arises if the absolute value of the density decrease created by the heat effect is larger.

The investigation of convective instability driven by reaction fronts started in the 1980's by studying the effect of the diameter and the orientation of narrow tubes on the speed and the shape of a moving front. Later the theoretical studies continued by describing the pattern formation in a Hele-Shaw cell where the fluid motion may be considered two dimensional. Because of the fast development of computer science, the theoretical investigations have been accelerated and several models have been developed to describe the phenomenon without experimental proof. In these theories the fluid motion and the chemical reaction are incorporated in different ways: the fluid motion was described by either Darcy's law or the Navier-Stokes equation. In several approaches chemistry was not included or was handled as an infinitesimally narrow dividing interface. More recently the whole reaction zone has been applied successfully.

Our goal is to quantitatively describe the initial and the long time evolution of pattern formation in an acid-catalyzed reaction front induced by fluid motion, as well as to determine the applicability of theoretical models developed for density fingering. We have given the characteristics of the density fingering by varying the orientation, the gapwidth, the width of the Hele-Shaw cell, the heat removal, the concentration of the reactants, and the decay of the autocatalyst. We have followed the change in temperature generated by the front and measured the isothermal density difference between the solution of the reactants and the products. Furthermore, the front velocity in the absence of convection was also determined.

2 Experimental

Front propagation in narrow and wide, so-called Hele-Shaw cells consisting of two parallel plexi plates separated by a spacer, was monitored using a monochrome CCD camera by collecting images in 0.40–2.00 s intervals. To give a quantitative description of the initial regime of the evolution of pattern formation (see images on the left in Figure 1), we have performed fast Fourier transformation (FFT) on the front profiles determined from consecutive images. From the temporal change of the Fourier amplitudes, the growth rates (ω) of perturbations with different wave number (k) were determined resulting in the dispersion relation ($\omega - k$) shown right in Figure 1. The growth rate (ω_m) and the wavenumber (k_m) of the fastest growing component of the perturbation, and the marginal wave number k_0, which separates the unstable modes from the stable ones, are characteristic of this relation. To characterize the long time evolution of pattern formation caused by simple convection, we have determined the front amplitude measured as the distance between the foremost and the hindmost segments of the reaction front in the direction of front propagation, and the power-average wave number calculated from the Fourier coefficients.

The change in temperature caused by the heat evolution in the reaction front has been determined by a thin iron-constantan thermocouple placed in the Hele-Shaw cell. The densities of the reactant and the product solutions were measured by a digital density-meter within 10^{-5} g/cm^3 precision, and the front velocities in the absence of convection were obtained from the distance traveled by the front per unit time.

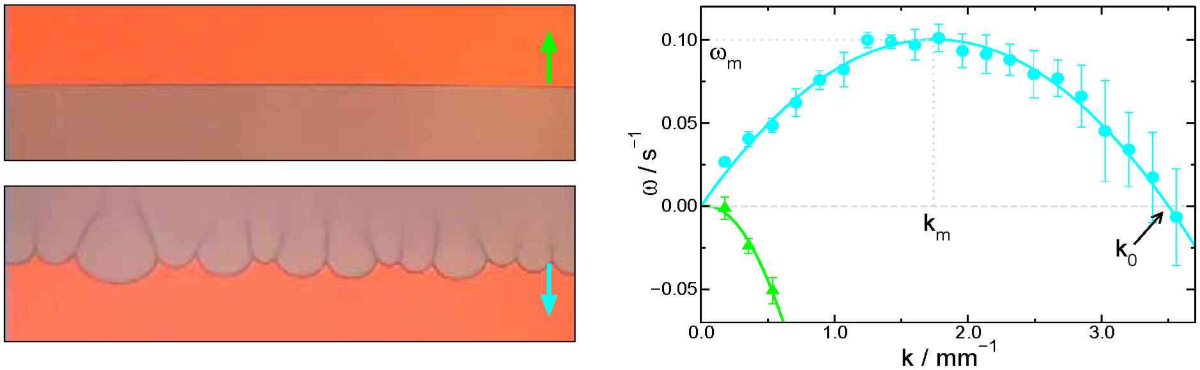

Figure 1: The linear regime of density fingering in simple convection: images of upward propagating front (upper left), downward propagating front (lower left), and dispersion curves for up- (▲) and downward (●) propagating fronts (right). The size of the images recorded by a VHS camera: 4.6×1.1 cm. Red regions represent the reactant while the blue regions the product solution.

3 New scientific results

I. *We have demonstrated that the high frequency components are stabilized by diffusion.* [1, 2]

By varying the orientation and the gapwidth of the Hele-Shaw cell we have determined the characteristics of the evolution of pattern formation driven by simple convection: the growth rates (ω_m) and wave number (k_m) of the most unstable modes, the marginal (k_0) wave numbers, and the k_0/k_m ratios. Based on the comparison of the experimental and the theoretical results we have proven that the high frequency modes are stabilized by diffusion instead of surface tension.

II. *It has been shown that Darcy's law describing the fluid motion is valid up to 0.6 mm of gapwidth.* [2]

We have investigated the density fingering by varying the gapwidth in the range of 0.40–1.04 mm. Our experimental results have revealed that for describing the behavior of the fluid motion the Navier-Stokes equation is valid without any restriction, whereas Darcy's law can only be used for narrow cells.

III. *The region of convective instability increases on increasing heat removal.* [2]

One of the plexi walls of the Hele-Shaw cell was replaced by an aluminum wall to enhance heat removal while the reactant concentrations and the gapwidth were kept constant. Because of the significantly smaller temperature increase the thermal density change was eliminated, thus the region of instability increased.

IV. *Rise in the autocatalyst removal yields a decrease in the instability of downward propagating front.* [4]

On increasing the initial concentration of sodium hydroxide while the reactant concentrations and the gapwidth were kept constant, the regime of instability decreased because of the growing autocatalyst neutralization. It has been shown that the instability decrease yields smaller k_m, k_0, and ω_m, therefore the shapes of the curves do not change, only the unstable regime for the downward propagating front becomes smaller.

V. *The evolution of pattern formation for upward propagating planar fronts led by multicomponent convection was quantitatively described.* [4]

The increase in the initial concentration of either sodium hydroxide or the reactants coupled by larger gapwidth yields multicomponent convection in the system and the upward propagating front presented in Figure 2. The loss of stability is quantitatively described by the dispersion curve with symbols (▲).

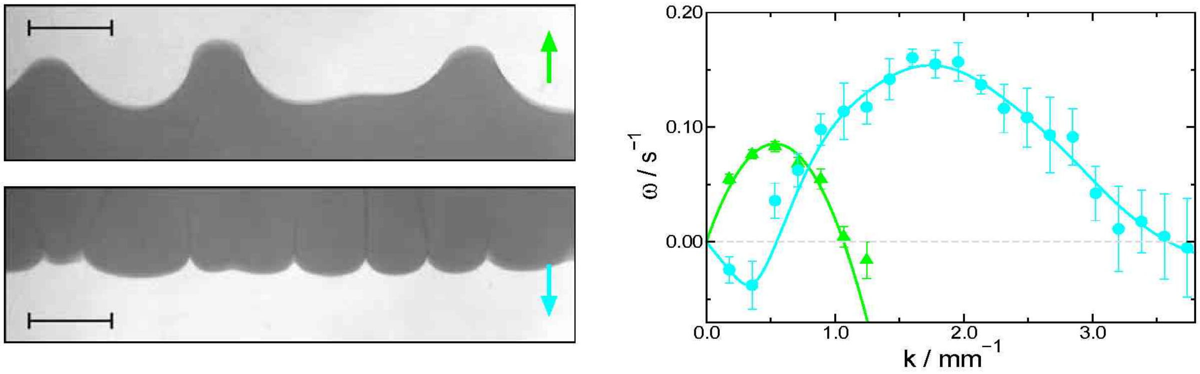

Figure 2: The linear regime of density fingering in multicomponent convection: front shapes (left), and dispersion curves for up- (▲) and downward (●) propagating fronts (right). An upward propagating front presented in the upper left image and a downward propagating front in the lower one (darker regions represent the product solution and lighter the reactant). The black bar corresponds to 5 mm.

VI. *We have characterized the qualitatively different partial stabilization of downward propagating reaction fronts led by multicomponent convection.* [3]

On increasing the reactant concentration in thicker cells downward propagating fronts are partially stabilized parallel to the destabilization of the upward propagating front demonstrated by the upper left image of Figure 2. The growth rates of a downward propagating front (see (●) symbol in Figure 2) in the short wave number regime decrease significantly resulting in a different type of dispersion curve.

VII. *The long time behavior of density fingering in simple convection has been quantitatively described.* [5]

We have characterized the long time regime of the evolution of pattern formation caused by simple convection. Both the front amplitude and the power-average wave number have been determined by varying the reactant concentrations and the width of the cell. We have found that at low initial concentration and in 1.0–3.0 cm wide vessels the structure emerging initially evolves to a single cell. At higher reactant concentration, however, continuous tip splitting is observed.

4 Publications related to the dissertation

1. D. Horváth, T. Bánsági, Jr., Á. Tóth: Orientation-dependent density fingering in an acidity front, J. Chem. Phys. **117**, 4399 (2002). (IF=3.147; NIC[1]=7)
2. T. Bánsági, Jr., D. Horváth, Á. Tóth: Convective instability of an acidity front in Hele-Shaw cells, Phys. Rev. E **68**, 026303 (2003). (IF=2.202; NIC=4)
3. T. Bánsági, Jr., D. Horváth, Á. Tóth, J. Yang, S. Kalliadasis, A. De Wit: Density fingering of an exothermic autocatalytic reaction, Phys. Rev. E **68**, 055301 (2003). (IF=2.202; NIC=1)
4. T. Bánsági, Jr., D. Horváth, Á. Tóth: Multicomponent convection in the chlorite-tetrathionate reaction, Chem. Phys. Lett. **384**, 153 (2004). (IF=2.438; NIC=2)
5. T. Bánsági, Jr., D. Horváth, Á. Tóth: Nonlinear interaction in the density fingering of an acidity front, J. Chem. Phys. – in press. (IF=2.950)

5 Lectures and poster presentations related to the dissertation

1. **T. Bánsági, Jr.**, D. Horváth, Á. Tóth: Convective instability in the chlorite-tetrathionate reaction, ESF Theme School: Methods for Realistic Modelling of Large and Complex Chemical Systems, Odense, D, 2002. (lecture)
2. **T. Bánsági, Jr.**, D. Horváth, Á. Tóth: Convective instability in the chlorite-tetrathionate reaction, ESF Theme School: Methods for Realistic Modelling of Large and Complex Chemical Systems, Odense, D, 2002. (poster)
3. **Bánsági T.**, Kiss A.: Konvektív instabilitás a klorit-tetrationát reakcióban, XXV. Kémiai Előadói Napok, Szeged, 2002. (lecture)
4. **T. Bánsági, Jr.**, A. Kiss, D. Horváth, Á. Tóth: Convective instability in the chlorite-tetrathionate reaction, Nonlinear phenomena in chemistry: An ESF REACTOR workshop, Budapest, 2003. (poster)
5. **T. Bánsági, Jr.**, Horváth, Á. Tóth: Density fingering in an acid-catalyzed reaction, The 2003 Younger European Chemist's Conference, ESRF, Grenoble, F, 2003. (poster)

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[1] NIC: number of independent citation

6. **T. Bánsági, Jr.**, A. Kiss, D. Horváth, Á. Tóth: Convective instabilities in an exothermic acid-catalyzed reaction, Dynamic Days, Palma de Mallorca, E, 2003. (lecture)
7. **Bánsági T.**: Konvekció-indukált mintázatok savkatalizált reakcióban, XXVI. Kémiai Előadói Napok, Szeged, 2003. (lecture)
8. **Bánsági T.**: Konvektív instabilitás a klorit-tetrationát rendszerben, Reakciókinetikai és Fotokémiai Munkabizottság, Balatonalmádi, 2004. (lecture)
9. **T. Bánsági, Jr.**, D. Horváth, Á. Tóth: Nonlinear density fingering in an acidity front, Gordon Research Conference on "Oscillation and Dynamic Instabilities in Chemical Systems", Lewiston, USA, 2004. (poster)

6 Poster presentation not related to the dissertation

1. **Bánsági T.**: Statistical investigation of heavy metals in trees and soils of Szeged, The 3rd International Conference of the Danube-Cris-Mures-Tisa Euroregion "Environment and Health", Petrosani, RO, 2001. (poster)