

The effect of polymer solutions on fluid motion in autocatalytic fronts

Thesis of the PhD dissertation

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1 Introduction

Naturally occurring patterns involve atmospheric formations, lava or oceanic streams. In most cases, density difference between the interacting media is responsible for their appearance, although contributions from viscosity or surface tension difference are also considered to be important. Factors influencing fluid motion were investigated through chemical model reactions, focusing on the effect of density difference and related reaction conditions. The effect of viscosity change is also discussed.

Investigation of fluid motion in laboratory conditions dates back to the 19th century that started with the characterization of distortion of interfaces between immiscible liquids followed by theoretical calculation of more and more complex systems. Turning from immiscible liquids to reactive chemical systems, interfaces of new properties were obtained. At the end of the previous century, along with the boom of computer technology, the number of established theoretical models rapidly increased. This demanded for the immediate experimental support of the proposed models, to which our group has also contributed.

Upon the investigation of the behavior of interfaces, a chemical front was generated, which separates the reactant and product solutions in autocatalytic reactions. Specifically, the reaction between chlorite and tetrathionate ions was investigated, which is autocatalytic with respect to hydrogen ion. Reactions were run in a Hele-Shaw cell, which is a thin vessel appropriate for the two dimensional visualization of interfaces. The densities of reactant and product solutions usually differ from each other. This difference is generated by the simultaneous effects of changing chemical composition and the density change due to the thermal solution contraction caused by the reaction heat liberated. The process is termed as complex convection when these density changes have opposite signs and the absolute value of that originating from the change of chemical composition is exceeded by the temperature-induced density change. In the vicinity of the reaction front, a local density change between the two sides can also occur due to the diffusion coefficients of the reaction and product particles and their mutual relation, besides the temperature change, which can induce an additional fluid motion. When the system contains certain polymer molecules, a viscosity change between the reactant and product solutions can be induced that influences the pattern formation.

My doctoral research aimed to reveal the effects of solution viscosity, both constant and varying in the course of the reaction and the diffusivities of particles present in the reaction system on the chemical pattern formation.

2 Experimental

To study the effect of bulk solution viscosity, polyacrylamide (Figure 1. (b)), an inert polymer, was added to the reaction mixture in the Hele-Shaw cell (Figure 1. (a)) and the front formed upon the reaction between chlorite and tetrathionate ions was studied. The viscosity of polyacrylamide solution exhibits a negligible change during the reaction which is accompanied a change in pH. Although the added polymer varies the isotherm densities of the reactant and product solutions, the density difference is very close to that of the polymer free system. When a polyelectrolyte (Figure 1. (d)) is applied instead of polyacrylamide for setting the initial viscosity of the reactant solution, the viscosity significantly decreases during the reaction. Upon addition of the sodium-polyacrylate, containing more carboxylic groups (Figure 1. (c)) to the reaction solution, one can minimize the change in viscosity, while the carboxylate groups of the polymer with low diffusivity reversibly bind the hydrogen ions acting as the autocatalyst, i.e. the carboxylate groups immobilize the hydrogen ions.

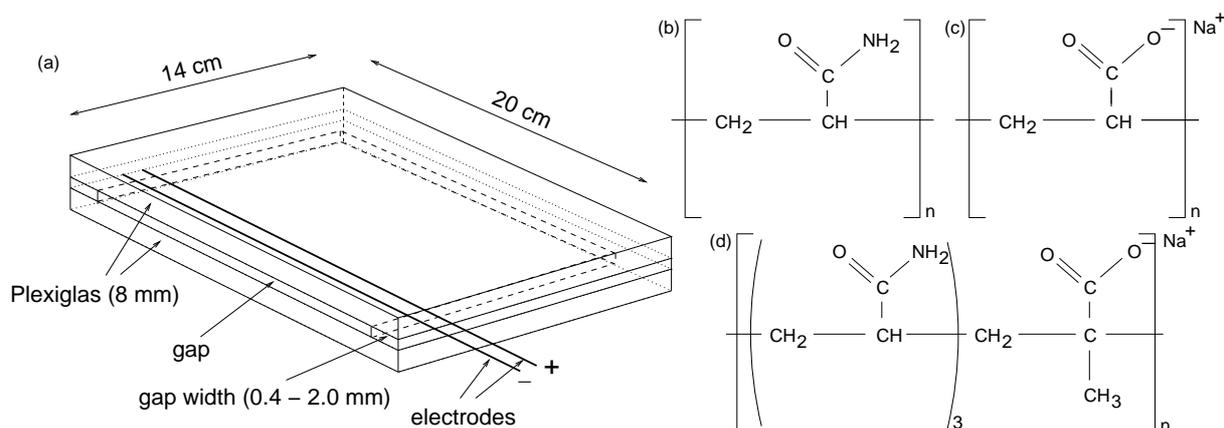


Figure 1: Schematic drawing of (a) the Hele-Shaw cell. Structures of (b) polyacrylamide, (c) sodium-polyacrylate and (d) polyelectrolyte molecule.

3 Evaluation methods

The velocity of front propagation was determined in capillaries by capturing a digital image sequence, that were analyzed by image processing software. The position of front was defined by the change in the grayscale caused by the color change in the cell during the reaction. The same method was applied to monitor the behavior of fronts in the Hele-Shaw cell, where the position and shape of the front was determined at the same intervals and the front shapes were decomposed into Fourier modes by Fourier transformation. For each mode the amplitude initially grows or decays exponentially, with the exponent termed as growth rate. The growth

rate vs. wavenumber function is the so-called dispersion curve that is used for the quantitative characterization of the pattern evolved from the original plane front. During the studies of the long-range behavior of the patterns, the front amplitude was determined once the front takes on a stationary structure. This was defined the standard deviation of the front from the average front position. For the fronts that lack a stationary shape, the deviation relates to the distance between the most advanced and most retarded parts of the reaction front. For additional quantitative characterization, the average number of waves in a given width was also introduced. The regular front shapes were characterized by autocorrelation functions, which provide quantitative information on the periodicity of the pattern.

4 New scientific results

- I. *The degree of front instability decreases and the wavelength of the front shape characteristic for the initial part of the pattern formation increases with the solution viscosity.* [1]

The instability of the reaction fronts propagating downwards decreases with the solution viscosity. The amplitude of the formed pattern is significantly, while its characteristic wavenumber value is only slightly decreased by the decreasing instability of the front, as demonstrated by the dispersion curves used for the quantitative characterization in Figure 2. The maxima of the dispersion curves characteristic for the initial part of pattern formation greatly decrease with the solution viscosity, in contrast to the slight variation of the wavelength values.

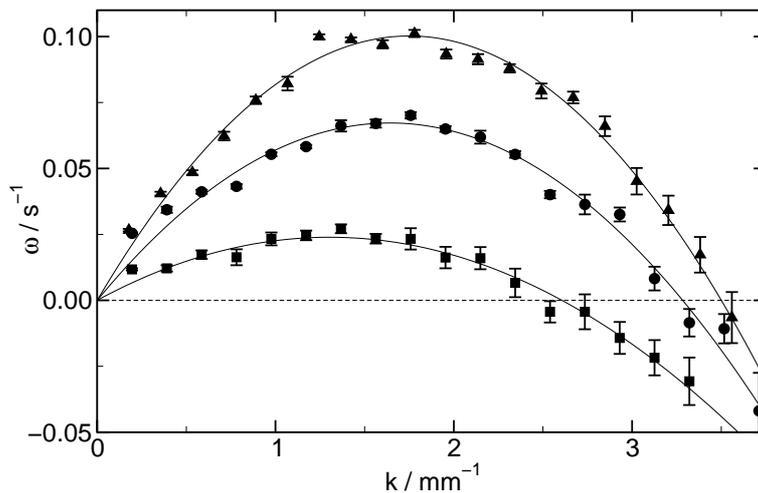


Figure 2: Dispersion curves at different viscosities, $\eta = 0.932$ cP (\blacktriangle), $\eta = 1.48$ cP (\bullet), and $\eta = 3.56$ cP (\blacksquare). Continuous lines are fitted parabolas, the maxima of which define the modus of the highest growth rate.

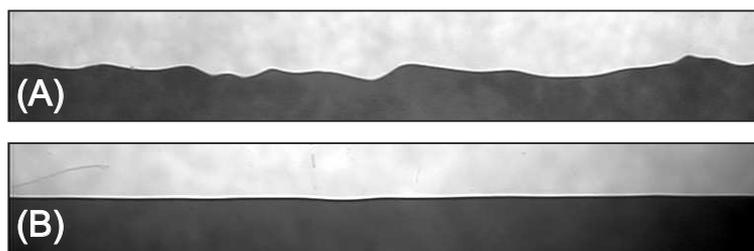


Figure 3: Photographs taken on reaction fronts propagating downward in (A) polyelectrolyte, and (B) polyacrylamide solutions. Black regions represent the reactant solution and light regions the product.

- II. *There is only a minor effect of the increasing solution viscosity upon the long-range behavior of the reaction front due to the continuous fusion of cells.* [1]

The effect of solution viscosity on the front behavior is less pronounced in the non-linear range than in the initial range, where the plane front is split into dense cells, while the fusion of cells due to the nonlinear interactions in the course of reaction results in the decrease of the average number of waves cells. This decrease has similar extent for the systems of both the lower ($\eta = 1.48$ cP) and the higher ($\eta = 3.56$ cP) viscosities. The front amplitude is also similar for these systems, although, in case of higher viscosity, the time for the stabilization of front amplitude is nearly one magnitude larger.

- III. *The decrease of viscosity at the reaction front in polyelectrolyte-containing front reactions resulting in pH-change highly destabilizes the planar reaction front.* [2]

The basic polyelectrolyte added to the reactant solution can reversibly bind the formed autocatalyst besides increasing the solution viscosity. Applying the polymer in a concentration lower than that required for a diffusive pattern formation, a pattern seen in Figure 3. (A) is observed for fronts propagating downwards. This front instability is caused by the magnitude-range decrease in the solution viscosity, which originates from the conformational change caused by the change of ionic properties of the partially protonated polymer. When setting the same viscosity value with an inert polyacrylamide solution, i.e. which cannot bind hydrogen ions, a state planar front show in Figure 3. (B) forms, while the bulk viscosity remains constant.

- IV. *When using polyelectrolyte that reversibly binds the autocatalyst, we have shown that a cellular front structure forms due to the changes in diffusion rate and the decrease in the velocity of propagation for horizontally traveling fronts. This structure appears at a concentration significantly lower than the critical value for diffusive instability.* [3]

When the reaction was conducted in a horizontal cell of 0.8 mm slit height containing sodium polyacrylate solution, a cellular front pattern was observed for autocatalyst bin-

ding smaller than that required for diffusive instability. The length and time scale of this wave pattern significantly differ from that of the diffusive pattern. There is a certain range of polymer concentration required for the formation of the diffusive and this novel pattern. Where neither of the patterns appears, the front retains its planar shape during the entire reaction. This signifies that the pattern formation at the lower wavelength does not originate from diffusive instability, rather convective instability, which forms because of the increased solution layer thickness. Convection is caused by the decreased velocity of front propagation, the non-monotonous density change in the course of the reaction and the difference in diffusion coefficients in the vicinity of the front.

V. *An alternating cellular pattern of the horizontally propagating front was detected in polyelectrolyte containing, 2 mm thick solutions.* [4]

Conducting the reaction in a horizontal, 2 mm high reaction cell in the presence of basic polyelectrolyte, major changes are observable in the build-up of the pattern, which (besides the increase in wavelength) mainly manifests in a structural change. A steady cellular structure (as those in the previous cases) does not form, rather the front wave is subjected to a half phase shift at even time intervals perpendicular to the propagation direction in Figure 4. This phenomenon occurs throughout the complete propagation of the front in the reaction cell.

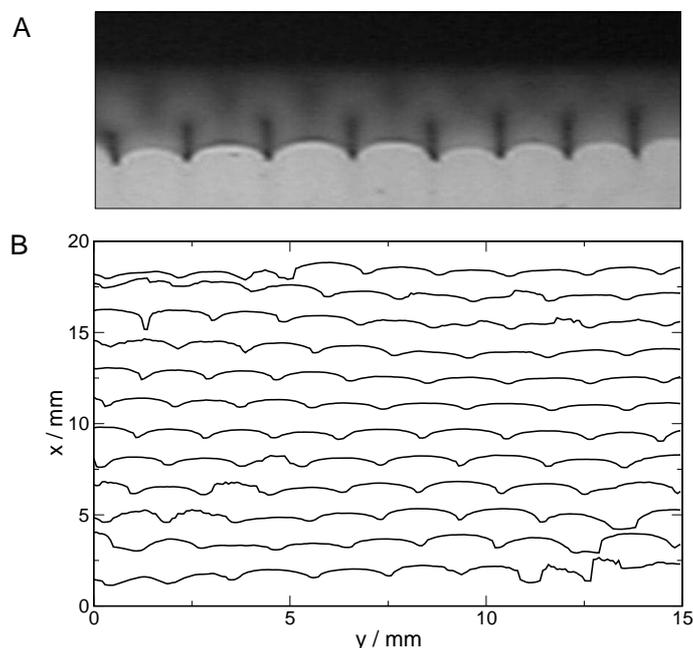


Figure 4: Photograph of the reaction front propagating in a horizontal (A). Black region represents the reactant solution and light region the product. 2 mm thick solution layer containing 25.0 mM Na-polyacrylate, and the related front profiles (B) at $\Delta t = 60$ s intervals.

5 Publications related to the dissertation

1. T. Rica, D. Horváth, Á. Tóth: "Density fingering in acidity fronts: Effects of viscosity", Chem. Phys. Lett., **408**, 422 (2005). (IF = 2.438)
2. T. Rica, D. Horváth, Á. Tóth: "Viscosity-change-induced density fingering in polyelectrolytes", J. Phys. Chem. B, **112**, 14593 (2008). (IF = 4.189)
3. T. Rica, É. Pópty Tóth, D. Horváth, Á. Tóth: "Double-diffusive cellular fingering in the horizontally propagating fronts of the chlorite-tetrathionate reaction", Physica D. **239**, 831 (2010). (IF = 1.568)
4. T. Rica, O. Miholics, D. Horváth, Á. Tóth: "Oscillatory and stationary convective patterns in reaction fronts" in preparation

6 Lectures and poster presentations related to the dissertation

1. T. Rica, D. Horváth, Á. Tóth: Spatiotemporal pattern formation in the chlorite-tetrathionate reaction, International Congress of Young Chemists 2007, Jurata, Poland, 2007. (poster)
2. Rica T., Horváth D., Tóth Á.: Savkatalizált frontok vizsgálata ionos polimeroldatokban, XXX. Kémiai Előadói Napok, Szeged, 2007. (presentation)
3. Rica T., Horváth D., Tóth Á.: Viskozitásváltozás indukált mintázatképződés polielektrolitokban, XXXI. Kémiai Előadói Napok, Szeged, 2008. (presentation)
4. T. Rica, D. Horváth, Á. Tóth: Density fingering of autocatalytic reactions in polyelectrolytes, Second European Science Foundation, Conference on Functional Dynamics, Rothenburg ob der Tauber, Germany, 2008. (poster)
5. T. Rica, D. Horváth, Á. Tóth: Self-organisation of reactive interfaces in an acid-catalysed autocatalytic reaction, Self-Assembly and Self-Organisation at Surfaces and Interfaces, Cambridge, England, 2008. (poster)
6. Rica T.: Polimeroldatok hatása a közegmozgásra autokatalitikus frontokban, Reakciókinetikai és Fotokémiai Munkabizottság, Gyöngyöstarján, 2009. (presentation)

7 Publications not related to the dissertation

1. Á. Veres, T. Rica, L. Janovák, N. Buzás, V. Zöllmer, T. Seemann, A. Richardt and I. Dékány: "Silver and gold modified plasmonic TiO₂ hybrid films for photocatalytic decomposition of ethanol under visible light", Catal. Today, Submitted: 2011. March 14.
2. "Plasmonic properties of gold and silver-gold alloys modified TiO₂ and their photocatalytic efficiency", in preparation

8 Poster presentations not related to the dissertation

1. T. Rica, Á. Veres, I. Dékány: Photodegradation of organic pollutants on gold functionalized TiO₂ surfaces using visible light, 11th International Symposium Interdisciplinary Regional Research, Szeged, 2010.
2. Á. Veres, T. Rica, L. Janovák, D. Sebők, I. Dékány: Effect of silver-modifying on TiO₂ for photocatalytic degradation of thiodiglycol on photocatalyst/polymer composite films, 11th International Symposium Interdisciplinary Regional Research, Szeged, 2010.