

# **Diffusive and convective instabilities in autocatalytic reaction fronts**

Thesis of the PhD Dissertation

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# 1 Introduction and objectives of the thesis

Materials surrounding us can move with various types of transport processes, and hence can have a great impact on our daily lives. It is sufficient to just think of the different atmospheric formations (like a hurricane or a simple cloud), the sea currents or the spreading of pollution. Because these phenomena affect us very strongly, it is essential to study them experimentally. Generally, through diffusion, convection, and in the presence of external electrical field, ion migration can the materials be transferred. The fluid motion can be influenced by three factors: the change in density, in viscosity and in the surface tension. From these three factors, the effect of the first and the third along with diffusion were investigated in detail through autocatalytic model reactions. The autocatalysis is one of the simplest nonlinear chemical phenomena, in which the concentrations and the speed of reaction does not change linearly, a sharp concentration "jump" and rate acceleration can be observed.

The interaction between autocatalytic chemical reactions and material transport processes result in a sharp interface between the reactant and product solutions creating a constant density difference at the two sides. This interface, developing in an autocatalytic reaction, is called a chemical front. In a homogeneous medium, propagating fronts usually keep their original planar shape, i.e., they are stable. However, the traveling planar fronts become unstable under certain circumstances where cellular structures developed from the experimental noise. The instability perpendicular to the direction of propagation is called lateral instability. In convection free medium, we call it diffusive instability, when two conditions fulfilled at the same time: first the autocatalysis should have adequate strength, i.e., the reaction order of the autocatalyst must be greater than one in the rate equation. Second, the flux of the autocatalyst must be less than that of the reactant, which can be influenced by the diffusion coefficient  $D$  and the concentration changes along the front.

Interfaces in the autocatalytic iodate-arsenous acid and the chlorite-tetrathionate systems were investigated to confirm the theoretical models. The density of reactants and products are different in both exothermic reaction because of the change in the chemical composition and the heat release. When these reactions are carried out in reaction vessel with different orientations in the presence of gravity field, fluid motion induced in the system leads to distortions in the interface. Convection can also create a new type of hydrodynamic instability, called Marangoni instability, when material is transported along the liquid/gas interface due to surface tension gradient. The interface is also distorted, since the liquid with a higher surface tension pulls the liquid with a smaller surface tension.

During my doctoral research, I investigated chemical fronts in various autocatalytic reactions. The first goal was to detect diffusive instability in the iodate-arsenous acid reaction with binding only the hydrogen ions. Besides monitoring the spatiotemporal pattern formations and quantitatively characterizing the evolving structures, I have measured the diffusion coefficients of kinetically important components *in situ* with pulsed field gradient spin echo (PFGSE) NMR

method. Theoretical calculations predicted that the mixing length, characterizing the pattern, increases with the square function of the vessel height when the height of the reaction vessel is increased. Previous studies, however, suggested that this proportionality is not valid, so my aim was to determine the scaling law experimentally in the iodate-arsenous acid reaction under several chemical compositions. In addition, I investigated the effect of widening in the third dimension on the self-organization of the chlorite-tetrathionate reaction. Finally, the Marangoni instability was studied in the two model reaction.

## 2 Experimental

The diffusive instability of the iodate-arsenous acid reaction was investigated with a reactor containing a 6 cm  $\times$  7.5 cm polyacrylamide gel between two plexiglas walls. The reaction was started with a filter paper soaked in sulfuric acid. The effect of fluid motion on the pattern formation was studied in the iodate-arsenous acid (IAA) and the chlorite-tetrathionate (CT) reaction. In most of the experiments, Hele-Shaw reaction vessels were used which consisted of two parallel plexiglas walls separated by spacers of different thickness depending on the purpose of the investigation. To describe the long time behavior of the horizontally propagating fronts in vertical Hele-Shaw vessels, we doubled their lengths while their widths were varied between 3 and 10 mm, as illustrated in Figure 1. For the investigation of Marangoni instability, 1 cm high and 1 mm wide extra walls were inserted to the two sides of the spacer in order to create a flat liquid/gas interface and facilitate the loading of the vessel (see the side-view in Figure 1(b)). A glass rectangular slab was the suitable cell for testing the three-dimensional structures, since it facilitated the recording of images parallel from side-view and top-view by using mirrors.

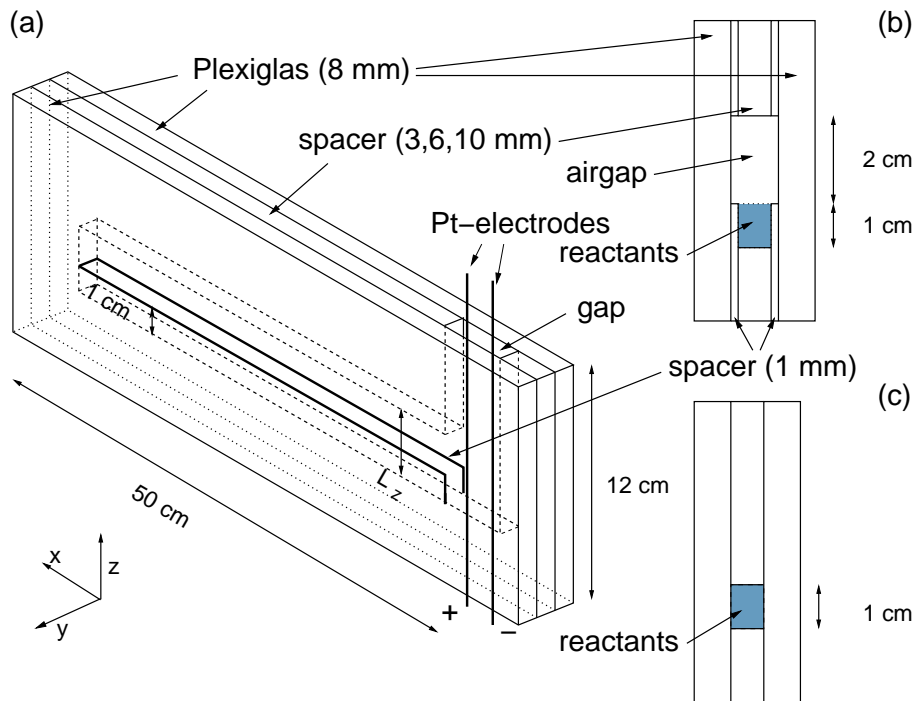


Figure 1: The scheme of the Hele-Shaw reaction vessel (front-view (a)) use for studying the long time behavior of fronts, with air gap (side-view (b)), without the free surface (side-view (c)).

In all cases, planar fronts were initiated electrochemically by electrolysis at 3 V potential difference between two thin parallel Pt-wires producing hydrogen ions in the acid-catalyzed reactions. A monochrome (Panasonic WV-BP330/B) and a color camera (Sony DFW-X710) connected to an image processing system were utilized to monitor the spatiotemporal changes

of the fronts.

The NMR measurements were carried out with a Bruker Avance DRX 500 spectrometer. The change in temperature along the front was monitored by a thin J-type Fe-CuNi thermocouple placed in the cell opposite to the direction of front propagation. The densities of the reactant and the product mixtures were determined by an Anton Paar DMA 58 and 500 digital density meters within  $10^{-5}$  g cm $^{-3}$  and  $10^{-4}$  g cm $^{-3}$  precision. The surface tensions were measured by the Wilhelmy-plate method implemented using Kruss easyDyne meter.

### 3 Evaluation methods

First the front profile and velocity were determined to characterize the long time behavior of the pattern formation. The image processing program assigned a gray scale value ranging from 0 to 255 to the different light intensities of images recorded at specified intervals by the computer. The front position was determined as the extreme of the first derivative of gray scale values as a function of space along the front propagation for every moment. The front profile was obtained by determining the front positions perpendicular to the front. The front velocity was defined as the slope of the linear region of the position vs. time curve.

Then the evolving pattern was quantitatively described by the mixing length ( $L_m$ ) and the amplitude ( $A$ ). The former was defined as the average deviation of the front profiles, while the latter as the distance between the most advanced and the slowest points. The mixing length is a better definition since it considers all points of the front, while the amplitude is given from only two points of the reaction front. The average front profile was prepared by subtracting the average front position from each point, and the curves were averaged in the direction perpendicular to the front propagation.

The free induction signals of NMR were evaluated by using the GIFA program successfully applied in our research group previously.

## 4 New scientific results

- I. *Cellular pattern formation can be induced by binding the hydrogen ion only in the iodate-arsenous acid system, which is supported by the diffusion coefficient measurements in the reactant mixture.* [1]

The autocatalyst must be slowed down to realize the diffusion-driven instability experimentally in convection free environment. The IAA system has two autocatalyst: iodide and hydrogen ions. Cellular patterns with greater amplitudes develop when hydrogen ions are immobilized selectively – in carboxylate containing polyacrylamide gels – when iodide ions were bound to cyclodextrin in a buffered medium. The cells, and hence, the instability are still small because two autocatalysts are in the system and one of them is hydrogen ion which has higher mobility. I measured the diffusion coefficients of kinetically important components in order to describe quantitatively the spatiotemporal pattern formation. Since the diffusion coefficients in acidic and basic solutions were sufficiently close to each other (see Table 1), the *in situ* PFGSE-NMR measurements were performed in the reactant mixtures only. The results showed that the horizontally front remained planar in the IAA system when sodium-polyacrylate used as an immobilizing agent, i.e., hydrogen ions could not be sufficiently slowed down, while the appearance of cellular structures was observed in the case of cross-linked acrylamide gels.

Table 1: Diffusion coefficients in basic and acidic solutions.

	$D_{\text{basic}} / \text{cm}^2\text{s}^{-1}$	$D_{\text{acidic}} / \text{cm}^2\text{s}^{-1}$
Acetate / acetic acid	$(1.21 \pm 0.01) \times 10^{-5}$	$(1.17 \pm 0.01) \times 10^{-5}$
Bromophenol blue	$(4.8 \pm 0.3) \times 10^{-6}$	$(4.9 \pm 0.2) \times 10^{-6}$
Polyacrylate / polyacrylic acid	$(3.64 \pm 0.06) \times 10^{-7}$	$(3.57 \pm 0.09) \times 10^{-7}$

- II. *The power exponents of scaling laws describing the shape of horizontally propagating fronts in the vertical reaction vessel depend on the stoichiometric ratio of the reactants in the IAA system, but they are independent of temperature between 4 °C and 25 °C.* [2]

In a sufficiently long and narrow reaction vessel, a front, characterized with its mixing length  $L_m$ , with constant shape evolves in the IAA reaction when the solution height is varied. I carried out experiments in the IAA reaction with three different ratios of initial concentrations  $R$  in a 3 mm thick and 1 – 4 cm high container. The  $L_m = CL_z^B$  power function was fitted to the experimentally determined mixing lengths for the various chemical compositions. The exponents are summarized in Table 2. The decrease in the ratio of the

initial concentration of arsenous acid to iodate ion results in the decrease of the exponent because of the increase in the reaction front thickness.

Table 2: Scaling exponents ( $R = [\text{H}_3\text{AsO}_3]_0/[\text{KIO}_3]_0$ ).

R	T / °C	B
3.9	25	$1.33 \pm 0.02$
2.8	25	$1.17 \pm 0.06$
2.6	25	$0.78 \pm 0.06$
2.8	4	$1.23 \pm 0.05$

We can conclude from the data shown in the table above that there is a significant difference between the results of the numerical modeling and the experiments. The exponent not only differs from the numerically predicted two but also depends on the stoichiometric ratio of the reactants. I have also investigated the effect of reducing the temperature from 25 °C to 4 °C without changing the reaction mechanism for a given chemical composition. The mixing length decreases by decreasing the temperature, as Fig. 2 illustrates, but the scaling exponent  $B$  remains constant within the experimental error. The constant  $C$  becomes smaller when the magnitude of the density difference is decreased, i.e., temperature is increased.

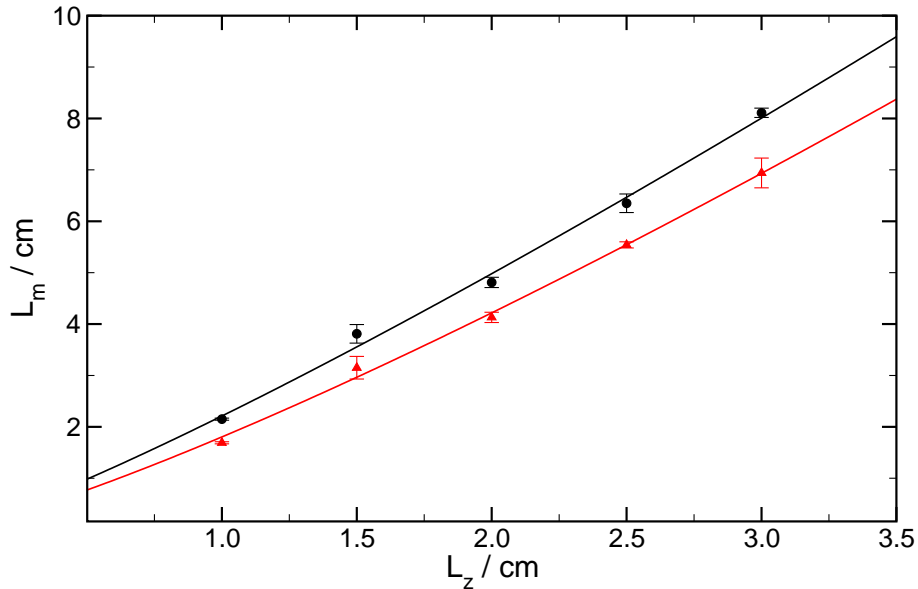


Figure 2: The mixing length  $L_m$  as a function of the vessel height  $L_z$  at 25 °C and at 4 °C. The solid lines correspond to the results of fitting as  $L_m = CL_z^B$ .



III. *There exists a universal scaling exponent ( $1.32 \pm 0.08$ ), which is valid for thin reaction fronts.* [2]

The scaling exponents are in a good agreement for thin reaction fronts propagating horizontally with opposite density changes. The use of the same reaction conditions for the chlorite-tetrathionate and the iodate-arsenous acid system, i.e., chlorite ion and arsenous acid are in excess, temperature is 25 °C and the thickness of the reaction vessel is three mm, the determined exponents equal within the experimental error: the exponent for the CT system is  $1.31 \pm 0.08$ , while for the IAA it is  $1.33 \pm 0.02$ . The density increases when the chlorite ion oxidizes the tetrathionate ion, while the density of the product mixture in the iodate-arsenous acid reaction is lower compared to that of the reactant solution, thus, the isothermal density difference is positive in the former and negative in the latter case.

IV. *The heat release stabilizes the pattern evolving in sufficiently thick solutions for horizontally propagating reaction fronts in the exothermic CT reaction.* [3]

During the experiments, continuously changing shapes were discovered when the 6 mm wide vessel was used, since the heat release and the heat transfer through the vessel wall became comparable. As the thickness of the glass-walled reaction vessel increased, structures with constant shape and velocity emerged at 11 mm thickness shown in Fig. 3. Presumably, the heat evolution during the exothermic reaction helps the stabilization of the pattern. In thick solution layers, chemical fronts of constant shape propagating with constant velocity emerge because the heat evolved on increasing the liquid thickness results in a inefficient cooling through the wall.

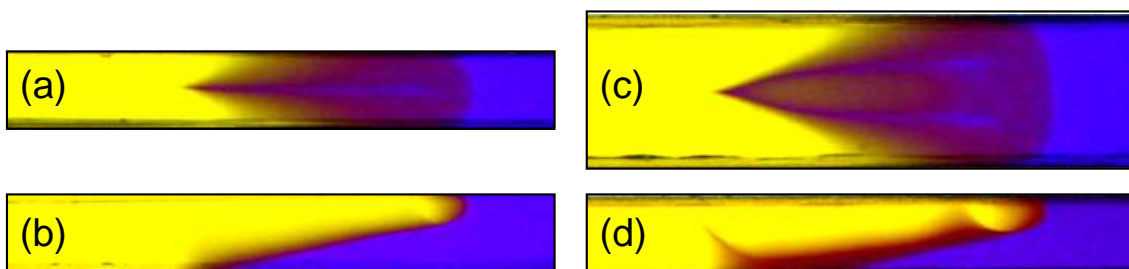


Figure 3: Images of fronts propagating from left to right at  $t = 100$  s: side (b)-(d) and top view (a)-(c), at 11 mm (a)-(b) and at 21 mm (c)-(d) wide of glass slabs.

V. *The mixing lengths, determined from the top and the side, characterize the stable patterns and they are independent of the solution thickness.* [3]

The three-dimensional stationary structure that has two characteristic regions: the leading symmetric edge and the V-shaped trailing cusp. The side view of the leading edge gives a single cell. For its quantitative characterization, the average front positions were divided by the corresponding thickness of the container resulting in a normalized front profile.

The overlap of these profiles indicates that the amplitude of the front is independent of the thickness of the vessel. The top view of the trailing cusps shows that the amplitude increases on increasing the solution thickness while the angle where the segments coalesce is constant. Overall, it can be stated that besides the front velocity certain characteristics of the top and side views are independent of the solution thickness in an 11 – 21 mm range.

VI. *Marangoni instability, altering the shape of a constant front profile, can evolve in the IAA system.* [4]

In the IAA reaction – due to surface tension difference – Marangoni instability was detected at appropriate arsenous acid and iodate concentration ratio, when sufficient amount of surface-active iodine is developed. The introduction of the air gap yields a different structure with greater mixing lengths (as illustrated in Fig. 4), since the reactant solution with higher surface tension pulls the product solution with lower surface tension. When the experiments carried out at  $R = 2.6$  ratio, at  $25\text{ }^\circ\text{C}$ , and at 10 mm thick spacer – where convection is the greatest – the doubling of the air gap does not cause any deviation in the profiles since they are the same within the experimental error. Using the more iodine-producing reactant composition in the narrow Hele-Shaw vessels, we obtain front shapes with longer mixing lengths due to the greater increase in the volume of air.

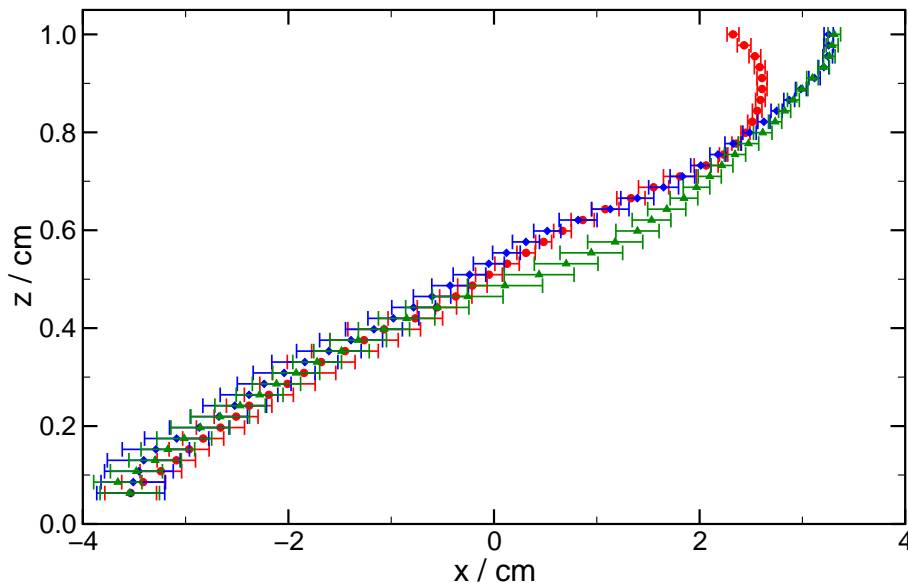


Figure 4: Temporal average profile of the stable patterns for selected container heights at  $[\text{As(III)}]_0/[\text{IO}_3^-]_0 = 2,6$  ratio: without free surface (●), 1 cm high air gap (◆), 2 cm high air gap (▲).

VII. *The Marangoni instability can be eliminated by lowering the temperature where the surface tension difference becomes negligible.* [4]

The iodate-arsenous acid reaction is exothermic, thus the heat released near the front causes further decrease in the overall density. In order to eliminate this effect, the reaction vessel is thermostated to 4 °C. Under these conditions, Marangoni instability is also eliminated, since the stable front profiles overlap within the experimental error. At  $R = 2.6$  ratio the characteristic mixing length increases in a greater manner in the case of thicker reaction vessels. The surface tension difference between the reactant and product solutions is reduced at 4 °C. Hence, when the temperature is reduced from 25 °C to 4 °C, the mixing length not only decreases but also Marangoni instability is eliminated.

## 5 Publications related to the subject of the dissertation

1. T. Rica, É. Pópity-Tóth, D. Horváth, Á. Tóth

*Double-diffusive cellular fingering in the horizontally propagating fronts of the chlorite-tetrathionate reaction,*

Physica D-NONLINEAR PHENOMENA **239**, 831-837 (2010).

IF = 1.555

2. É. Pópity-Tóth, D. Horváth, Á. Tóth

*The dependence of scaling law on stoichiometry for horizontally propagating vertical chemical fronts,*

J. Chem. Phys. **135**, 074506 (2011).

IF = 2.920

3. É. Pópity-Tóth, D. Horváth, Á. Tóth

*Horizontally propagating three-dimensional chemo-hydrodynamic patterns in the chlorite-tetrathionate reaction,*

(in press Chaos) (2012).

IF = 2.081

4. É. Pópity-Tóth, V. Pimienta, D. Horváth, Á. Tóth

*Marangoni instability in the iodate-arsenous acid system,*

(under preparation J. Chem. Phys.) (2012).

(IF = 2.920)

$\Sigma_{IF} = 6.556$

## 6 Lectures and poster presentations related to the dissertation

1. T. Rica, É. Sz. Tóth, D. Horváth, Á. Tóth

*Density fingering of autocatalytic reactions in polyelectrolytes,*

2nd ESF Conference on Functional Dynamics,

Rothenburg ob der Tauber, Germany, 2008. (poster)

2. T. Rica, É. Sz. Tóth, D. Horváth, Á. Tóth  
*Self-organization of reactive surfaces in an acid-catalyzed autocatalytic reaction,*  
Self-assembly and self-organization at surfaces and interfaces,  
Cambridge, England, 2008. (poster)
3. Pópity-Tóth É., Horváth D., Tóth Á.  
*Diffúzió instabilitás vizsgálata a jodát-arzénessav reakcióban,*  
XXXII. Kémiai Előadói Napok,  
Szeged, 2009. (lecture)
4. É. Pópity-Tóth, D. Horváth, Á. Tóth  
*Scaling laws of convective patterns in autocatalytic reactions,*  
Women Chemists and Innovation in the Visegrad Countries,  
Keszthely, 2010. (poster)
5. E. Czeglédi, É. Pópity-Tóth, D. Horváth, Á. Tóth  
*Diffusion coefficient measurement in polyelectrolytes and hydrogels,*  
Women Chemists and Innovation in the Visegrad Countries,  
Keszthely, 2010. (poster)
6. Pópity-Tóth É., Horváth D., Tóth Á.  
*Konvektív mintázatok skálázási törvénye a jodát-arzénessav rendszerben,*  
XXXIII. Kémiai Előadói Napok,  
Szeged, 2010. (lecture)
7. D. Horváth, É. Pópity-Tóth, Á. Tóth  
*Marangoni Instability in the Iodate-Arsenous Acid System,*  
ESA Workshop on chemo-hydrodynamic instabilities at interfaces,  
Szeged, 2011. (lecture)
8. Á. Tóth, É. Pópity-Tóth, D. Horváth  
*Stoichiometry-dependent scaling-law in the IAA system,*  
ESA Workshop on chemo-hydrodynamic instabilities at interfaces,  
Szeged, 2011. (lecture)

9. Pópity-Tóth É., Horváth D., Tóth Á.  
*Marangoni instabilitás a jodát-arzénessav reakcióban,*  
XXXIV. Kémiai Előadói Napok,  
Szeged, 2011. (lecture)
10. D. Horváth, É. Pópity-Tóth, Á. Tóth  
*Horizontally propagating three-dimensional chemo-hydrodynamic patterns,*  
ESA Workshop on chemo-hydrodynamic patterns and instabilities,  
Brussels, Belgium 2012. (lecture)
11. Pópity-Tóth É.  
*Instabilitások tanulmányozása autokatalitikus reakciókban,*  
Reakciókinetikai és Fotokémiai Munkabizottság,  
Siófok, 2012. (lecture)
12. É. Pópity-Tóth, D. Horváth, Á. Tóth  
*Horizontally propagating three-dimensional chemo-hydrodynamic patterns in the chlorite-tetrathionate reaction,*  
Oscillations and Dynamic Instabilities in Chemical Systems,  
Waterville, USA, 2012. (poster)