

# Migration– and diffusion–driven instability in autocatalytic ionic reactions

Theses of PhD dissertation

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# 1 Introduction

Nonlinear chemical dynamics covers a wide scale of special phenomena and patterns, among which the dissertation gives insight into two types of instabilities that occur in autocatalytic ionic reactions: lateral front instability and Turing instability.

The interaction of autocatalytic chemical reaction and transport processes lead to a propagating chemical front. The front structure can be influenced in several ways depending on the type of transport process coupled with the reaction. Under appropriate circumstances a planar front propagating in a homogeneous medium may lose its stability and build cellular structures. This phenomenon is called lateral instability, when along the interface between the initial and final state, i.e., along the chemical front, concentration gradients perpendicular to the direction of propagation arise.

If diffusion acts only among the transport processes of the reaction system, namely we exclude the effect of convection, perturbations along the propagating chemical front decrease as a result of the diffusion of the autocatalyst. The diffusion of the reactants works to the contrary, hence the condition of lateral instability in a reaction-diffusion system is that the flux of the reactant across the front overcomes that of the autocatalyst. Consequently, pattern formation becomes controllable via altering the flux of the key species.

Turing structures can arise as a diffusive instability in systems including positive feedback, where the key species are intermediates. The condition of instability—similarly to the diffusion-driven front instability—is the lower diffusional flux of the autocatalyst with respect to the inhibitory species. Upon this condition, a homogeneous stationary state loses its stability to spatial perturbations resulting in a stationary spatial pattern with distinct wavelength.

In reactions between ionic species external or internal electric field may modify the onset of instability by creating migrational fluxes in or opposite to the direction of the diffusional fluxes. The dissertation gives a description on the processes and conditions underlying the instability in these reaction-diffusion-migration systems.

The migration-driven lateral instability has been examined experimentally in the chlorite–tetrathionate reaction by applying external electric field parallel to the direction of front propagation. Theoretical investigations have been carried out in simple prototype autocatalytic systems, supporting the experimental study. The results are not only in a good agreement, but also give basis for the general conditions to observe migration-driven front instability in various reactions.

The theoretical investigations furthermore have considered the effect of local electric field built up by the system itself due to the ionic species. The extent of diffusion-driven instability from species

with different mobility and charges has been examined in various models exhibiting lateral front and Turing instability.

## **2 Applied methods**

### **2.1 Experimental**

The convection-free medium was ensured by using acrylamide-N,N'-methylene-bisacrylamide-methacrylate copolymer, containing carboxylate groups, as an immobile binding agent for decreasing the amount of free autocatalyst. The hydrogel was placed in an external electric field maintained with Pt-electrodes parallel to the direction of front propagation. Planar fronts were initiated with electrolysis and the pattern formation was monitored by an imaging system. From the evolution of front profiles the velocity of front propagation and the degree of front instability were determined with Fourier transformation. The fronts were characterized quantitatively by dispersion relations and front amplitudes. The dispersion curves are the growth rate coefficients of Fourier modes as a function of wave number. The wave number corresponding to the maximum of the curve shows the mode initially determining the loss of stability; the marginal wave number separates the positive and negative growth rate coefficients, i.e., the domain of unstable and stable modes.

### **2.2 Modeling**

The balance equations describing the reaction-diffusion-migration system augmented with the charge balance of the ionic species yield a boundary value problem for planar fronts in a moving coordinate system, which was solved with the relaxation method. The appropriate boundary conditions outside the finite grid were obtained from the exponential concentration profiles resulting from the phase space analysis of the trajectory corresponding to the planar front. We used linear stability analysis for determining the stability of planar fronts with respect to transverse spatial perturbation, that of homogeneous steady state to spatial perturbation, and constructed the dispersion curves that quantitatively characterize the onset of instability. The evolving front structures and concentration profiles were also calculated in the two-dimensional system with the Euler-method.

### 3 New scientific results

#### 3.1 Migration-driven front instability in the chlorite-tetrathionate reaction

- I. *The effect of inhomogeneous electric field fundamentally differs from that of constant electric field, because it acts independently of  $H^+$ -binding.* [1]

Experiments carried out applying inhomogeneous electric field with immobilization of some amount of autocatalyst showed that in positive electric field ionic migration in the direction of diffusion enhances the instability, while the opposite orientation stabilizes the planar front by reducing the initial perturbations. These tendencies were the same using different immobilization. In inhomogeneous electric field the driving force of instability resides in the difference between the migrational fluxes of the key species.

- II. *In the chlorite-tetrathionate reaction, we have shown experimentally that in reaction-diffusion-migration system lateral instability can be induced by applying an inhomogeneous electric field which selectively increases the flux of reactants.* [2]

In the absence of external electric field and without any immobilization of hydrogen ions, the planar front remains stable as indicated by the negative growth rates in the dispersion curve (see Fig. 1,  $\square$ ). Placing the front in positive electric field the loss of stability is distinctly observable: cellular structure develops as shown in Fig. 1. The corresponding dispersion curve (x), describing the contribution of the different Fourier-modes, contains positive growth rate coefficients in a wide range. The dispersion curves also illustrate that the extent of instability increases on increasing the current density, since both the wave number of the most unstable mode and

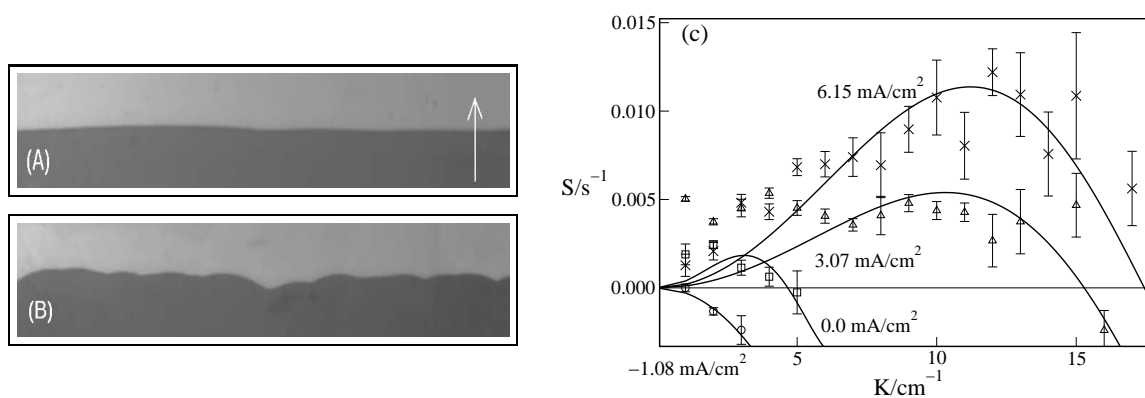


Figure 1: Experiments without immobilization: Images of fronts with  $J = 0.0 \text{ mA/cm}^2$  (A), and  $J = +6.15 \text{ mA/cm}^2$  (B) current density, and dispersion curves (c) reflecting the consequences of increasing current density. Arrow shows the direction of front propagation.

the marginal wave number increase with current density, which also indicates that more cells evolve with smaller wavelength. The negative field, however, reduces the experimental noise and flattens the planar front completely ( $\circ$ ).

### 3.2 Migration-driven lateral instability

III. *The conditions and the driving force of migration-driven instability have been established. For simple cubic autocatalysis, the critical current density required for the onset of instability is determined by the ratio of the electric conductance of the product and the reactant solution and by the difference between the charge of the autocatalyst and that of the reactant.* [3]

Five different autocatalytic models have been investigated theoretically where both the charge difference between the key species and the order with respect to the autocatalyst in the rate law have been varied. Based on our results, the migration-driven instability arises under the following conditions: For the existence of lateral front instability a "pushed" chemical front is required, i.e., in a simple autocatalytic reaction, the order with respect to the autocatalyst must be greater than one. Furthermore, the electric conductance must increase in the course of the reaction, giving rise to an inhomogeneous electric field followed from the stoichiometry of the reaction.

The higher is the difference in specific conductance—and so the difference of electric field strength—between the product and reactant side, the greater is the extent of instability as illustrated by Fig. 2. The dispersion curves, and hence the instabilities, are different due to the

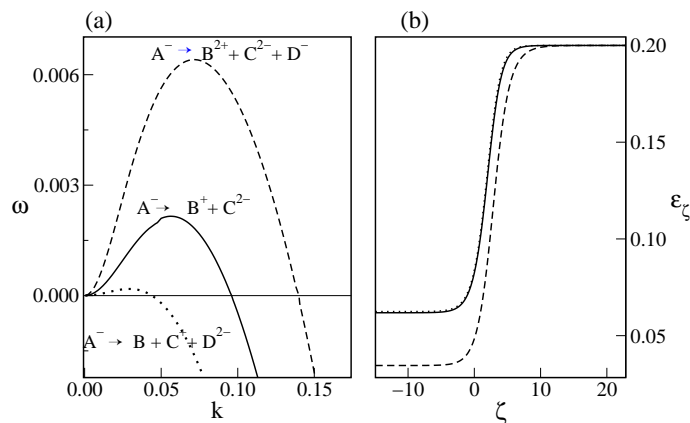


Figure 2: Dispersion curves (a) and local fields (b) in three different systems with  $j = 0.4$  current density. In the reactions B corresponds to the autocatalyst.

difference in the increase of net charge. This supports the statement that with increasing charge difference of the key species the degree of instability also extends.

The critical current density necessary for the loss of stability may be described by the formula

$$j_{cr} \approx \frac{C}{(z_B - z_A) \kappa_{-\infty} / \kappa_{\infty}},$$

where  $C = 0.9 \pm 0.1$ ,  $\kappa_{-\infty} / \kappa_{\infty}$  is the ratio of specific conductance in the product and the reactant solution,  $z_B - z_A$  is the charge difference between the key species.

### 3.3 Diffusion-driven front instability in ionic systems

IV. *We have demonstrated theoretically that in ionic systems the local electric field built up by the species with different charge and mobility may significantly alter the extent of lateral instability.* [4]

In autocatalytic fronts with the autocatalyst diffusing at slower rate, the extent of diffusion-driven front instability depends on the charges of the species as shown in Fig. 3 for cubic autocatalysis. In these systems a local electric field is built up due to the difference in diffusion coefficients.

Depending on the charges of species, the local field may either increase the extent of instability or decrease it. For positively charged autocatalyst in cubic autocatalysis, a positive electric field at the front further enhances lateral instability, while in case of negative autocatalyst a negative field tends to stabilize transverse perturbations. In the latter case, complete stabilization of the planar front is observed for the  $A^- \rightarrow B^-$  system.

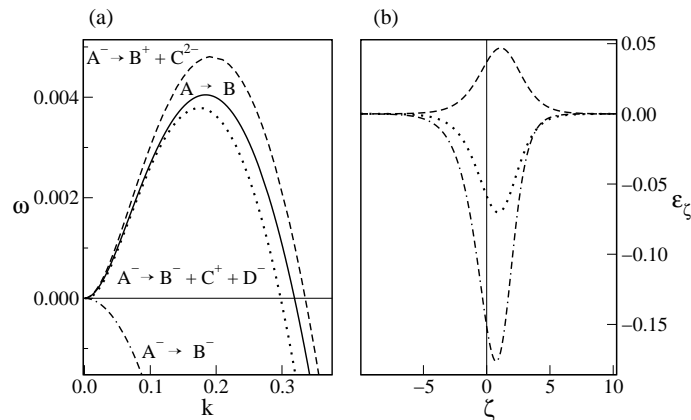


Figure 3: Dispersion curves calculated in different systems with the same diffusion coefficient of autocatalyst (a) and the corresponding local fields (b).

### 3.4 Turing instability in ionic systems

V. We have shown that the charge distribution of the species alters the extent of Turing instability similarly to the tendencies observed in the case of diffusion-driven lateral front instability. [4]

Turing instability in the Schnakenberg model has been studied with various charges on the species. When the homogeneous state is unstable to spatial perturbations, a local electric field is built up as the pattern appears due to the difference in diffusion coefficients. Depending on the charges of species, the local field may either increase the extent of Turing instability or decrease it, similarly to that observed for lateral front instability. If the key species have opposite charge, the local field increases the extent of Turing instability, while stabilizing effect is observed in the model where they have the same charge as shown in Fig. 4.

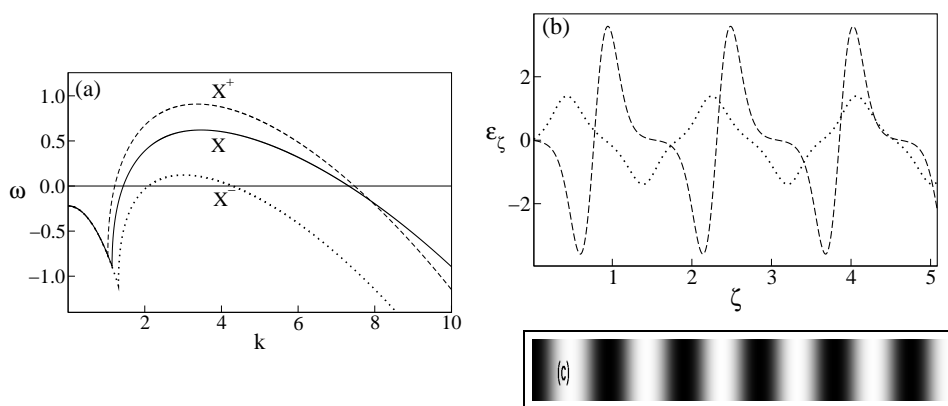


Figure 4: Dispersion curves of models including differently charged autocatalyst (a) and the corresponding local electric fields (b). The inhibitor is in both cases negatively charged. Grey scale representation of the one dimensional Turing pattern (c) .

## 4 Publications related to the subject of the dissertation

1. **Zs. Virányi**, Á. Tóth, D. Horváth, *Lateral instability induced by an inhomogeneous electric field*,  
Chem. Phys. Lett. 401, 575-578 (2005)(IF=2.438)
2. **Zs. Virányi**, D. Horváth, Á. Tóth, *Migration-driven instability in the Chlorite-Tetrathionate Reaction*,  
J. Phys. Chem. A 110, 3614-3618 (2006)(IF=2.898)



3. To appear: **Zs. Virányi**, Á. Tóth, D. Horváth, *Modeling study of migration-driven instability in autocatalytic systems*,  
J. Eng. Math. (2007)(IF=0,885)
4. Under preparation: **Zs. Virányi**, Á. Tóth, D. Horváth, *Diffusion-driven instability in ionic systems*

## 5 Further publications

1. **Zs. Virányi**, A. Szommer, Á. Tóth, D. Horváth, *Lateral instability controlled by constant electric field in an acid-catalyzed reaction*,  
Phys. Chem. Chem. Phys. 6, 3396-3401 (2004)(IF=1,959)
2. R. Patakfalvi, **Zs. Virányi**, I. Dékány, *Kinetics of silver nanoparticle growth in aqueous polymer solutions*,  
Colloid and Polymer Science 283, 299-305 (2004)(IF=1,11)
3. To appear: **Zs. Virányi**, I. Szalai, J. Boissonade, P. De Kepper, *Spatiotemporal Pattern Formation in the Bromate – Sulfite Reaction*

## 6 Posters and talks related to the dissertation

1. **Zs. Virányi**, Á. Tóth, D. Horváth, *Electric field controlled pattern formation in the chlorite-tetrathionate reaction*, GRC on Oscillations and Dynamic Instabilities in Chemical Systems, Lewiston, ME (US), (2004)(E)
2. **Zs. Virányi**, Á. Tóth, D. Horváth, *Electric-field induced lateral instability in an acid-catalyzed reaction*,  
ESF REACTOR Workshop 5, Prague (2004)(P)
3. **Virányi Zs.**, *Migráció által vezérelt laterális instabilitás*,  
XXVIII. Kémiai Előadói Napok, Szeged (2005)(E)
4. **Zs. Virányi**, Á. Tóth, D. Horváth, *Migration-driven front instability*, Summer School on Design and Control of Self-Organization in Physical Systems, Trieste, (2005)(E)

5. **Zs. Virányi, Á. Tóth, D. Horváth**, *Effect of charge on cellular pattern formation in cubic autocatalysis*,  
Gordon Research Conferences, Oxford (2006)(P)
6. **Virányi Zs.**, *Migráció által vezérelt laterális instabilitás*,  
MKE QSAR és Modellezési Szakcsoport, 6. KeMoMo - QSAR miniszimpózium, Szeged (2006)(E)
7. **Virányi Zs.**, *Front és Turing instabilitás ionos rendszerekben*, Reakciókinetikai és Fotokémiai Munkabizottság, Balatonalmádi (2007)(E)