Study of reaction-diffusion phenomena in hydrogen-ion autocatalytic reactions

Theses of PhD dissertation
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1 Introduction

In our environment we can find many form of time and space periodic phenomena. Especially, the study of the biological pattern formation is a really interesting topic, because those often have physiological functions. Alan Turing, a British mathematician pointed out the possibility of the development of self-organized pattern from an originally homogeneous spatial state, in his paper in 1952, and titled "The Chemical Basis of Morphogenesis". At the same period Belousov was looking for a model reaction of intracellular oxidation of organic compounds: he examined the cerium(III)-ions catalyzed oxidation of citric acid in acidic medium by bromate ion. Surprisingly he observed that during the reactions the color of the solution became yellow and colorless periodically. This reaction turned into familiar, after the systematic examination of Zhabotinsky. One of the most striking property of the Belousov–Zhabotinsky reaction (BZ), that it can produce moving spatial patterns and waves in a non-mixed, thin liquid layer. However, it is very difficult to produce stationary patterns in this reaction. According to Turing’s paper the requirement of stationary pattern formation is that the diffusion of the inhibitor (the compound of the negative feedback) must be faster than the activator. This prerequisite can fulfilled only in special circumstances. The first documented experimentally observation of Turing pattern was reported by De Kepper and co-workers in the chlorite–iodide–malonic acid reaction. The development of stationary spatial patterns in this reaction resulted in the presence of starch, because it binded the triiodide ions in a reversible way. This binding causes smaller effective diffusion factor of the activator. In 2009 a systematic method to design stationary patterns in activator-inhibitor type chemical reaction have been developed by De Kepper and co-workers. Since then by using this method four different chemical reactions were found to be able to produce stationary patterns.
2 Objectives

The aims of my PhD study were to look for new reaction-diffusion system, to perform numeric simulation of that system and investigate the effect of the diffusion feed which is a crucial parameter of the reaction-diffusion system.

- Examination of the effect of the gel thickness in pattern formation: the diffusive feed has a determining role in chemical pattern development. One of the easiest way to control experimentally the time-scale of diffusive feed is the changing of the gel thickness. My goal was to study the results of the operation of this parameter in the pattern formation.

- Generating of a stationary pattern using the systematic design method in a new system: when I started my PhD work only three aqueous-phase chemical system were known to produce stationary pattern: chlorite–iodide–malonic acid (CIMA), iodate–sulfite–ferrocyanide (FIS), iodate–sulfite–thiourea (TuIS). According to the above mentioned systematic design method, all of the pH oscillators are suitable to form stationary pattern. My goal was to go step by step through this design method with hydrogen-peroxide–sulfite–ferrocyanide reaction and produce stationary pattern.

- Perform numeric simulation to explain the observations of the experiments: We recognized that it is necessary to find the well known known CFUR approximation (continuous flow unstirred reactor) to make a better fit to the experiments.
3 Experimental methods

To perform the experiments I used a thermostated batch reactor \((V=25\, \text{cm}^3)\), a thermostated, continuous fed, stirred reactor (CSTR, \(V=45\, \text{cm}^3\)), a conical, cylindrical and disc shaped gel reactors (Figure 1). pH was measured by a HI1330B glass electrode and a Consort C861 and recorded by a computer. A digital camera and Streampix (Norpix) recorded the pictures, image processing was accomplished by ImageJ and GIMP. Warmlaser 200 mW laser pointer was used to control the pattern formation.

Experiments on the effect of gel thickness were performed in the conical and cylindrical shaped gel reactor with FIS and TuIS systems. The new, stationary pattern formation was executed in the disc shaped gel reactor with the HPSF system.

Numeric simulations were performed with the finite difference method using XPPAUT and CVODE programs.

Figure 1: Schematic drawings of the disc and conical shaped gel reactors.
4 New scientific results

- I have pointed out that chemical waves appear only above a critical gel thickness in the FIS and TuIS systems.

- I have shown that in the development of spatial oscillations in the FIS and TuIS reactions, the negative feedback is provided by the kinetics and by the diffusion feed.

Figure 2: Stationary iodine front and moving pH front in the TuIS system at different sulphuric acid concentrations, in the gel reactor.

- I have observed the appearance of stationary iodine (triiodide) front in TuIS system, in parallel at larger gel thickness. (Figure 2)

- I have systematically found chemical fronts, waves and stationary pattern formations in the HPSF system (Figure 3).

Figure 3: Picture of a stationary pattern and its time-space development figure of HPSF system, in a disc shaped reactor.
• I have proved experimentally that the light sensitivity of the HPSF system is suitable to control the pattern formation (Figure 4 a).

![Image](image1.png)

**Figure 4:** Disposal of labyrinth in the HPSF system (a) and stationary pattern in the numeric simulation (b).

• I have refined the CFUR approximation to make a better description of the mass transport between the CSTR and the gel (DFUR approximation).

• I have showed that the experiment results, like spatial bistability and stationary pattern can be qualitatively reproduced by numeric simulations using the Rábai model of the pH oscillators and by the DFUR approximation (Figure 4 b).
Scientific publications

Related to the dissertation:


Not related to the dissertation: