Self-organization in autocatalytic chemical systems: pH and calcium ion pattern formation

PhD thesis

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Introduction

Periodic phenomena can occur in many fields of nature including biological systems, and also have important regulatory function in living organisms. The heart rate provided by the sinus node and the circadian rhythm are good examples for that. Periodicity may appear not only in time but also in space, a special case of that is the patterns of animal integument.

Chemical periodicity can be occurred in time and space under certain circumstances. During temporal oscillation the concentration of an intermediate changes periodically. The spatial oscillations may appear as reaction-diffusion waves. Another form of spatial periodicity is the formation stationary structures from a homogeneous initial state. By studying chemical reaction-diffusion systems the fundamental aspects of periodic biological phenomena can be studied in relatively simplified way.

Objectives

The objectives of my research were:

(1) Investigation of the basic properties of Landolt-type autocatalytic reactions using different oxidizing agents. Mathematical description of the inflection time and the pH change during the autocatalytic reactions. Studying the effect of reversible proton-binding agent on autocatalytic reactions.

(2) Generation of spatiotemporal waves in bromate – sulfite – ferrocyanide (BSF) system. Investigation of the effect of the thickness of the gel and the temperature, the parameters which has fundamental effect on reaction diffusion systems. Study of the role of the different negative feedback mechanisms: the partial oxidation of sulfite ion and the long-range activation in the bromate – sulfite reaction-diffusion system.

(3) Creation and characterization stationary patterns in BSF system using the known design method.

Comparison of the results with patterns developed in other Landolt type pH oscillators.

(4) Generation of calcium ion waves and patterns by coupling the pH-dependent formation of $CaEDTA^{2-}$ to the BSF reaction.

Methods

In batch experiments a thermostated and mixed reactor was used. The pH of the content of the reactor was measured by a combined pH electrode, the analog signals were digitized and processed on a PC.

Two different types of one side fed open reactors (OSFRs) were used: a ring-shaped and a disc-shaped reactor. In the ring-shaped reactor the direction of the observations was perpendicular direction to the diffusive fed. To monitor the state of the continuous stirred tank reactor (CSTR) content, the potential of a bright platinum electrode was measured against the reference electrode connected via salt bridge. The reactor was illuminated from above and pictures were taken from the same direction. Disk-shaped OSFR was used for observations along the feed direction. The content of CSTR flowed behind a 25 mm diameter gel disk. The reactor was illuminated from the direction of the CSTR, pictures were taken from the opposite side. The reactors were immersed in a thermostated vessel and were mixed. Feeding was provided by a four-channel peristaltic pump.

Reagent solutions were added from four separated containers, and were mixed only in the reactor. In each case, the gel was prepared from 2% agarose. Bromocresol green pH indicator and arsenazo (III) metal indicator were used for visualization the reaction-diffusion phenomena. The reactors were illuminated through a band-pass filter. The pictures were taken by using CCD camera. To reduce the noise level, image averaging was used during image capture. The image processing was made by using ImageJ software.

The Rábai-model was used for numerical simulations at batch phenomena. The hydrogen ion consuming reaction was omitted.

In OSFR simulations the partial differential equations were discretized with a standard second-order finite difference scheme. The resulting system was solved by the SUNDIALS CVODE solver.

Dirichlet boundary condition was applied at CSTR/gel surface, and Neumann boundary condition at gel/impermeable wall surface.

Results

In my doctoral thesis the results related to the study of the bromate – sulfite – ferrocyanide reaction–diffusion system are presented.

(1) The autocatalytic oxidation of sulfite ion was experimentally investigated using hydrogen peroxide, bromate ion and iodate ion as oxidizing agent. Numerical simulations were carried out based on the Rábai model. The experiments and simulations showed that the pH change in the course of the oxidation and the inflexion time are independent of the nature of the oxidant in all the three cases. These observations can be described by simple mathematical equations which are modified if reversible proton acceptor is present.

(2) In the BSF reaction spatial bistability and spatiotemporal oscillation were experimentally produced and observed in parallel and perpendicular direction to diffusive feed. The effect of temperature and thickness of the gel on the spatiotemporal oscillation were studied.

Numerical simulations were used to characterise the BSF reaction-diffusion system. In this system the oscillations can appear as result of three different negative feedbacks.

(3) Stationary hydrogen ion patterns were produced in BSF system using the known design method. The appearance of these patterns was found to depend on the feeding concentration of ferrocyanide. The negative effect of the ionic strength on the pattern formation was experimentally verified.

(4) Calcium ion waves and patterns were produced by coupling protonation and complex formation equilibria of CaEDTA to BSF reaction – diffusion system. Formation of calcium patterns were explained and described.

Conclusions

(1) In Landolt-type autocatalytic reactions the pH-change were significantly reduced in the presence of reversible proton-binding agent. The ΔpH is independent of hydrogen sulfite concentration, but in the presence of a protonatable weak acid ΔpH does it. The proton-binding compound significantly slows down the reaction rate. In oscillators based on Landolt-type autocatalytic reactions, the pH change influences the amplitude and the inflexion time influences the period. The reversible proton-binding compound used in different couplings modifiy the properties of the oscillator: the driven system affects the driving pH oscillator.

(2) In the bromate – sulfite – ferrocyanide system oscillation can be developed via three different types of negative feedback routes. In the experiments the oxidation of ferrocyanide gives negative feedback, the parameter range of oscillations determined by long-range activation and partial sulfite oxidation is narrow.

(3) The success of the known design method is supported by the experiments: using NaPAA to reduce the mobility

of autocatalytic hydrogen ions lateral front instability and stationary pattern formation have been observed. The formation of calcium ion patterns in BSFCaEDTA oscillator has confirmed the application of this systematic design method.

(4) The formation of the calcium ion pattern indicates a decrease in hydrogen ion diffusion speed, which was proved by calculations. Based on these simulations, a small molecular proton-binding compound is capable of reducing effectively of the mobility of hydrogen ions.

Publications

Publications related to the PhD thesis:

1. Molnár, I.; Takács, N.; Kurin-Csörgei, K.; Orbán, M.; Szalai, I. (2013) Some General Features in the Autocatalytic Reaction between Sulfite Ion and Different Oxidants. International Journal of Chemical Kinetics, 45(7): 462-468. IF: 1,566
2. Molnár, I.; Kurin-Csörgei, K.; Orbán, M.; Szalai, I. (2014) Generation of spatiotemporal calcium patterns by coupling a pH-oscillator to a complexation equilibrium. Chemical Communications, 50(32): 4158-4160. IF: 6,834
3. Molnár, I.; Szalai, I. (2015) Pattern Formation in the Bromate–Sulfite–Ferrocyanide Reaction. The Journal of Physical Chemistry A, 119(39): 9954-9961. IF: 2,883
4. Molnár, I.; Szalai, I. (2017) Kinetic and Diffusion-Driven Instabilities in the Bromate-Sulfite-Ferrocyanide System. Journal of Physical Chemistry A, 121(9): 1900-1908. IF: 2,836

Publications not related to the PhD thesis:

5. Molnár, I.; Kurin-Csörgei, K.; Szalai, I. (2018) Spatiotemporal dynamics of minimal bromate oscillators in an open one-side-fed reactor. Phys Chem Chem Phys, 20(20): 13851-13857. IF: 3,567