Spatial-gradient-driven Self-organization and Self-assembly of Chemical Systems

Final report for K_16 119795

1 Motivation

The motivation in this project was the construction of chemical systems where gradients play a central role in the self-organization of dissipative structures. These gradients, controlled externally or spontaneously emerging from autocatalysis, bring about transport processes in the form of diffusion, advection, and by coupling with chemical reactions generate a reaction-diffusion-convection system far-from-equilibrium. The quantitative description of these emerging phenomena is an essential step in the understanding of self-organization in natural processes. This interdisciplinary research was conducted in four parallel work packages: precipitation processes in confined geometry, flow-driven systems, autocatalytic systems related to supramolecular self-assembled structures, and emergent behavior of gradient-driven systems.

2 Precipitation processes in confined geometry (WP1)

The characterization of the kinetics of chemical precipitation reactions has been proved to be important in understanding the processes in confined geometries with different reactants. Benchmark experiments have shown that precipitation kinetics must be studied on two different time scales in accordance with the various reactions. Therefore, we have elaborated a high-speed-camera-based and a UV-vis-spectrometer-based method for the study of reactions described by short (< 5 s) and long (> 5 s) characteristic time scales, respectively.[1,2] With those protocols in hand, we have then performed a systematic kinetic analysis applying sodium oxalate as a common precipitant in the reactions with various alkaline earth and transition metal ions. It is found that an equation, which had been known to be only phenomenological, in fact provides information about the pathway of the reaction, i.e., whether it occurs via complex formation or precipitate forms directly from ions, or via parallel routes.[3]

Flow-driven precipitation experiments applying radial injection have been performed with numerous chemical systems in a confined geometry in order to investigate the effect of reaction rate on pattern formation. It is found that even if the experimental conditions, such as injection rate, gap height, reactant concentration, and the host solution, are kept constant, significantly different patterns can be obtained upon changing the chemical character of the injected solution. If reactants are brought together such that the time scale of the reaction is long compared to the injection, the characteristics of the evolving pattern only rely on the hydrodynamic instability present in the system according to the apparent solution properties. If the time scale of the reaction and that of the flow are comparable, a radially expanding pattern grows, which conserves the flow field present during precipitation. When the reaction is significantly faster than the flow and provides a large amount of precipitate, the coupling of precipitation and hydrodynamics becomes strong, leading to complex pattern formation.[4] It has also been observed that the relative contribution of nucleation to crystal growth changes the pattern characteristics. If a large number of small crystals are produced, precipitate tube formation is favored. On the contrary, fast crystal growth providing large particles in small amount counteracts less with hydrodynamics (Fig. 1).[5] We have also attempted to modify the characteristic pattern of a selected flow-driven precipitation. Benchmark experiments have shown that magnesium ion cannot provide tube-like pattern formation with carbonate precipitant even if the flow rate and reactant concentrations are high, in contrast to, e.g., the similar calcium and strontium ion systems. Therefore, experiments have been performed with solutions containing either Ca(II) or Sr(II) next to Mg(II). We have observed that, at a given [Mg(II)], the increase of Ca(II) or Sr(II) concentration leads to precipitate tube formation even in the case of three times Mg(II) excess. Also, these tubes form under conditions where neither Ca(II) nor Sr(II) is able to provide precipitate tubes during injection.

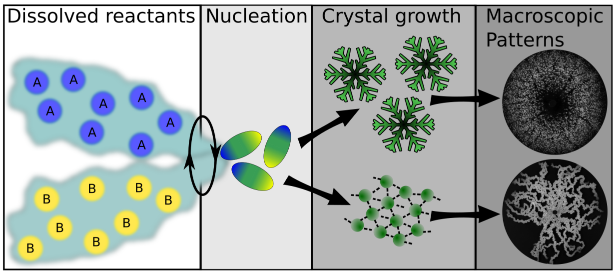

Figure 1: Relation of time scale determines both the crystal growth and the final precipitation pattern.[5]

Furthermore, as an outreach of the project, ZIF-8 formation (zinc ion and 2-methylimidazole) has been investigated under the same flow conditions to search for novel product microstructures. As an unexpected result, Liesegang type macroscopic pattern has been observed when the reactant solution contained some calcium and magnesium contaminants (doping). Those composites have been investigated via SEM and XRD as well. By varying the stoichiometric ratio of the reactants and by spanning their concentration range, we have found that, although tube-like pattern formation cannot be obtained, characteristic patterns discovered in other chemical systems (e.g., $CaCO_3$) are present. Structure analysis is in progress in order to see whether any effect of flow on particle size and shape could be tracked. In parallel, we perform UV-vis photometer aided kinetic measurements to shade light on possible recrystallization of the product. A scientific publication will soon (ca. 2 months) be submitted based on the results.

Finally, although it had not proposed for the project, obstacles have been placed within the confined geometry to investigate how the modified flow field interacts with pattern formation. It is found that the originally uniform flow field splits into small segments around the obstacles which increases the yield of the reaction.[6]

3 Flow-driven systems (WP2)

We have produced hollow precipitate tubes with the flow-injection technique, and characterized their linear and volume growth using the reaction between copper ions and phosphate or silicate ions. We have shown that the ratio of volume increase rate to pumping rate is constant independently of chemical composition. Osmosis contributes to the tube growth, since the inward flux of chemical species dominates during the precipitate pattern formation. While the tubes have smooth outer surface, the inner walls are covered with nanoflowers for copper phosphate and nanoballs for copper silicate.[7]

In a different experimental setup we have created a spreading gravity current by adjusting the appropriate density difference between the solutions. This forms a radially symmetric precipitate pattern that contains spatially separated copper oxalate monohydrate and cobalt oxalate tetrahydrate (Fig. 2), indentified by X-ray diffraction measurements. In the transition zone, a unique crystalline composite containing copper oxalate plates with cobalt oxalate coating also forms.[8]

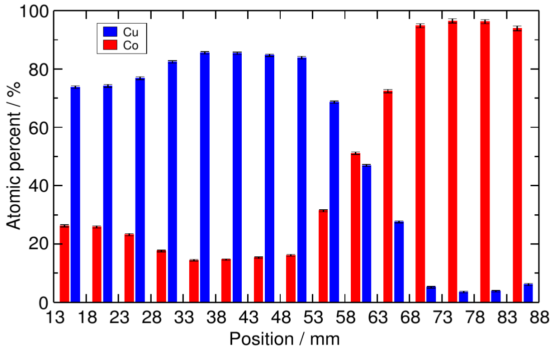

Figure 2: Spatial separation of copper(II) and cobalt(II) oxalates driven by a gravity current.[8]

We have demonstrated that a simple mechanical effect (an oscillatory pressure change) can be used to shape the evolving structure. It is seen that multiple, oscillatory banded copper phosphate membranes can be yielded by injecting one solution into the other one via a sufficiently slowly rotating peristaltic pump simply because the solution is delivered in an oscillatory manner with well-defined pressure variations leading to pulsating flow. Changing the reaction for another one providing more cohesive and faster precipitation may allow the investigation of how the length, diameter, and periodicity of the bands can be tuned by adjusting the peristalticity of the pump. The published work became the editor's pick and produced a cover image.[9]

For characterizing the spatial distribution of nucleation we have shown that a precipitation reaction can be driven by a gravity current that spreads on the bottom as a denser fluid is injected into an initially stagnant liquid. Supersaturation and nucleation are restricted to locations where the two liquids come into contact, hence the flow pattern governs the spatial distribution of the final product. In a numerical study we have quantitatively characterized the flow associated with the gravity current prior to the onset of nucleation and distinguish three zones where the coupling of transport processes with reaction can take place depending on their time scales. A scaling law associated with the region of Rayleigh–Taylor instability behind the tip of the gravity current has also been determined.[10]

4 Autocatalytic systems of supramolecular structures (WP3)

An extensive literature survey has led us to the hydrolysis of Schiff-bases that can be autocatalytic with respect to hydroxide ion. The experimental studies using a couple of custom-synthesized Schiff-bases have revealed that the hydrolysis of the selected Schiff-bases is characterized with weak positive feedback. The thorough investigation of the reaction steps involved has shown that a single autocatalytic step cannot be identified within the net reaction, instead the entire scheme comprises an autocatalytic network. Hydroxide ion plays the role of the autocatalyst due to the difference in the strength of basicity of the reactant imine and the product amine. The former is weaker, hence pH increases in the course of the reaction. This, in turn, results in an increase of reaction rate for the hydrolysis. Although the autocatalysis is weak, this switch in pH takes place in a biofriendly environment of 7.0-8.0. Using the selected Schiff-bases, the steady-state is found to be stable in the pH range of 5–9. This is attributed to the significant contribution of the reaction of water with the protonated imine to the net process.

Theoretical and numerical studies based on the empirical rate laws have led to the construction of an 8-variable model. The model parameters have been obtained from the fitting to the experimental results in closed, well-stirred system. In order to achieve a quantitative description, the reactions between hydroxide ion and both the imine and its protonated form, as well as that between and water and the protonated imine to yield amine have to be incorporated in the network. We have also shown that this autocatalytic network itself in a continuously-stirred tank reactor, provided the direct hydrolysis is sufficiently slow, can produce not only bistability, but also sustained oscillations with the addition of a hydroxide ion consuming reaction. By separating the time scales, the 8-variable model can be reduced to a two-variable back bone that carries the essential features of this autocatalytic network. A manuscript is in preparation on the chemical characteristics of the reaction in a closed system. The results have been presented in an invited lecture in the "Chemical Systems Meeting" and in the "15th International Conference on Fundamental and Applied Aspects of Physical Chemistry" conferences.

Hydrogen ion plays a crucial role in several spatially extended autocatalytic systems where diffusion couples with the reactions, hence both chemical and diffusion time scales determine the behavior. In an effort to determine the diffusion coefficient of hydrogen ion, we have constructed a custom-made conductometric cell designed to measure the effective diffusion coefficient of a pair of strong electrolytes containing sodium ion or hydrogen ion with a common anion. This, together with the individual diffusion coefficient for sodium ion obtained from PFGSE-NMR spectroscopy, has allowed the determination of the diffusion coefficient for hydrogen ion in agarose. Numerical calculations have also been performed to study the behavior of a diffusion-migration model describing ionic diffusion in our system.[11] This general method can be extended for other hydrogels.

The systematic study of a redox system based on the reactive oxygen species (ROS) dynamics in the rhizosphere has been extended to search for oscillatory dynamics. An extensive stoichiometric network analysis has demonstrated that both Hopf-bifurcation and saddle-node transition can exist under pool chemical approximation (Fig. 3). This suggests that transient oscillations and sharp transitions can be observed with an appropriate parameter set.[12]

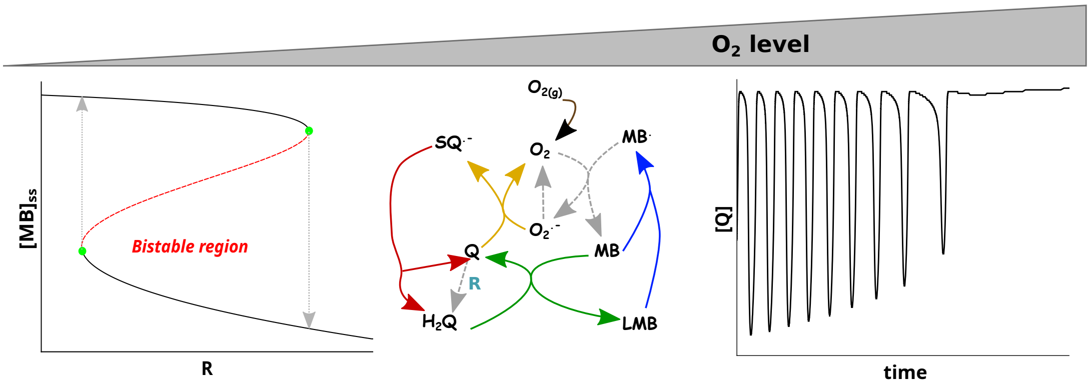

Figure 3: Oxygen level controls the behavior from bistability to oscillations in autocatalytic network for ROS dynamics in the rhizosphere.

By studying the behavior of this ROS dynamics in a spatial distributed system, we have found that diffusional spreading can create a transiently sharp reaction front when it drives an autocatalysis backwards. With a systematic numerical study we have shown that these thin reaction fronts can generally be maintained by a diffusion front in reversible autocatalytic systems that epxlains the experimental observations. We have presented the result in a lecture at the "Solvay Workshop on Nonlinear Phenomena and Complex Systems" and a manuscript is in preparation.

Biologically relevant oscillatory reactions can couple to precipitation reactions. We have performed a kinetic investigation of the precipitation of calcium phosphate using a process widely found in microorganisms: the hydrolysis of urea by enzyme urease. Under certain conditions, periodic precipitation has been obtained accompanied by pH oscillations in a well-stirred, closed reactor. We proposed that an internal pH-regulated change in the concentration of phosphate ion is the driving force for periodicity. A simple model involving the biocatalytic reaction network coupled with burst nucleation of nanoparticles above a critical supersaturation reproduced key features of the experiments.[13] We have extended the experimental investigation of precipitation reactions coupled to the hydrolysis of urea by enzyme urease and found that periodic production of calcite accompanied by pH oscillation can also be observed in the absence of phosphate contamination. The model construction and theoretical study are planned for future.

5 Gradient-driven systems (WP4)

The effect of three different gradients have been addressed: magnetic field, surface tension and concentration.

By pumping gadolinium(III) salt solution into sodium phosphate solution in the presence of magnetic field, we have produced tubular precipitate structures. The growth dynamics depends on the injection rate and the magnetic field strength. We have found two distinct growth regimes in the parameter space. In the first the magnetic field acts on the flow of the paramagnetic solution and the precipitation process follow the flow pattern. In the second the precipitate formation is directly influenced by the magnetic field, in which case the flow is oriented towards the higher magnetic field faster than in the absence of precipitation. We have also shown that Lorenz force does not play a role in the confined space around the precipitate. X-ray tomography of the produced tubular structure has revealed that the surface morphology of the precipitate tubes can be controlled by the magnetic field.[14]

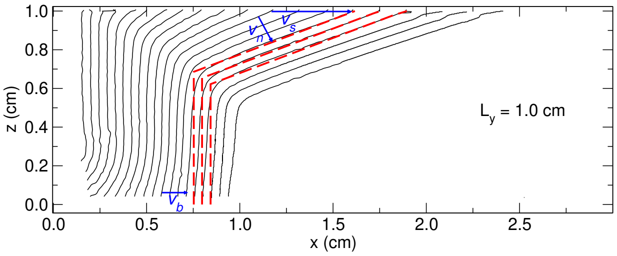

Figure 4: Front propagation driven by Marangoni instability on the upper surface corresponds to geometric spreading (red dashed lines).[15]

We have performed modeling calculations of the reaction-diffusion-advection system in three dimensions to reconstruct the experimental observations in our earlier microgravity experiments and validated a model based on geometric spreading (Fig. 4). According to the calculated flow field, the direction of significant fluid flow follows the concentration gradients and hence coincides with the propagation of the reaction front, allowing only negligible transverse flow in the upper fluid layer.[15,16]

Controlling self-organization in precipitation reactions has received growing attention in the efforts of engineering highly ordered spatial structures. Experiments have been successful in regulating the band patterns of the Liesegang phenomenon on various scales. We have shown that by adjusting the composition of the hydrogel medium, we can switch the final pattern between the classical band structure and the rare precipitate spots with hexagonal symmetry. The accompanying modeling study reveals that besides the modification of gel property, tuning of the time scale of diffusional spreading of hydroxide ions with respect to that of the phase separation drives the mode selection between one-dimensional band and two-dimensional spot patterns.[17]

6 Outcome

At the start of the project we sought answers to five general questions. The following statements can be formulated based on our results.

How is the dynamics of the precipitate formation affected by the flow in gradient-driven systems?

Fluid motion introduces an additional transport process that has a substantial effect on the spatial distribution of local supersaturation. Hence with initially separated reactants, macroscopic precipitate pattern formation is characterized by strong advective currents along the flow, and diffusional fluxes transverse to that. The interplay of these two factors has a dominating effect on the structure of the precipitate.

How does the chemical character of precipitants influence the precipitate properties?
Reaction rates, determined by the chemical properties of the components, are crucial. The relation between chemical time scale and that of advection and diffusion determines the structures and eventually the properties of the precipitate.

Can we find new systems exhibiting oscillations or reaction fronts using organic reactions?
The network based on the hydrolysis of Schiff-bases containing phenolic hydroxyl groups can support sustained oscillations in an open system in the presence of a reactant consuming hydroxide ion. With the particular Schiff-bases selected for the experiments, the OH-independent hydrolytic step is sufficiently fast to stabilize the steady state in the entire pH-range applicable. The chemical time scale of this step is significantly shorter than that of diffusion, therefore reaction fronts chosen the experiments cannot evolve in closed distributed systems.

Can we drive the self-assembly of soft matter with autocatalysis?
This question was meant as a pathfinder based on the knowledge acquired in the work packages. We have only managed to assemble the oscillatory precipitation of calcite driven by an enzyme reaction, due to the time spent on the specific points in the work packages. Hence the question remains to be answered and indeed we plan to continue the research along this path.

What are the major effects on pattern formation in the presence of externally induced spatial gradients?
We can identify two major factors that can drive pattern formation: direct contribution from the transport process associated with the spatial gradient and the spatial distribution of chemical time scales. Both of these can dominate the spatial pattern and properties of the product.

Besides the 17 publications, three Ph.D. dissertations[18–20] and five M.Sc. theses[21–25] (one with "Nívódíj"[22]) were among the results of the conducted research. This work by its nature is a fundamental research, however, the external control of gradients can be utilized to fine tune products and their properties. This idea can be exploited in a specific reaction to enhance the manufacture of a desired product.

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