Control of precipitation patterns in two-dimensions by pH field

Ferenc Molnár Jr. [a], László Roszol [b], András Volford [b], István Lagzi [c,d,*]

[a] Department of Theoretical Physics, Eötvös Loránd University, Budapest, Hungary
[b] Department of Physics, Budapest University of Technology and Economics, Budapest, Hungary
[c] Department of Meteorology, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary
[d] Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL, USA

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ABSTRACT

Systematic deformation of a moving precipitation front into a 2D stationary profile by a pH field generated by acidic and basic reservoirs and its design procedure are discussed. Results indicate that in some pattern formation systems, where the pattern emerges by a precipitation reaction of metal and hydroxide ions, phenomena can be governed by a complex pH field. The pattern formation can be described and discussed by taking into account acid–base chemistry. Our approach, which relies on solving either time-dependent reaction–diffusion equations or derived Laplace's equation, provides a reasonable description of the system.

1. Introduction

Precipitation structures can spontaneously evolve in not only inanimate systems [1,2] (e.g., structure of agates), but also in animate systems [3] (e.g., seashell pattern formation) by self-organizing way. Even though nature has been creating fascinating patterns from the very beginning, the first man-made precipitation system was designed and the results were published only a hundred years ago [4]. There are many precipitation reactions in various media (usually gelled media: either hydrogels [5–8] or aerogels [9]) available for pattern formation that allow creating different precipitation structures in two- or three-dimensions. Despite the enormous efforts, pattern formation is currently in a somewhat precarious position. Therefore, to survive a next few decades, this field should provide soon some real scientific and industrial applications (e.g., special materials, sensors, electronic devices, catalyst). The focus of the precipitation pattern formation must gradually shift from the investigation of individual and specific systems to their control in macro- and microscales and use them in material science. Therefore, a real challenge is how the pattern formation (not only in precipitation systems) can contribute to development of new and robust ways of designing specific materials in bulk phase via controlling patterns.

In the usual experimental setup of these systems (Liesegang phenomenon), the inner electrolyte is homogeneously distributed in a gel, while the outer electrolyte diffuses into the gel from the specific reservoir. It is a general argument that the role of the gel is just to prevent the sedimentation of the precipitate and the hydrodynamic instability. However, there are few recent results on the effect of the gelled medium on pattern formation [10–14]. Pattern formation occurs due to interplay between the precipitation reaction and diffusion of the electrolytes. The produced pattern consists of a set of precipitation bands or rings (depending on the geometry of the system), which are always perpendicular to the diffusion flux of the invading (outer) electrolyte. These patterns should be considered as static ones in the sense that these precipitation zones stay at a given position where these zones formed. However, there is another family of precipitation patterns. In some systems, the formed precipitate (e.g., $Al(OH)_3$ [15–19], $Cr(OH)_3$ [20–23], $Co(OH)_2$ [24], HgI_2 [25]) can be redissolved in the excess of the outer electrolyte via formation of the soluble complex, resulting in a moving precipitation front. Here the precipitate forms from metal cation and hydroxide ion. Therefore, any reactions or techniques which can affect the global pH field are capable of controlling precipitation patterns [26]. Recently, we developed a technique for controlling and distorting precipitation fronts into stationary and appropriately shaped structures in $Al(OH)_3$ system [15]. This method provides an alternative way to control precipitation structures compared to the method that uses the ionic nature of the reagents [27,28] and realizing specific control through time-dependent electric field [29].

Pattern formation phenomenon can be described by reaction–diffusion systems which are mathematical models that describe the spatial and temporal variations of concentrations of chemical species involved in precipitation and mass transport processes. Usually, models consist of two parts: the first is the diffusion term of electrolytes, and the second one is the kinetic term, which describes the precipitation process [30]. Models can differ from each

* Corresponding author at: Department of Meteorology, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary. Fax: +36 1372 2904.
E-mail address: lagzi@vuk.chem.elte.hu (I. Lagzi).

other by complexity of this term. There are several models in which the kinetics of the precipitation is represented by integro-differential equations [31–34] or by very complex reaction network containing many chemical species [35]. In some cases these complex models can overcomplicate the understanding on the pattern formation mechanism.

In this Letter, we will show that in pH-driven precipitation systems the front propagation and pattern formation can be modelled by a simple way, just taking into account acid–base chemistry and such stationary patterns can be successfully designed and controlled by a pH field.

2. Experimental

An agarose gel containing AlCl₃ (inner electrolyte) was prepared as follows. Agarose (Reanal) was dissolved in distilled water (1% w/v), which was heated up to 80 °C and stirred until the solution became crystal clear. The solution was then mixed with the given amount of $AlCl_3 \cdot 6H_2O$ (Reanal) to prepare the inner electrolyte with a concentration of 0.040 M in a Petri dish, which was held firmly horizontally to obtain a uniformly thick gel. After polymerization (1 h) the outer electrolyte (NaOH, 2.50 M) was placed into a central reservoir (cut out from the gel) and other reservoirs (from three up to six) around the central one were arranged to have special geometric orientations. These reservoirs were filled with the HCl solution (3.02 M). Front evolution was monitored using a digital camera.

3. Numerical model

Diffusion of the acid and base and the fast neutralization reaction ($H^+ + OH^- \rightarrow H_2O$) between them were considered to simulate the evolution of the pattern formation and the stationary shape of the font. During this investigation we excluded the reversible reaction ($H_2O \rightarrow H^+ + OH^-$), because high acid and base concentrations were used (in molar range). This condition ensures that the reaction shifts toward the formation of water. This process can be modelled using reaction–diffusion equations. From the mathematical point of view, a reaction–diffusion system is a set of parabolic partial differential equations (PDEs), and it has a specific form in this case:

$$\frac{\partial c_{H^+}}{\partial t} = D_{H^+} \nabla^2 c_{H^+} - k c_{H^+} c_{OH^-}, \qquad (1)$$

$$\frac{\partial c_{OH^-}}{\partial t} = D_{OH^-} \nabla^2 c_{OH^-} - k c_{H^+} c_{OH^-}, \qquad (2)$$

where c_{H^+}, c_{OH^-} and D_{H^+}, D_{OH^-} are the concentrations and diffusion coefficients of the H^+ and OH^- ions. k is a chemical rate constant, and ∇^2 symbol represents the Laplacian operator. We followed two different strategies. The first is solving equations (1) and (2) using a 'method of lines' technique. This approach reduces the set of PDEs to a system of ordinary differential equations (ODEs) in one independent variable, time. The system of ODEs can then be solved as an initial value problem. Using this technique the evolution of the pattern can be obtained from the numerical simulations.

Our second approach is the stationary form of these differential equations, which can be combined (subtracting Eq. (1) from Eq. (2)) to the Laplace's equation:

$$\nabla^2 u = 0, \qquad (3)$$

where $u = D_{H^+} c_{H^+} - D_{OH^-} c_{OH^-}$. This equation does not contain any time derivative, which means that here the numerical task is less time consuming compared to solving Eqs. (1) and (2). However, this method provides only the final and stationary front profiles, and cannot say anything about its evolution.

The Laplace's equation was solved using Comsol Multiphysics' finite element method in a two dimensional domain (with Neumann boundary condition) containing a 'base' container at the centre and from three up to six 'acid' containers around the 'base' container (with Dirichlet boundary conditions) corresponding to the experimental setup. The solution of u can be visualized as contour lines for different u values and the shape of these contour lines are defined by the geometry only. The solution of $[H^+]$ and $[OH^-]$ can be derived from the solution of u and the water equilibrium. It is important to note that the $u \rightarrow [H^+]$ transformation changes only the values of the contour lines but not their shapes, which means that the solution for $[H^+]$ is equal to the u contour lines with the transformed values. Consequently, the initial acid and base concentrations in the containers and the diffusion coefficients of acid and base will determine the position of the sharp neutral pH zone, which is a contour line of u.

4. Results and discussion

After filling the reservoirs with acidic and basic solutions a well visible, sharp and thin aluminum hydroxide front appears around the central reservoir due to the interplay of the precipitation process and formation of the aluminum hydroxide anionic complex via equilibrium reactions:

$$Al^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Al(OH)_3(s), \qquad (4)$$

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons [Al(OH)_4]^-(aq). \qquad (5)$$
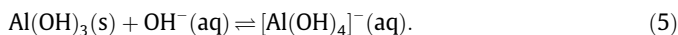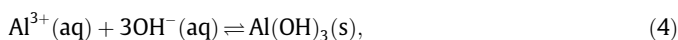
This circular front moves by the diffusive kinetics and the width of the front slightly increases with time. Aluminum hydroxide exists only in a specific range of pH (between pH ∼4 and 9.5) [36], while outside this range either soluble complex (behind the front, at pH higher than 9.5) or free Al^{3+} (ahead of the front, at pH below 4) is present. After an hour, the propagating aluminum hydroxide front can 'feel' the effect of acid concentration profiles from the surrounding reservoirs (Figure 1). Acid–base neutralization reaction and continuous acid and base influx from the reservoirs create a stationary pH field after few hours with a very sharp pH gradient. This results in a very thin, white and not moving (stationary) front around the central reservoir with different shapes. Figure 1 shows the evolution of the aluminum hydroxide front into a stationary triangular shape obtained from the numerical simulation solving the time dependent PDEs (Eqs. (1) and (2). This simple reaction–diffusion model can capture the evolution and deformation of the precipitation front as observed in an experiment. We determined the error between the calculated and experimentally observed positions of the front, which was around a few hundred microns. Our finding supports the fact that the pattern formation and front deformation are governed by the pH field through the neutralization reaction of hydrogen and hydroxide ions, and a sophisticated description of the precipitation mechanism can be neglected. In this special case, the model does not need to contain any complicated terms corresponding to the nucleation followed by the Ostwald ripening or phase separation [37]. Design of an arbitrary distorted and shaped front is quite easy using symmetric or asymmetric setup of containers around the central one. Figure 2 shows the experimental and numerical results of the front distortion using different arrangement of the acidic reservoirs into the various geometrical shapes. Results of the numerical simulations are in a good accordance with the experimental findings in case of solving reaction–diffusion equations (Eqs. (1) and (2)), however we found that the solution of the Laplace's equation (Eq. (3)) differs slightly where the precipitation curvature is high (mainly at the 'vertices' of the polygons). This is due to the fact that the system has not reached the real stationary state and in these positions the difference in the shape is more significant.
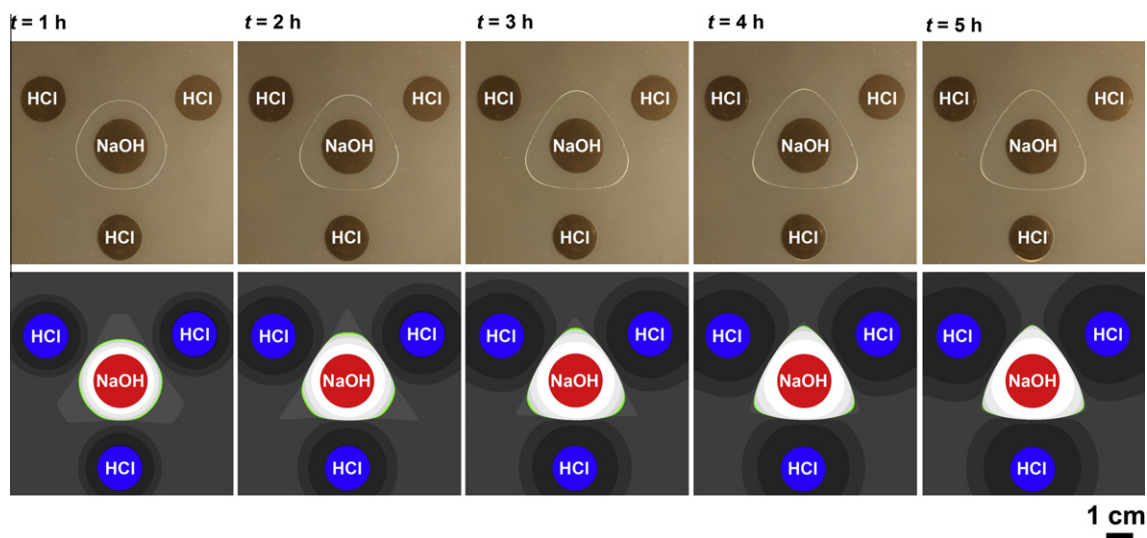
Figure 1. Evolution of fronts in the Al(OH)$_3$ system in an experiment (top row) and in the numerical simulation of reaction–diffusion equations (Eqs. (1) and (2), bottom row). The precipitation front started to move at the interface of the NaOH (central) reservoir towards acidic reservoirs. After 3 h the front profile became stationary and practically did not change anymore. In numerical simulations the colors correspond to the different concentration levels of H$^+$.
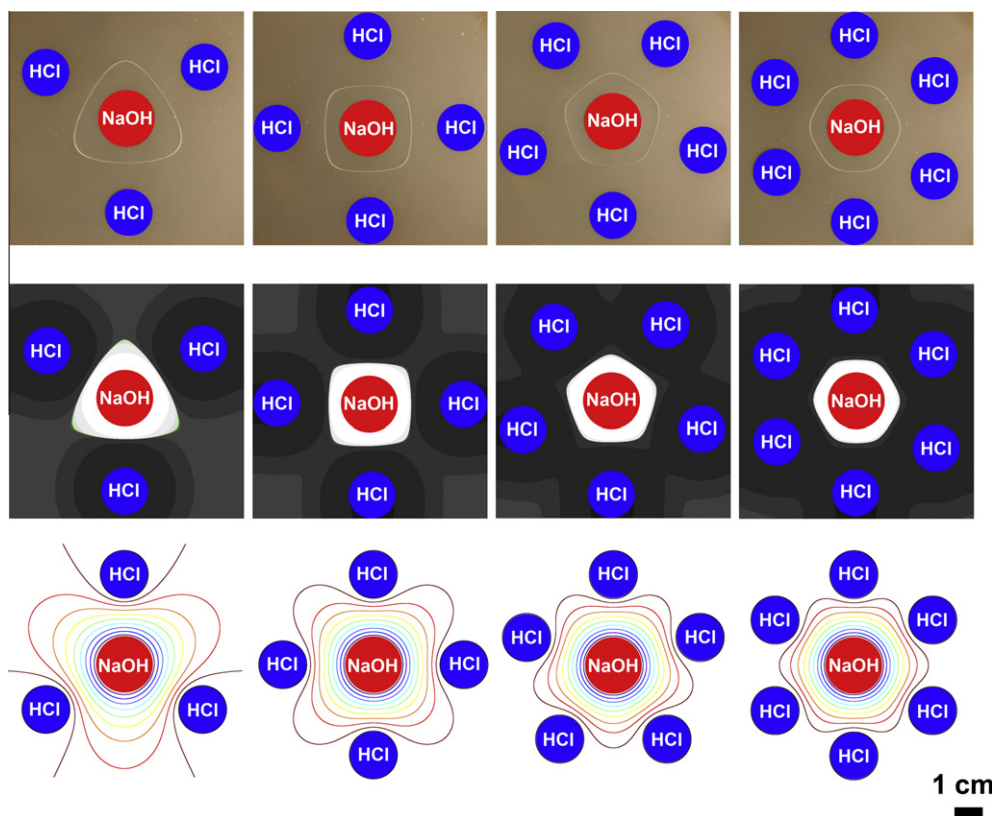

Figure 2. Stationary front profiles simulated using different arrangements of the peripheral acidic reservoirs: experiments at t = 5 h (top row); numerical simulation results of reaction–diffusion equations at t = 5 h (Eqs. (1) and (2), middle row); numerical simulation results of Laplace's equation (Eq. (3), bottom row). In numerical simulations the colors correspond to the different concentration levels of H$^+$.

Solving the Laplace's equation (3), we have also examined the situation, where the domain boundary condition was changed from Neumann to Dirichlet and we found that it had no impact on the solution of u. Moreover, shrinking the domain results in a shape distortion of u between the domain boundary and the containers, but not between the containers. We also revealed that choosing domain size four times larger than the distance of acid

and base centres is a good choice with negligible effect on the results.

5. Conclusion

Pattern control and distortion of structures in a bulk phase are among the important topics in material science. We provided a

simple way to distort and control the evolution of the precipitation structure resulting in stationary profiles in 2D. Our approach is based on the simple fact that the precipitation appears in a given pH range, and the actual precipitation processes (the chemical reactions describing the precipitation formation) are not included in the calculations. Numerical approach, solving either time-dependent reaction–diffusion equations (without reaction for precipitate formation) or solving derived Laplace's equation, provide a reasonable description of the system. Our results indicate that in some systems, where the precipitation occurs by reaction of metal cations with hydroxide ions, our simple approach is valid and the system is governed by a complex pH field and the pattern formation can be described and discussed by taking only acid–base chemistry into account. This strategy can be extended to the design and control of complex structures by acid–base chemistry in 3D.

Acknowledgements

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