# Systematic Front Distortion and Presence of Consecutive Fronts in a Precipitation System

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A new simple reaction−diffusion system is presented focusing on pattern formation phenomena as consecutive precipitation fronts and distortion of the precipitation front. The chemical system investigated here is based on the amphoteric property of aluminum hydroxide and exhibits two unique phenomena. Both the existence of consecutive precipitation fronts and distortion are reported for the first time. The precipitation patterns could be controlled by the pH field, and the distortion of the precipitation front can be practical for microtechnological applications of reaction−diffusion systems.

Technological application of precipitation reaction−diffusion systems has a great and highly increasing relevance.[1−3] Precipitation patterns (PP) can emerge, where the diffusion of two, usually inorganic, species are coupled with their reaction.[4−6] The existence of such patterns is usually explained by the instability of colloidal substances arising from the reactants.[6,7] The classical precipitation (Liesegang) patterns are static and stationary in the sense that the formed precipitation objects (bands, rings, or more complex patterns) stay at the given formed position. Instead of static patterns, dynamically changing precipitation patterns can be formed, if the complex formation of precipitate is possible; for example, in a classical Liesegang experimental setup a precipitation front moves through the reaction domain.[8−11]

Recently, focusing to micro- and nanotechnological applications of reaction−diffusion systems a detailed study on small-scale phenomena provides an alternative way of designing microstructures (diffraction gratings, planar Fresnel-like lenses)[1] and control pattern formation in small scales.[12−14] An advanced application of such a structure is the fabrication of surfaces with nanoscopic waves of linearly increasing heights.[15]

There are several systems in which a moving precipitation front has been observed ($Hg^{2+}/I^-$, $Co^{2+}/NH_4OH$, $Cr^{3+}/OH^-$; inner/outer electrolyte). In a usual setup, the inner electrolyte (represented by cations) is distributed homogeneously in a gel (e.g., gelatine, agar−agar, agarose, PVA), while the outer electrolyte diffuses into this medium from outside. Sedimentation and hydrodynamic instability are thus ignored. Precipitate formation ($HgI_2$, $Co(OH)_2$, $Cr(OH)_3$) is preferred at the junction point of the electrolytes; at the same time, the excess of the outer electrolyte behind the front reacts with precipitate by complex formation ($[HgI_4]^{2-}$, $[Co(NH_3)_6]^{2+}$, $[Cr(OH)_4]^-$) producing a soluble complex (redissolution). In such a way one single precipitation pulse can be detected,[11−13] which evolves in the gel driven by diffusion with a decreasing velocity.

We have constructed a new system ($Al^{3+}/OH^-$), which can produce several well-separated fronts varying periodically the pH of the central reservoir because of the amphoteric property of aluminum hydroxide. An agarose gel containing $AlCl_3$ (inner electrolyte) of a given concentration was prepared as follows. Agarose (Reanal) was dissolved in distilled water in such a way that it produced a solution 1 V/m %, which was heated to 70−80 °C and stirred until the solution became crystal clear. The solution was then mixed with the given amount of $AlCl_3*6H_2O$ (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 the completion of the gelation process (1 h) the outer electrolyte (NaOH, 2.50 M) was placed into a hole (reservoir, cut out from the gel). The pattern formation was monitored in transmitted light perpendicular to the gel surface by a digital camera (EOS-20D). Precipitation process and complex formation produced a well-visible and sharp thin aluminum hydroxide front by the following reactions

$$Al^{3+}(aq) + 3H_2O \leftrightarrow Al(OH)_3(s) + 3H^+(aq) \qquad (1)$$

$$Al(OH)_3(s) + H_2O \leftrightarrow [Al(OH)_4]^-(aq) + H^+(aq) \quad (2)$$

The front moved from the central reservoir by diffusive kinetics as the width of the pulse increased (Figure 1a). After the front left, the base in the reservoir was replaced by acid (HCl, 3.020 M) and precipitate appeared at the interface due to the reversible step (eq 2). Excess of $H^+$ redissolved the formed precipitate (eq 1) and a second, thin precipitation front evolved following
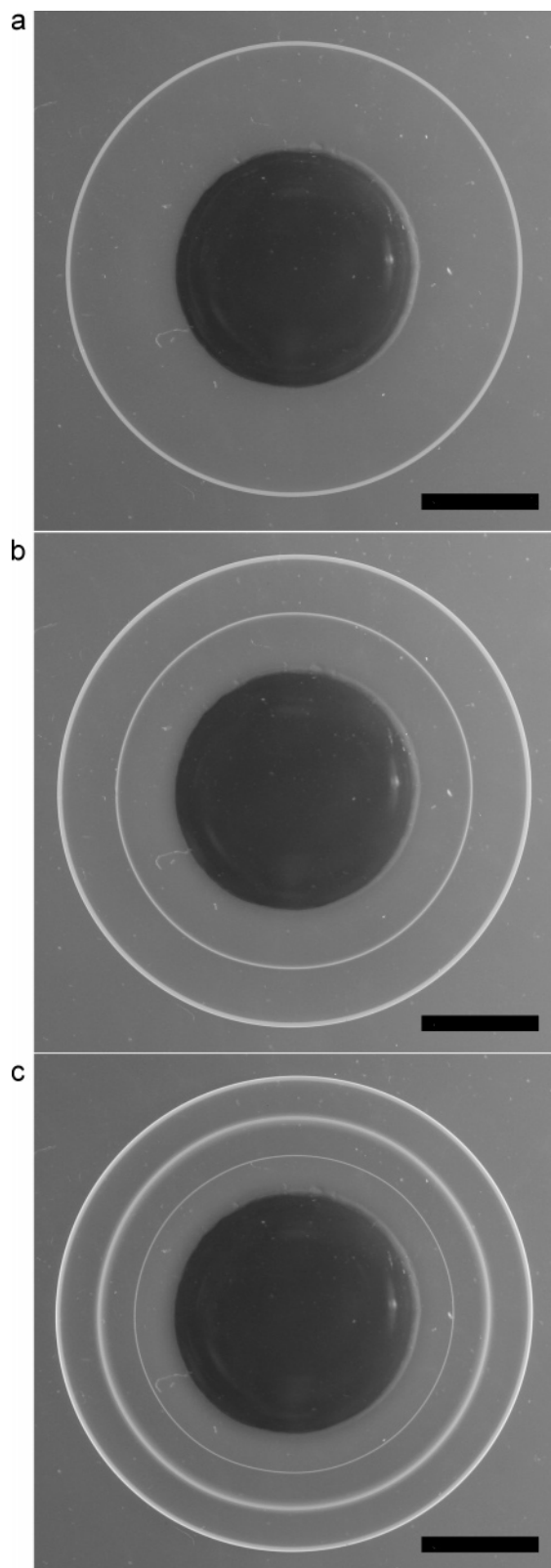
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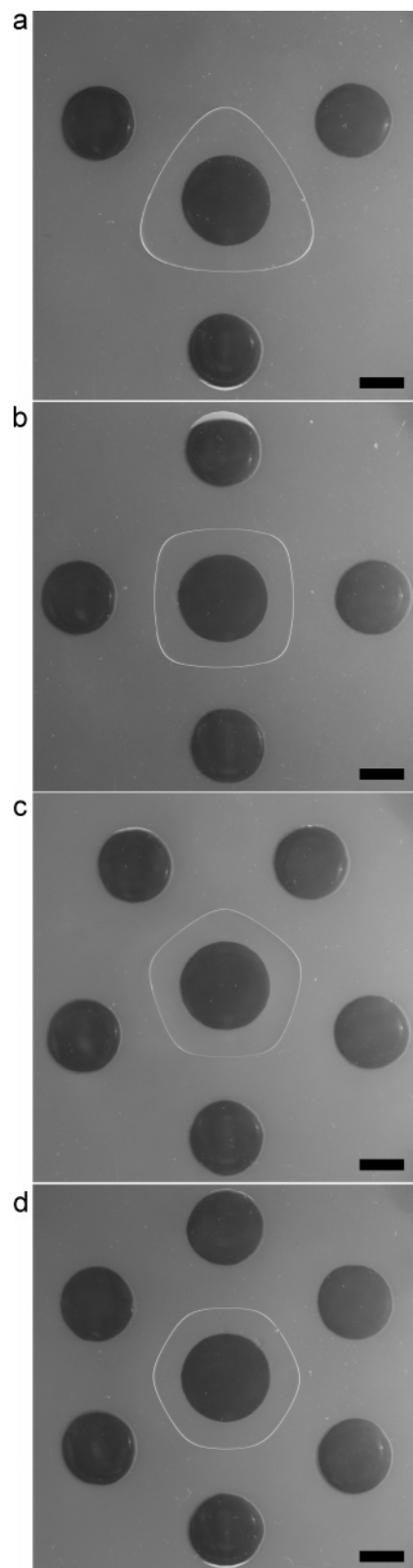‡ Department of Applied Analysis, Institute of Mathematics, Eötvös University.
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**Figure 1.** Evolution of aluminum hydroxide precipitation fronts varying the pH in the central reservoir. (a) The single precipitation front after 2 h. (b) Two consecutive fronts after 2.5 h. (c) Three precipitation fronts after 2.8 h. Initial conditions: $[Al^{3+}] = 0.040$ M; $[NaOH] = 2.50$ M (750 $\mu$L); agarose gel thickness: 3.2 mm; central hole radius: 10 mm. After 2 h NaOH was replaced by acid ($[HCl] = 3.020$ M; 750 $\mu$L). Half an hour later the reservoir was filled again with a base. The scale bar represents 1 cm.



**Figure 2.** Systematic distortion of the precipitation fronts after 5 h: using (a) three, (b) four, (c) five, and (d) six peripheral reservoirs. Initial conditions: (1) agarose gel: $[Al^{3+}] = 0.040$ M, thickness: 3.2 mm; (2) radius of the central hole: 10 mm, $[NaOH] = 2.50$ M (750 $\mu$L); (3) radii of the peripheral holes 9.0 mm, $[HCl] = 3.020$ M (505 $\mu$L). The distance of the peripheral reservoirs from the central one is 3.4 cm. The scale bar represents 1 cm.

Further fronts cannot be produced because the free aluminum and its hydroxo complex diffuse from the gel to the reservoir. The periodic change of pH in the central reservoir produces a

the first, wider one (Figure 1b). A third front can still be produced by replacing acid with a base (NaOH) (Figure 1c).

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new pattern formation phenomenon compared to previous systems using the amphoteric property of the precipitate.

In micro- and nanotechnological applications of the reaction−diffusion systems (WETS: wet stamping technique),[13] pattern formation is determined by the geometrical restriction of the stamp (e.g., the pattern inherits the shape of the stamp). Beyond such geometrical constraints, it can be important to distort the pattern structure. In macroscales, the symmetric or asymmetric distortion of PP by electric field has been done already;[16−18] at the same time, in microscales despite of some promising experimental investigations[19] the theoretical background along with the numerical simulations have not yet been completed.

Aluminum hydroxide exists only in a range of pH; anyway, either soluble complex or free $Al^{3+}$ is present. Applying this fact, various geometries of pattern can be produced, if the central reservoir filled with NaOH is surrounded by some other reservoirs containing HCl with a given setup: radius of reservoir, distance from the central one, and concentration of acid.

At the first stage, as described above, a radially symmetric front propagated from the boundary of the central reservoir. This evolution is driven mainly by the diffusion of $OH^-$ from the central one. Pattern formation did not occur around the peripheral holes because $H^+$ does not produce precipitate with $Al^{3+}$ (inner electrolyte); however, it may react with the precipitate $Al(OH)_3$ (eq 1). Relatively far from the central reservoir, the pH field, determining the position and width of the front, is affected by $H^+$ diffused from the peripheral holes (Figure 2). After some time the pH field becomes stationary because of the continuous fluxes of $H^+$ and $OH^-$ and neutralization reaction between them. Consequently, PP will be stationary as well. Variation of the pH field ensures a systematic control and distortion of a primarily radially symmetric precipitation front even in microscales.

In conclusion, we designed a new precipitation system in which unique phenomena have been observed because of the amphoteric property of the precipitate employed.

**Supporting Information Available:** The movie shows the evolution of aluminum hydroxide precipitation fronts using three peripheral reservoirs setup. It contains six frames (one frame per hour). Initial conditions: (1) agarose gel: $[Al^{3+}] = 0.040$ M, thickness: 3.2 mm; (2) radius of the central hole: 10 mm, $[NaOH] = 2.50$ M (750 $\mu$L); (3) radii of the peripheral holes: 9.0 mm, $[HCl] = 3.020$ M (505 $\mu$L). The distance of the peripheral reservoirs from the central one is 3.4 cm. This material is available free of charge via the Internet at http://pubs.acs.org.

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