

Liesegang patterns: Complex formation of precipitate in an electric field

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Abstract. Formation of 1D Liesegang patterns was studied numerically in precipitation and reversible complex formation of precipitate scenarios in an electric field. The Ostwald's supersaturation model reported by Büki, Kárpáti-Smidróczki and Zrínyi (BKZ model) was extended further. In the presence of an electric field the position of the first and the last bands (X_n) measured from the junction point of the outer and the inner electrolytes can be described by the function $X_n = a_1\tau_n^{1/2} + a_2\tau_n + a_3$, where τ_n is the time elapsed until the n th band formation, a_1 , a_2 and a_3 are constants. The variation of the total number of bands with different electric field strengths (ϵ) has a maximum. For higher ϵ one can observe a moving precipitation zone that becomes wider due to precipitation and reversible complex formation.

Keywords. Liesegang; precipitation patterns; electric field; complex formation.

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1. Introduction

Liesegang patterning is a well-known example of spatio-temporal pattern formation in reaction-diffusion systems [1,2]. Interdiffusion of two electrolytes and the precipitation reaction between them produces the quasi-periodic patterns. One of the electrolytes (called outer electrolyte) diffuses into the reaction space, which contains the other one (inner electrolyte), and the precipitation process produces rhythmic precipitation patterns. In the absence of an electric field, the time law $X_n = c_1 t_n^{1/2} + c_2$ [3] characterizes the evolution of the system. Here X_n is the position of the n th band measured from the junction point of the electrolytes, t_n is the time of appearance of the n th band and c_1 and c_2 are constants. Many detailed studies were performed to investigate the influence of geometry [4], the effect of gravitational field [5,6] and the effect of moving boundary [7,8] on Liesegang pattern formation. Recently, experimental pattern transitions have been found in a Liesegang system [9]. Various precipitate pattern structures have been reported

by Hantz [10–12]. Reaction of gas compounds can cause precipitate patterns in aerogels, observed in ref. [13].

Electric field has a significant effect on the formation of Liesegang bands, because the precipitation process is evoked by reaction of ions. This effect was studied in various systems experimentally [14–21] and by numerical simulations [20–22]. Both types of examinations showed that for the case of any electric field strength, the kinetics of last band formation can be described by the function $X_n = a_1 t_n^{1/2} + a_2 t_n + a_3$, where a_1 , a_2 and a_3 are appropriate constants.

Recently, Sultan and his co-workers [19,23–25] have presented experimental studies on some features and characteristics of the $\text{NH}_4\text{OH}/\text{CoCl}_2/\text{gelatine}$ system. The formed precipitate $\text{Co}(\text{OH})_2(\text{s})$ dissolves due to complex formation in excess ammonia. Zrínyi *et al* [26], Sultan and Panjarian [17] and Hilal and Sultan [27] observed and studied experimentally similar patterns in $\text{NaOH}/\text{Cr}(\text{NO}_3)_3$, while Das *et al* [28] performed it in KI/HgCl_2 system.

The aim of this paper is to continue investigation of the new features of the precipitation and complex formation scenarios in an electric field using numerical simulation method.

2. Model

The simple skeleton mechanism of the precipitation and the complex formation is



where $A^+(\text{aq})$ and $B^-(\text{aq})$ are the ionic species ($A^+(\text{aq})$ denotes the outer electrolyte and $B^-(\text{aq})$ denotes the inner electrolyte), $P(\text{s})$ is the precipitated product, $D(\text{aq})$ is the complex forming species and $C(\text{aq})$ is the complex. We assumed that the complex forming species and the complex do not have charge. Under the influence of an electric field the 1D Liesegang system is governed by the following set of partial differential equations:

$$\frac{\partial \alpha}{\partial \tau} = D_\alpha \frac{\partial^2 \alpha}{\partial x^2} - z_\alpha \epsilon \frac{\partial \alpha}{\partial x} - \Delta(K_s, L, \alpha\beta), \quad (4)$$

$$\frac{\partial \beta}{\partial \tau} = D_\beta \frac{\partial^2 \beta}{\partial x^2} - z_\beta \epsilon \frac{\partial \beta}{\partial x} - \Delta(K_s, L, \alpha\beta), \quad (5)$$

$$\frac{\partial \gamma}{\partial \tau} = D_\gamma \frac{\partial^2 \gamma}{\partial x^2} + \kappa_2 \pi \delta - \kappa_3 \gamma, \quad (6)$$

$$\frac{\partial \delta}{\partial \tau} = D_\delta \frac{\partial^2 \delta}{\partial x^2} - \kappa_2 \pi \delta + \kappa_3 \gamma, \quad (7)$$

$$\frac{\partial \pi}{\partial \tau} = \Delta(K_s, L, \alpha\beta) - \kappa_2 \pi \delta + \kappa_3 \gamma, \quad (8)$$

where the symbols denote dimensionless physical quantities as follows: α , β , γ and δ are the concentrations of $A^+(\text{aq})$, $B^-(\text{aq})$, $C(\text{aq})$ and $D(\text{aq})$, respectively, π is the amount of the precipitated product $P(s)$. D_α , D_β , D_γ and D_δ are the diffusion coefficients, z_α and z_β are the charges of the ions $A^+(\text{aq})$ and $B^-(\text{aq})$, respectively. κ_2 and κ_3 are chemical rate constants for the (2) and (3) reactions. The parameter ϵ is the electric field strength, τ is the dimensionless time and x is the dimensionless length. The function $\Delta(K_s, L, \alpha\beta)$ is defined by the following equations:

(i) If $\pi = 0$ (there is no precipitate at the grid point, precipitate formation),

$$\Delta(K_s, L, \alpha\beta) = \Sigma_P \Theta(\alpha\beta - K_s).$$

(ii) If $\pi \neq 0$ (there is some precipitate at the grid point, precipitate growth)

$$\Delta(K_s, L, \alpha\beta) = \Sigma_P \Theta(\alpha\beta - L),$$

where

$$\Sigma_P = \frac{1}{2} \left[(\alpha + \beta) - \sqrt{(\alpha + \beta)^2 - 4(\alpha\beta - L)} \right].$$

Σ_P is the amount of the precipitate, which can be formed [29,30], L is the precipitation product, K_s is the nucleation product and Θ is the Heaviside step function. Partial differential equations (4)–(8) were solved numerically using a forward Euler method with the following initial conditions:

$$\alpha(\tau = 0, x) = \alpha_0 \Theta(-x), \quad \beta(\tau = 0, x) = \beta_0 \Theta(x), \quad \delta(\tau = 0, x) = \delta_0 \Theta(-x)$$

and

$$\pi(\tau = 0, x) = \gamma(\tau = 0, x) = 0,$$

and with the following boundary conditions:

$$\left. \frac{\partial \alpha}{\partial x} \right|_{x=l} = \left. \frac{\partial \beta}{\partial x} \right|_{x=l} = \left. \frac{\partial \beta}{\partial x} \right|_{x=0} = \left. \frac{\partial \gamma}{\partial x} \right|_{x=l} = \left. \frac{\partial \gamma}{\partial x} \right|_{x=0} = \left. \frac{\partial \delta}{\partial x} \right|_{x=l} = 0,$$

$$\alpha|_{x=0} = \alpha_0,$$

$$\delta|_{x=0} = \delta_0.$$

Here l is the length of the diffusion column; we chose in the simulations $\alpha_0 = \delta_0 = 60.0$ and $\beta_0 = 6.0$. Here we assigned the same initial concentrations for the complex forming species and the outer electrolyte, and they diffused from outside in the same way. The following parameter set was used in the simulation: $D_\alpha = D_\beta = D_\gamma = D_\delta = 0.4$, $L = 0.100$, $K_s = 0.101$, $z_\alpha = 1$, $z_\beta = -1$, $\kappa_2 = 1 \times 10^{-4}$, $\kappa_3 = 1 \times 10^{-8}$, $l = 3360$ and $\pi_{\max} = 5.0$. Most of these parameters were proposed and reported in the work of Büki *et al* [29]. The grid spacing and the time step were $\Delta x = 0.8$ and $\Delta \tau = 0.05$, respectively.

3. Results

Position of the first and the last bands are shown in figure 1. For the case of any electric field strength the position of the first and the last bands, measured from

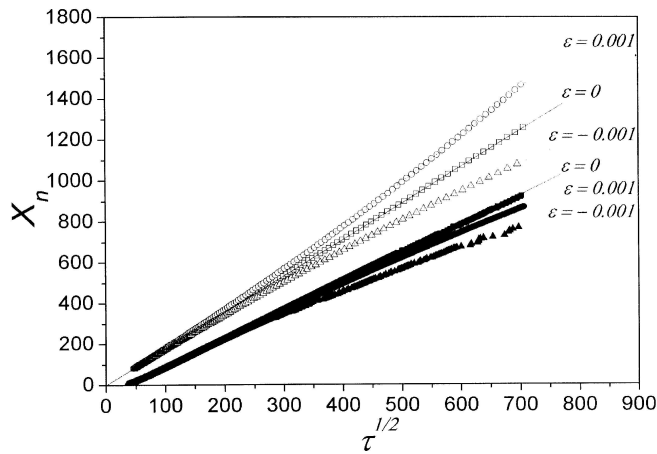


Figure 1. Variation of the positions of the first and the last bands measured from the junction point of the two electrolytes with square root of time at different values of ϵ . The solid line represents the fitted linear curve for the electric field-free case. The dotted lines represent the fitted second-order curves for various electric field strengths. The open and filled symbols correspond to the last and the first bands, respectively.

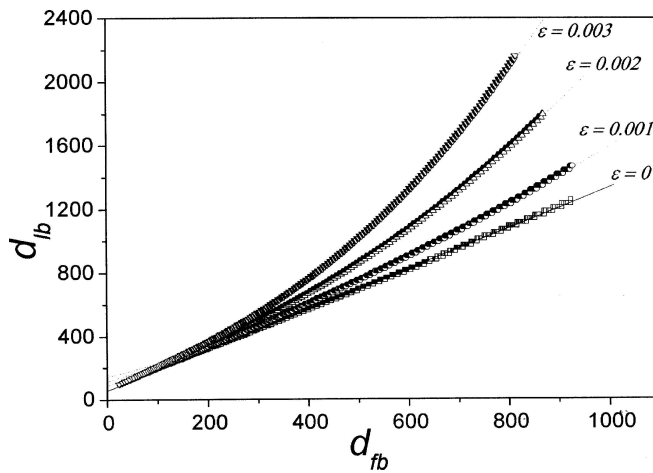


Figure 2. Correlation plot of the distance of the last band vs. the first band measured from the junction point of the two electrolytes at different values of ϵ . The solid line represents the fitted linear curve for the electric field-free case. The dotted lines represent the fitted second-order curves for various electric field strengths.

the junction point of the two electrolytes can be described very accurately by the function $X_n = a_1\tau_n^{1/2} + a_2\tau_n + a_3$, where a_1 , a_2 and a_3 are constants. The first term ($a_1\tau_n^{1/2}$) corresponds to the diffusion and the second one ($a_2\tau_n$) to the advection.

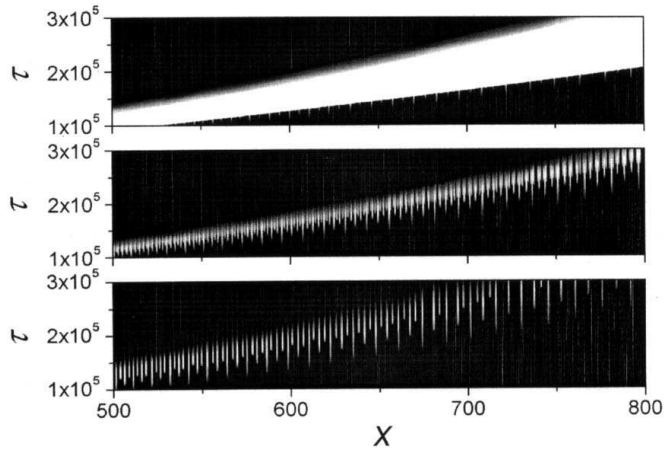


Figure 3. Evolution of 1D Liesegang patterns for various electric field strengths: $\epsilon = -0.001$ (bottom), $\epsilon = 0$ (middle) and $\epsilon = 0.001$ (top). The lighter territory represents the amount of the precipitate.

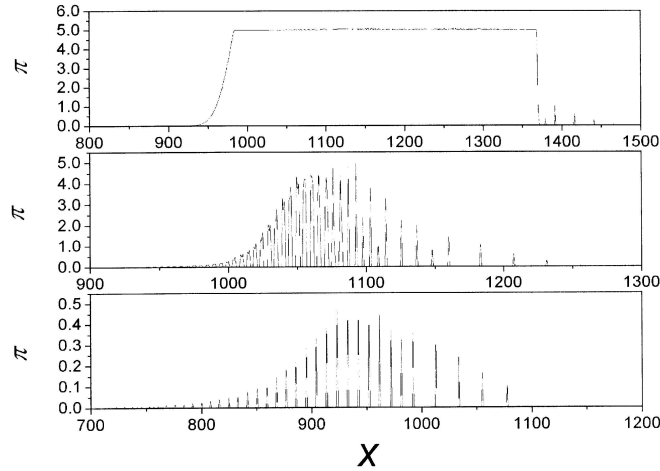


Figure 4. Spatial distribution of the amount of precipitate measured from the junction point of the outer and the inner electrolytes for three different values of ϵ at $\tau = 5 \times 10^5$: $\epsilon = -0.001$ (bottom), $\epsilon = 0$ (middle) and $\epsilon = 0.001$ (top). The amount of precipitate for $\epsilon = -0.001$ is one order lower than in case $\epsilon = 0$.

Therefore, it must be $a_1(\epsilon) \rightarrow a_1(\epsilon = 0)$, $a_2(\epsilon) \rightarrow 0$ and $a_3(\epsilon) \rightarrow a_3(\epsilon = 0)$, if $\epsilon \rightarrow 0$. These results are similar to that reported in refs [14–21] which mostly correspond to the regular Liesegang pattern formation in an external electric field. Figure 2 shows the position of the last bands (d_{lb}) vs. the position of the first bands (d_{fb}). The dependence of d_{lb} on d_{fb} is second-order in the case of $\epsilon > 0$. In electric field-free situation, the dependence of distance of the last band on the first one is linear as displayed in figure 2 and shown experimentally [24].

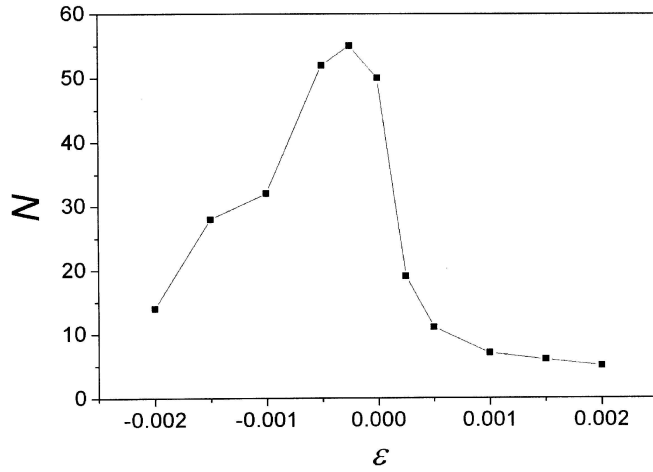


Figure 5. Dependence of the total number of bands (N) on electric field strength (ϵ) at $\tau = 4 \times 10^5$.

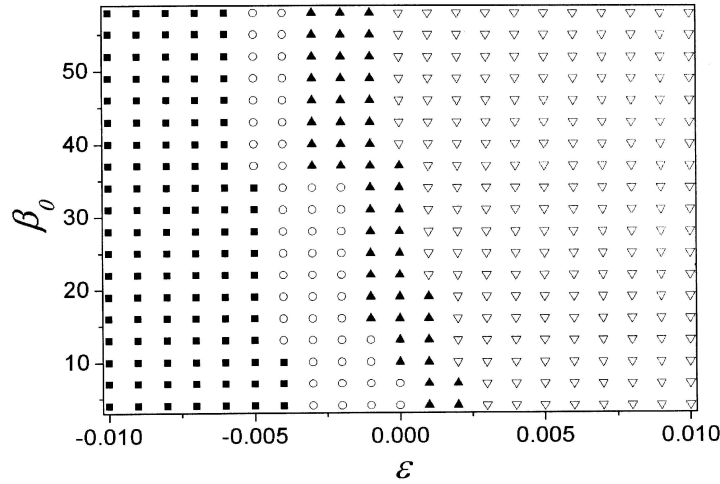


Figure 6. Existing patterns as a function of the initial concentration of the inner electrolyte (β_0) and the electric field strength (ϵ) at $\tau = 5 \times 10^5$. The pattern formation was classified as (■) no precipitation; (○) moving Liesegang bands; (▲) precipitation wave and moving Liesegang bands; and (▽) precipitation wave. (Parameters: $\alpha_0 = \delta_0 = 60.0$, $D_\alpha = D_\beta = D_\gamma = D_\delta = 0.4$, $L = 0.100$, $K_s = 0.101$, $z_\alpha = 1$, $z_\beta = -1$, $\kappa_2 = 1 \times 10^{-4}$, $\kappa_3 = 1 \times 10^{-8}$ and $\pi_{\max} = 5.0$.)

Figure 3 presents spatio-temporal evolution of Liesegang patterns and figure 4 shows the spatial distribution of $P(s)$ in various electric field strengths. For higher ϵ the first wide band propagates and grows thicker in time. Several bands after the first wide band can be observed. As electric field strength increases, one can observe

a crossover from moving Liesegang pattern (moving precipitation bands) to moving precipitation pulse (traveling precipitation wave). The above phenomenon is driven by the electric field strength (as a control parameter). The spatial distribution of the precipitate has also Gaussian characteristics when $\epsilon < 0$, but the amount of the precipitate at the grid point is smaller than in the absence of an electric field. Figure 5 illustrates the dependence of the total number of bands (N) on various electric field strengths (ϵ) at the same simulation time. The bands are countable if the amount of the precipitate at the grid point is higher than or equal to 0.01 ($\pi \geq 0.01$). N increases to a maximum value and then decreases with the electric field strength.

4. Conclusions

Several types of precipitation patterns can exist depending on ϵ , κ_2 , κ_3 , K_s , L , α_0 and β_0 . It is trivial that at low α_0 and β_0 (or at high K_s , L) there is no pattern formation, because the local concentration product of the electrolytes does not exceed the nucleation (precipitation) product. In case of low κ_2 the complex formation of the precipitate does not play an important role. Therefore regular Liesegang pattern formation is expected. The most interesting result can be observed, if the electric field strength is changed. At very low (negative) ϵ (electric field retards the diffusion of the invading electrolyte) there is no pattern formation due to the spatial separation of the electrolytes. In the case of higher (still negative) ϵ , or in the absence of an electric field, or for moderately positive ϵ moving Liesegang patterns exist. At the same time for higher ϵ precipitation waves evolve. A detailed numerical study has shown that the pattern formation is highly influenced by the electric field strength and the initial concentration of the inner electrolyte. Figure 6 illustrates this dependence for some different values of ϵ and β_0 .

The novel features of numerical simulations are the following:

- (i) In the case of applied constant DC electric field the position of the first and the last bands can be described by the second-order function of the square root of time.
- (ii) The correlation between the distance of the last and the first bands are also characterized by a second-order function for $\epsilon > 0$.
- (iii) The total number of bands increases to a maximum value and then decreases as electric field strength is increased.
- (iv) A crossover from moving bands to precipitation wave is reported as ϵ is changed.

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