

Stabilization and destabilization effects of the electric field on stochastic precipitate pattern formation

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Abstract

Stabilization and destabilization effects of an applied electric field on the Liesegang pattern formation in low concentration gradient were studied with numerical model simulations. In the absence of an electric field pattern formation exhibits increasingly stochastic behaviour as the initial concentration difference between the outer and the inner electrolytes (Δ) approaches to zero. Our numerical simulation results have shown that, if the electric field promotes the transport of the reaction front of the outer electrolyte into the diffusion column, then the electric field stabilizes the stochastic pattern structure. This means that Liesegang patterns in the simulations will be decreasingly stochastic, in terms of reproducibility of band locations and of the band formation. Destabilization behaviour was observed in the reverse case, if the electric field retards the diffusion of the outer electrolyte. Simulation of pattern formation is presented using concentration perturbations in a deterministic model. The precipitation process is based on ion-product supersaturation theory (Ostwald's model).

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1. Introduction

Variety of spatial patterns arises from the interaction of chemical reaction and diffusion, such as chemical waves [1], autocatalytic fronts [2], Turing structures [3] or precipitation patterns (Liesegang phenomenon) [4]. In most of such systems the reaction occurs between the ionic species, hence electric field has a significant influence on the evolution of pattern formation. Detailed investigations have been pursued on this topic in the last two decades; deformation of spiral waves [5,6], splitting [7,8] and deformations of waves [9] were presented. Effects of an electric field on autocatalytic front propagation in iodate–arsenous acid system were studied by Forstova et al. [10]. Tóth et al.

[11] and Horváth et al. [12] investigated the influence of external electric field on diffusion driven front instability. Interaction of Turing patterns with electric field was also observed [13].

Liesegang patterns appear due to the diffusion and precipitation of two, initially separated electrolytes [14]. One of them (inner electrolyte) is uniformly distributed in a gel (diffusion column) and the other one (outer electrolyte) diffuses from outside into the diffusion column. In the absence of an electric field dependence of band position on the square root of its formation time is linear. Experimental [15–23] and numerical studies [22–24] have shown that the applied electric field modified the spatiotemporal evolution of Liesegang patterns. Dependence of the band position on formation time in the presence of an electric field is

$$X_n = \alpha_0 \tau_n + \beta_0 \tau_n^{1/2} + \gamma_0,$$

where X_n is the position of the n th band measured from the junction point of the two electrolytes, τ_n is the time

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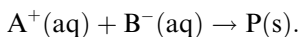
elapsed until its formation, while α_0 , β_0 , and γ_0 are constants.

In experiments the necessary condition for the pattern formation is that the ratio of the initial concentrations (b_0/a_0 , where a_0 and b_0 are the initial concentration of the outer and inner electrolytes, respectively), is small. In study of Antal et al. [25] the authors proposed that $0.005 \leq b_0/a_0 \leq 0.1$ and in this case they obtained well reproducible regular Liesegang patterns. Kai et al. [26], Kai and Müller [27], and Müller and Ross [14] presented that low initial concentration difference ($\Delta = a_0 - b_0$) in the absence of an electric field leads to considerable uncertainty, in terms of the location of bands and of the appearance time. Experimental investigations have shown that pattern formation exhibits increasingly stochastic behaviour as Δ approaches to zero. Recently, this fact has been reproduced by numerical simulations [28].

The aim of this paper is to show by using concentration perturbations in a deterministic model that the external electric field is able to stabilize or destabilize the stochastic precipitate patterns in the case of low initial concentration difference.

2. The model

The simplest precipitation reaction, which can be used to reproduce pattern formation is



Here the reagents $A^+(aq)$ and $B^-(aq)$ (outer and inner electrolytes, respectively), turn into an immobile precipitation product $P(s)$. Like in our previous study [28] we decompose the concentrations a of $A^+(aq)$ and b of $B^-(aq)$ as $a = \bar{a} + a'$ and $b = \bar{b} + b'$, where \bar{a} , \bar{b} are the average concentrations, while a' , b' are the concentration fluctuations. All of these quantities depend on spatial (x) and time (τ) variables. Based on a standard deterministic model [29,30] (using Ostwald's supersaturation theory [31]), evolution of pattern formation can be described by the following system of equations:

$$\frac{\partial \bar{a}}{\partial \tau} = D_a \frac{\partial^2 (\bar{a} + a')}{\partial x^2} - z_a \epsilon \frac{\partial (\bar{a} + a')}{\partial x} - \delta((\bar{a} + a')(\bar{b} + b'), K, L), \quad (1a)$$

$$\frac{\partial \bar{b}}{\partial \tau} = D_b \frac{\partial^2 (\bar{b} + b')}{\partial x^2} - z_b \epsilon \frac{\partial (\bar{b} + b')}{\partial x} - \delta((\bar{a} + a')(\bar{b} + b'), K, L), \quad (1b)$$

$$\frac{\partial p}{\partial \tau} = \delta((\bar{a} + a')(\bar{b} + b'), K, L), \quad (1c)$$

where all quantities are dimensionless. During the computations variation $\partial a'/\partial \tau$ of fluctuation a' and that

of b' are usually considered to be zero, since the average effect of these terms for any time interval is zero. Taking $\lim a' = 0$ and $\lim b' = 0$ would lead us to the deterministic case. p is the amount of the precipitate. D_a , D_b and z_a , z_b denote the diffusion coefficients and the charges of the electrolytes, respectively, while ϵ is the electric field strength. $\delta(ab, K, L)$ is the precipitation reaction term defined as follows:

$$\delta(ab, K, L) = \begin{cases} \kappa S_p \Theta(ab - K) & \text{if } p = 0 \\ \kappa S_p \Theta(ab - L) & \text{if } p > 0, \end{cases}$$

where κ is the rate constant of the precipitation reaction, L is the solubility product, K is the nucleation product and Θ is the Heaviside step function.

$$S_p = \frac{1}{2} \left[(a + b) - \sqrt{(a + b)^2 - 4(ab - L)} \right],$$

yields the amount of the precipitate proposed by Büki et al. [29,30]. In our calculations the amount of the precipitate was not limited at any space position.

During the computation process, first the concentrations of the two electrolytes were perturbed, then the diffusion and the reaction terms were consecutively calculated using the perturbed concentrations. This process has been repeated in every time step. At the microscopic level the only assumption was that the displacement of each particles are identically distributed. The mean of this distribution is related to the electric field strength (ϵ), while its variance is proportional to the fluctuations in the system.

Application of the central limit theorem gives that the change of concentration (which can be described by the displacement of particles) is normally distributed: the mean is determined again by ϵ , while its standard deviation is proportional to the square root of the number of ions, i.e., that of the concentration. Therefore, the perturbations of the concentrations were calculated as follows:

$$a' = (0.5 - \text{rand}(x, \tau))d\sqrt{\bar{a}}, \quad (2a)$$

$$b' = (0.5 - \text{rand}(x, \tau))d\sqrt{\bar{b}}, \quad (2b)$$

where d is related to the magnitude of the fluctuations and $\text{rand}(x, \tau)$ is a normally distributed random number between 0 and 1. It has been generated for the different electrolytes in every position in each time step.

In the numerical solution of Eqs. (1a)–(1c) we applied the “method of lines” with a second order Runge–Kutta method using the following boundary conditions:

$$\frac{\partial a}{\partial x} \Big|_{x=0} = a_0 \quad \text{and} \quad \frac{\partial b}{\partial x} \Big|_{x=0} = \frac{\partial a}{\partial x} \Big|_{x=l} = \frac{\partial b}{\partial x} \Big|_{x=l} = 0,$$

where l is the length of the diffusion column. In all simulations the parameter set $D_a = D_b = 0.4$, $K = 0.13$, $L = 0.1$, $\kappa = 250$, $z_a = 1$, $z_b = -1$, $l = 480$ and $d = 0.0003$ was used. The initial conditions were

$$a(0,x) = a_0\Theta(-x), \quad b(0,x) = b_0\Theta(x) \quad \text{and} \quad p(0,x) = 0.$$

Here we chose $a_0 = 1.4$, $b_0 = 1.0$, while ϵ was varied between -0.0025 and 0.0025 . The grid spacing was $\Delta x = 0.4$ and we performed numerical simulations with the time step $\Delta\tau = 0.004$.

3. Results and discussions

We performed 100 simulations for each case corresponding to the various electric field strengths, which was sufficient for the statistical analysis. Earlier, in the order of 10 real experiments were carried out at low concentration difference in the absence of an electric field. Fig. 1 shows the empirical density function of band locations along the diffusion column for various electric field strengths. In the present case (since the ions A^+ have a positive charge) $\epsilon > 0$ means that the electric field promotes the transport of the outer electrolyte into the diffusion column. During the simulations, we did not limit the amount of the formed precipitate. In this way, if in a given cell the precipitation process occurred, it could not “spread over” to the neighbor cells. Therefore, in each (independent) runs each of the bands occupies only one grid cell.

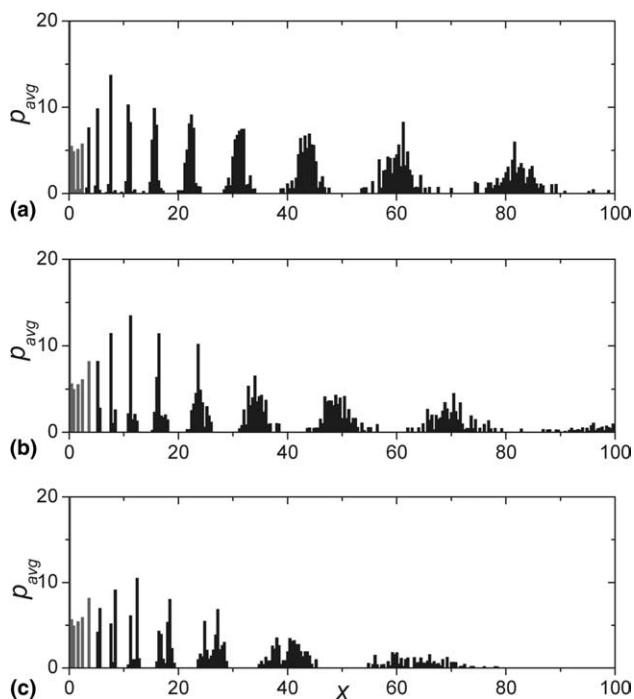


Fig. 1. Variation of the average amount of the precipitate (p_{avg}) in the diffusion column for: (a) $\epsilon = 0.0025$, (b) $\epsilon = 0$, and (c) $\epsilon = -0.0025$ as a function of distance measured from the junction point of the two electrolytes at $\tau = 5 \times 10^6$. The distribution of the precipitate corresponds to the average of 100 independent simulations. The black and gray color correspond to the deterministic and to the stochastic band positions, respectively.

The evolution of the band systems is displayed in Fig. 2. The band position does not depend linearly on the square root its formation time (as mentioned for the electric field free case). We found that the formation of the bands can be described by the function

$$\bar{X}_n = \alpha_0(\epsilon)\bar{\tau}_n + \beta_0(\epsilon)\bar{\tau}_n^{1/2} + \gamma_0(\epsilon), \quad (3)$$

where \bar{X}_n and $\bar{\tau}_n$ are the average of the n th band positions and formation time, respectively. $\alpha_0(\epsilon)$, $\beta_0(\epsilon)$, and $\gamma_0(\epsilon)$ depend on the electric field strength. The first term of the right hand side of Eq. (3) corresponds to the migration of ions and the second one to the diffusion.

The stabilization–destabilization effect of an electric field is reflected more evidently in Figs. 3 and 4. We investigated the dependence of the standard deviation of band positions and formation time on the number of bands (Fig. 3) and on spatial position (Fig. 4). In Fig. 3, both types of standard deviations increase exponentially with the number of bands. We obtain a more realistic picture for the effect of the electric field strength, if the standard deviations are plotted as a function of the spatial position. In this case, we obtained a similar dependence but standard deviation of band formation time depends polynomially (of order 3) on space position, and standard deviation of band positions increases with space position as a second order polynomial (Fig. 4). The summary of our findings is that the standard deviations increase as electric field strength is decreased. Dependence of standard deviation of band formation time on space position is higher than the standard deviation of the band positions. The precipitate pattern exhibits more deterministic behaviour in space than in time.

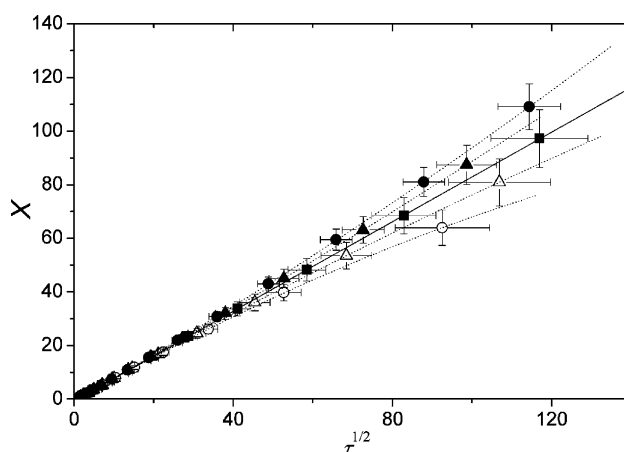


Fig. 2. Dependence of the average distance of bands (measured from the junction point of the two electrolytes) on the average square root of formation time. The spatial and square root time standard deviations of 100 simulations are also shown. The solid line corresponds to the fitted linear curve in the absence of an electric field. The dotted lines represent the fitted second-order curves in the presence of an electric field. (\bullet) $\epsilon = 0.0025$; (\blacktriangle) $\epsilon = 0.00125$; (\blacksquare) $\epsilon = 0$; (\triangle) $\epsilon = -0.00125$; (\circ) $\epsilon = -0.0025$.

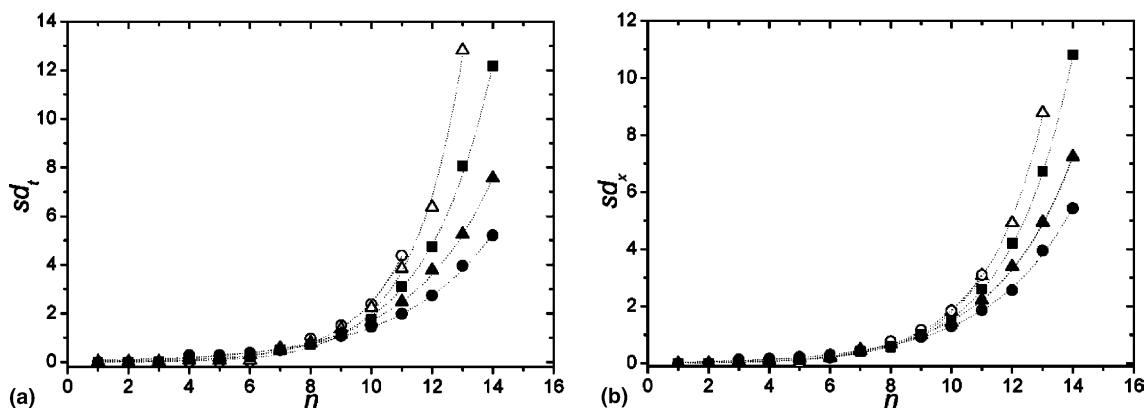


Fig. 3. (a) Dependence of the standard deviation of band formation time (sd_t) on the band number; (b) Dependence of the standard deviation of the band positions (sd_x) on the band number. ((●) $\epsilon = 0.0025$; (▲) $\epsilon = 0.00125$; (■) $\epsilon = 0$; (△) $\epsilon = -0.00125$; (○) $\epsilon = -0.0025$).

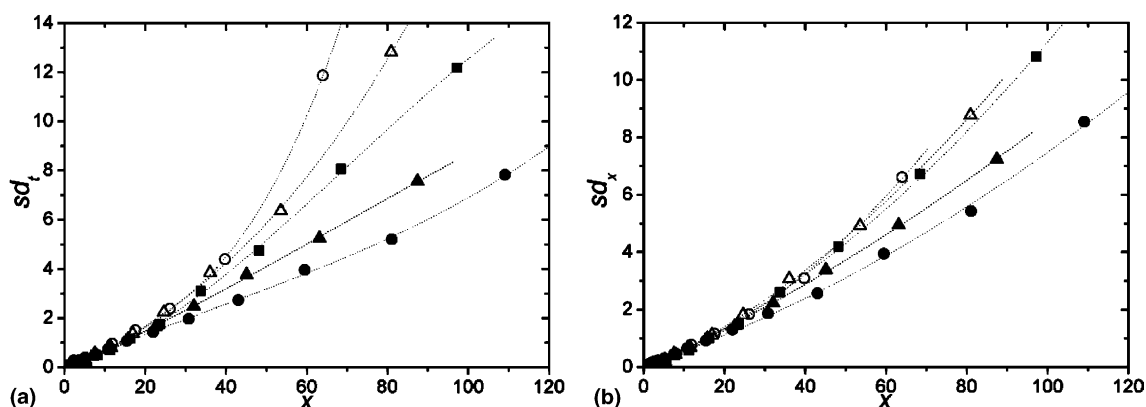


Fig. 4. (a) Dependence of the standard deviation of band formation time (sd_t) on band position; (b) Dependence of the standard deviation of the band positions (sd_x) on band position. ((●) $\epsilon = 0.0025$; (▲) $\epsilon = 0.00125$; (■) $\epsilon = 0$; (△) $\epsilon = -0.00125$; (○) $\epsilon = -0.0025$).

4. Conclusions

Decreasing ϵ , the spatial distribution of bands becomes more stochastic as shown in Fig. 1. We called a precipitate band position stochastic if after the averaging process this band occupies more than one spatial grid cell. Otherwise it was considered deterministic. The high values of standard deviation in the experiments can be recognized as a stochastic behaviour of the reaction-diffusion system. Fig. 2 reflects the experimental finding that the electric field modifies the diffusion characteristics of the electrolytes. Ionic migration flux of the outer electrolyte changes the spatiotemporal evolution of Liesegang patterns. Fluctuations and stochastic behaviour of the phenomenon can be described by standard deviation of the band position and formation time as we did in Fig. 3 (in dependence of band number) and in Fig. 4 (in dependence of spatial position). In both cases standard deviations are monotone increasing with the number of bands and the position. The bands belonging to the same band number occupies different position depending on the electric field strength.

We predicted that the stochastic precipitate pattern distribution depends on the electric field strength using perturbed concentration in a deterministic model. Liesegang patterns have been found to be increasingly deterministic, in terms of reproducibility of the band locations and of band formations as the electric field promotes the transport of the outer electrolytes.

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