



Pattern transition between periodic Liesegang pattern and crystal growth regime in reaction–diffusion systems

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ABSTRACT

The pattern transition between periodic precipitation pattern formation (Liesegang phenomenon) and pure crystal growth regimes is investigated in silver nitrate and potassium dichromate system in mixed agarose–gelatin gel. Morphologically different patterns were found depending on the quality of the gel, and transition between these typical patterns can be controlled by the concentration of gelatin in mixed gel. Effect of temperature and hydrodynamic force on precipitation pattern structure was also investigated.

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1. Introduction

It was more than 110 years ago when Ralph Eduard Liesegang observed and reported a unique phenomenon [1]. The interaction of diffusion of ions with precipitation reaction between them can produce inhomogeneous distribution of formed precipitate [2–11]. In the typical experimental setup, one chemical reagent (inner electrolyte) is uniformly distributed in a test tube in a gel, while the other reagent (outer electrolyte) diffuses from outside. The gel prevents sedimentation of precipitate and hydrodynamic turbulence. On the other hand, the gelled medium provides an ideal medium for crystal growth. Initially, both electrolytes are spatially separated. The initial concentration of the outer (invading) electrolyte is usually higher than that of inner one. This condition ensures the higher diffusion flux of the outer electrolyte into the gel. In some circumstances, in the wake of the chemical front precipitation bands are formed, following each other according to the spacing regularity [12]. This law states that the ratio of positions of the consecutive bands (X_{n+1}/X_n) measured from the junction point of the outer and inner electrolytes (gel interface) are constant and this is called spacing coefficient (p ; $p = X_{n+1}/X_n$).

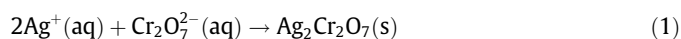
Pattern formation phenomena serve frequently the basis for the design of micro-structures, which gained recently great interest and importance in material science [13,14].

Recently, the morphological pattern transition between periodic precipitation pattern and tree-like crystal aggregates has

been reported with varying gel (agar) concentrations in a lead iodide precipitation system [15,16]. The aim of this study is to investigate the robustness of Liesegang pattern formation in reaction–diffusion systems, and describe the pattern transition through the variation of chemical quality and concentration of the gel.

2. Experimental

Pattern formation was observed in the silver nitrate/potassium dichromate system, where the following precipitation reaction occurs between two ions producing insoluble precipitate:



Here the silver nitrate and the potassium dichromate are the outer and inner electrolytes, respectively.

Agarose (Reanal, puriss grade) and gelatin (Reanal, puriss grade) were used to prepare agarose, gelatin or mixed agarose–gelatin gel. The prescribe amount of gel or gels and potassium dichromate (Reanal, analytical grade) were dissolved in distilled water to produce solution of potassium dichromate of concentration 0.0036 mol/L. The solution was continuously stirred and heated up to 90 °C, and this was poured into a test tube (1.6 cm in diameter and 16 cm in length). After gelation process (2 h for agarose and agarose–gelatin mixed gel; 24 h for gelatin), 5 cm³ silver nitrate (Reanal, analytical grade) solution of fixed concentration (0.25 mol/L) was placed onto the gel interface. Shortly after then, a reddish brown precipitate appeared at the gel interface. Pattern formation was monitored after 1 week, and different types of patterns were observed depending on the concentration of the gel containing one or two monomers.

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3. Results and discussion

3.1. Effect of the gel

Firstly, the effect of the gel was investigated. From earlier works it is known that the gel and the chemical grade of the monomer of the gel as well as impurities play crucial role in precipitation pattern formation [17,18], and these could affect the pattern structure. However, no model ever developed has reflected this fact. In all models, which have successfully reproduced the Liesegang phenomenon, the direct effect of the gel have not been incorporated [19–25]. From the mathematical point of view, the description of pattern formation is simple. In prenucleation and phase separation models the precipitation process starts if the local concentration product of the outer and inner electrolytes or the concentration of the intermediate species (which produces during the reaction of the outer and inner electrolytes) reaches a threshold (nucleation or coagulation threshold, spinodal point). However, these models represent a general picture of the Liesegang pattern formation. For the review please see Ref. [26]. There have been some efforts to take into account the effect of the gel through addition some noise and fluctuation [24,27–29]. Recently, a new reaction–diffusion model was proposed, which includes stochastic term [30,31] describing the stochastic process of the nucleation. It is shown numerically that the amplitude of the stochastic term sensitively affect the final pattern [31].

Fig. 1 shows the effect of the gel and how the gel concentration affects the pattern structure. In these investigations only the quality of the gel and its concentration were varied. All the same time, the final pattern structures show very different morphologies. In case of gelatin the well defined banded (Liesegang) pattern structure can be observed (Fig. 1a and b). One can see that the concentration of the gelatin significantly affects pattern structure, namely: spacing coefficient, diffusion coefficient of the front (D_f)

Table 1

Dependence of the spacing coefficient on the gelatin (gel) concentration at 20.2 °C. The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 mol/L and 0.25 mol/L, respectively.

Gelatin concentration (w/w%)	5.0	7.5	10.0	12.5
Spacing coefficient	1.124	1.112	1.087	1.074

and width of the bands (w_n). The spacing coefficient linearly depends, within experimental errors, on the concentration of the gelatin (Table 1). Furthermore, D_f shows slightly nonlinear characteristic as a function of the gelatin concentration (Fig. 2) and $D_{f5\%}/D_{f10\%} = 1.49$, where $D_{f5\%}$ and $D_{f10\%}$ are the measured diffusion constant of the front for 5 w/w% and 10 w/w% gelatin, respectively. It can be obtained from nonlinear fitting for D_f on gelatin concentration that the intersection of the diffusion coefficient of the front at zero gelatin concentration equals to $0.95 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ (Fig. 2). This is one order of magnitude higher than that of the diffusion constant of small ions in water. It can be noted that the D_f value found at zero gelatin concentration is a hypothetical value because there is no pattern formation in this case due to the lack of the gelled medium. However, the gel concentration affects both the diffusion coefficients of the chemical species and front. The gel concentration also influences the width of the bands. At higher gelatin concentration the bands are thicker. This silver nitrate/potassium dichromate/gelatin system is the most famous one producing Liesegang type pattern formation. However, it can be observed that the width law, which states that the width of the bands is linearly proportional to its position measured from the junction point of the electrolytes ($w_n \sim x_n$) [32,33], has distortion especially at lower gel concentration. This linear proportionality originates from the mass conservation and the assumptions that the concentration of the sol (intermediate product) is constant behind the moving diffusion front and the density of precipitate

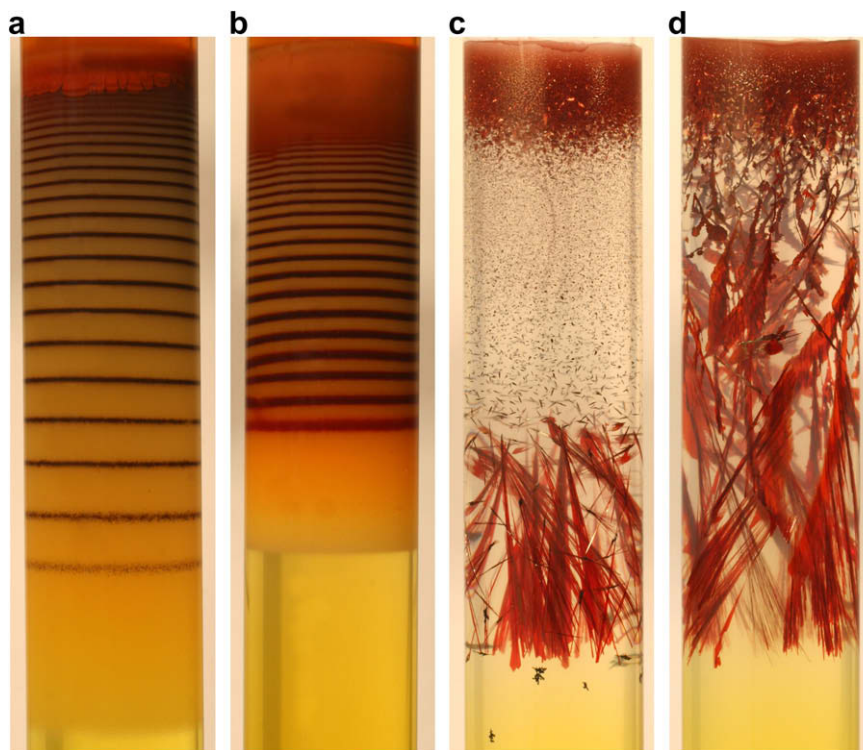


Fig. 1. The silver dichromate precipitation patterns after 1 week at 20.2 °C ± 0.4 °C in gelatin gels: (a) 5 w/w%, (b) 10 w/w% and in agarose gels: (c) 0.25 w/w% and (d) 0.5 w/w%. The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 mol/L and 0.25 mol/L, respectively. The scale bar represents 1 cm.

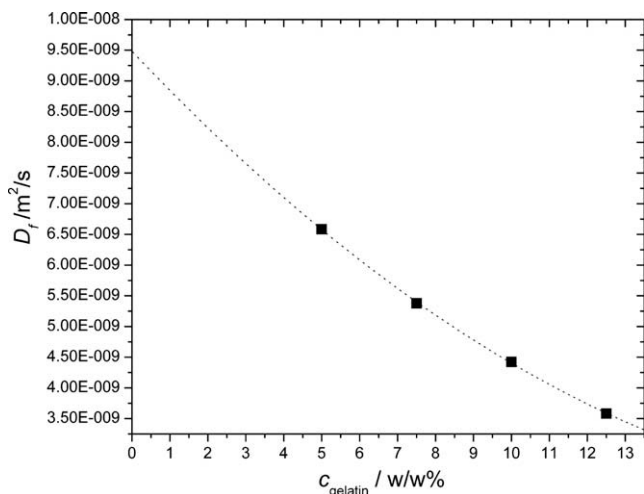


Fig. 2. Dependence of the diffusion constant of the front on the gelatin (gel) concentration at 20.2 °C. The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 mol/L and 0.25 mol/L, respectively.

Table 2

Dependence of exponent α in the width law for the Liesegang pattern formation on gelatin (gel) concentration at 20.2 °C. The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 mol/L and 0.25 mol/L, respectively.

Gelatin concentration (w/w%)	5.0	7.5	10.0	12.5
α	0.612	0.692	0.842	0.940

inside the bands is also constant. In lower gelatin concentration regime this discrepancy may be interpreted by the variation of the density of formed precipitate. However, the width law has a more general form in which the width of the bands increases with their

position as a power law ($w_n \sim x_n^\alpha$) with $\alpha > 0$ [26,33]. Here the $\alpha = 1$ case corresponds to the linear proportionality between two quantities discussed above. Our investigation shows that at lower gelatin concentrations these exponents are very close to those obtained from the reactive lattice-gas [34,35] and the discrete stochastic model simulations [27] (Table 2). Exponent α tends to 1.0 in experiments if the gel concentration is increased (Table 2).

The patterns show different structure if the agarose gel was used. These needle- and plate-like pattern structures (Fig. 1c and d) are completely different from the classical Liesegang structures (Fig. 1a and b), however only gel was changed. One can see that the agarose gel provides different environment for precipitation than gelatin, and pure crystal growth is preferred. After a transient period, which depends on agarose gel concentration (spatially higher at lower agarose concentration), the pure crystal growth regime is observed.

3.2. Effect of temperature

The effect of temperature was also investigated in both gels (Fig. 3). In case of pattern formation in gelatin (Liesegang phenomenon) there are two main differences at lower temperature (5.0 °C). First of all, the diffusion constant of the front is smaller by a factor of 0.65 at lower temperature compared to the higher temperature case (20.2 °C). This is a trivial consequence that the temperature affects the diffusion constant of electrolytes. On the other hand, the structure of the band looks more defined and width of the bands is dominantly thinner compared to room temperature case (Fig. 3a and b). Patterns in agarose show very straight needle-like crystal growth with smaller branch points on the crystal surface due to lower noise and fluctuation in system at lower temperature (Fig. 3c and d).

3.3. Pattern transition

In former works the gel concentration has been varied, which can induce pattern transition [15,16]. In this Letter, a new type of pattern transition was found: by adding a small amount of gelatin

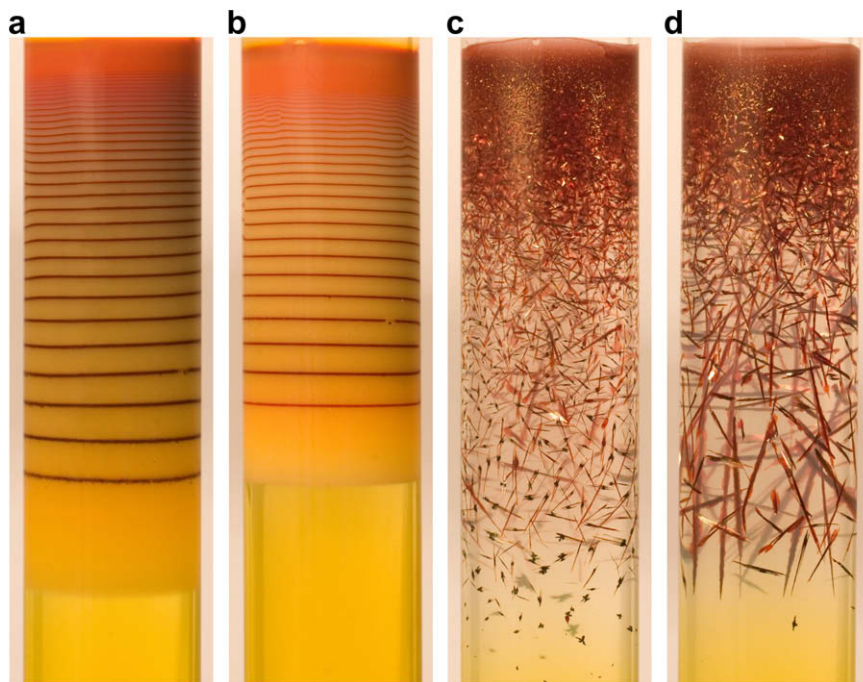


Fig. 3. The silver dichromate precipitation patterns after 1 week at 5.0 °C ± 0.2 °C in gelatin gels: (a) 5 w/w%, (b) 10 w/w% and in agarose gels: (c) 0.25 w/w% and (d) 0.5 w/w%. The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 mol/L and 0.25 mol/L, respectively. The scale bar represents 1 cm.

into agarose, different type of pattern formation can be observed depending on gelatin concentration. Fig. 4 depicts the precipitation pattern structures after the 1st week of the experiments. In experiments with 0.001 w/w% gelatin periodic precipitation occurred near the gel interface. Furthermore, needle- and plate-like crystal

aggregates appeared after Liesegang bands (Fig. 4a). By increasing the gelatin concentration, the periodic precipitation with needle-like crystals pattern structure becomes dominant (Fig. 4b). At gelatin concentrations equal to or above approximately 0.01 w/w%, only periodic precipitation (Liesegang) pattern can be observed

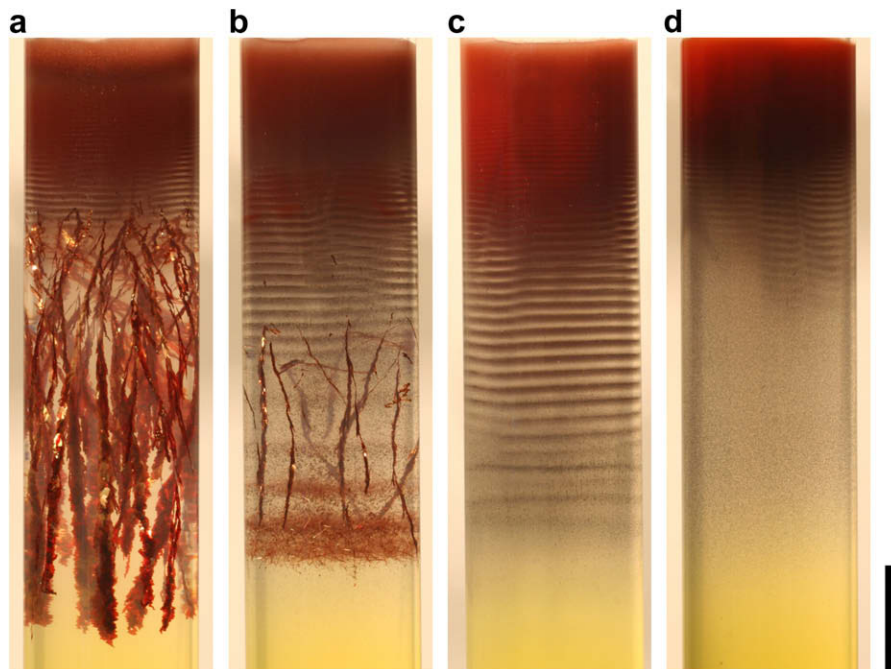


Fig. 4. Pattern transition from crystal growth to periodic precipitation after 1 week at $20.2 \text{ }^\circ\text{C} \pm 0.4 \text{ }^\circ\text{C}$ in mixed agarose–gelatin gels: (a) 0.5 w/w%/0.001 w/w% (b) 0.5 w/w%/0.005 w/w% (c) 0.5 w/w%/0.01 w/w% and (d) 0.5 w/w%/0.1 w/w% (gelatin/agarose concentration). The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 mol/L and 0.25 mol/L, respectively. The scale bar represents 1 cm.

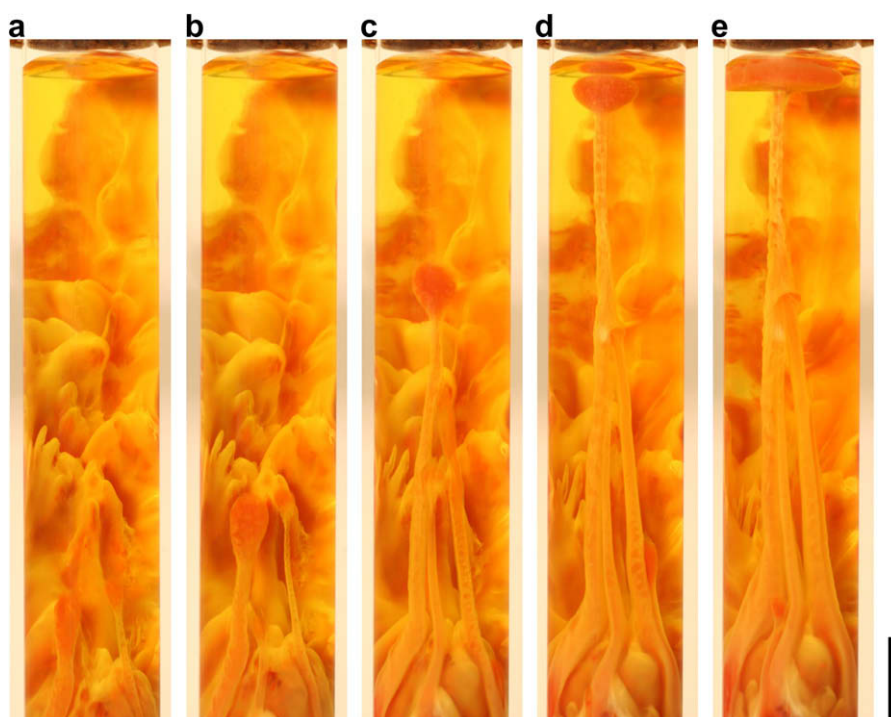


Fig. 5. Tubular pattern formation in silver dichromate precipitation system at $20.2 \text{ }^\circ\text{C} \pm 0.4 \text{ }^\circ\text{C}$ in a viscous gelatin gel with concentration 2.5 w/w%. The concentrations of the inner (potassium dichromate) and the outer (silver nitrate) electrolytes are 0.0036 mol/L and 0.25 mol/L, respectively. The outer electrolyte can invade into the gel by hydrodynamic way producing tubular structures. The time intervals between images are 60 s. The scale bar represents 1 cm.

(Fig. 4c and d). However, further from the gel interface the banded pattern formation disappears (Fig. 4d).

One can see that very small amount of gelatin can induce pattern transition in reaction–diffusion systems. There are several important effects that influence pattern formation, namely rates of heterogeneous and surface nucleation (nucleation on crystal surface) and variation of supersaturation. In such systems, there is practically no homogeneous nucleation because the gel matrix has internal structure which provide nucleation sites (and also may contain impurities) so the dominant nucleation process is the heterogeneous nucleation. This internal structure (pore size etc.) depends on the gel type, its chemical grade and as well as the gel concentration [36]. The gelatin provides higher nucleation rate and number density of crystal than agarose. In case of higher nucleation rate there is no surface nucleation [15,16], which favours to formation of periodic precipitation (Liesegang phenomenon). Inside the Liesegang bands the number of crystals is very high, but the size of crystals is small (1–10 μm) [37]. In contrast to this fact, the agarose ensures lower nucleation rate, the number density of crystal is also lower compared to gelatin. Therefore, in this case the initial dominancy of heterogeneous nucleation will be exceeded by the nucleation on crystal surface and the growth of crystal aggregates reduce the supersaturation at a high enough to suppress further heterogeneous nucleation [15,16]. These result in growth of macroscopic needle- and plate-like crystal aggregates. This is a simple interpretation why the patterns have different morphologies in different gels. It can be controlled by gel quality, gel concentration and quality and concentration of reacting species [15,16]. The pattern transition can be explained in a similar manner. Small amount of gelatin can induce heterogeneous nucleation and the number density of crystals is high because of higher supersaturation at the interface. This involves the occurrence of periodic precipitation near to the junction point of the electrolytes. The higher the distance from the interface is, the lower the supersaturation becomes, resulting in a continuous decrease in the number of density of crystals. Small crystals can grow and the surface nucleation will be preferred producing needle- and plate-like crystal aggregates after periodic precipitation zone (Fig. 4a). Increasing the gelatin concentration in the mixed gel, the heterogeneous nucleation rate and the number density of crystals will be so high in the diffusion medium that only periodic precipitation will be dominant (Fig. 4c and d) (or some needle- and plate-like aggregates can be observed (Fig. 4b)). However, at higher gelatin concentration continuous precipitation can be observed after the periodic precipitation region due to high nucleation rate (Fig. 4d).

3.4. Tubular pattern formation

Recently, tubular pattern formation has been extensively studied in precipitation systems [38–42]. Additionally, we report here a tubular pattern formation in silver nitrate/potassium dichromate/gelatin system (Fig. 5), where the concentration of the gelatin was low enough (2.5 w/w%) that the solid gelled medium was not formed at room temperature. Instead of solid gel a very viscous medium was created. Therefore, at the beginning of experiments the solution of the outer electrolyte was able to invade into the gel by hydrodynamic way producing tubular pattern structures.

4. Conclusions

Precipitation pattern formation in different gels and pattern transition in mixed agarose–gelatin gel were investigated. Different type of pattern structures can be designed using chemically different gels, and pattern transition from Liesegang pattern to crystal

growth can be controlled by addition of gelatin to agarose gel. Based on our investigations it is implied that the Liesegang pattern formation (periodic precipitation) is not a robust phenomena [43], and such type of pattern formation can be expected only in systems, where the diffusion matrix (hydrogel, aerogel, liquid, etc.) provides high heterogeneous (or homogeneous) nucleation rate and number density of particles. Furthermore, this rate should not be too high because at very high rate the diffusion cannot deplete the inner electrolyte from the vicinity of bands due to continuous nucleation and precipitate formation. This means that Liesegang pattern formation occurs only in a moderate nucleation regime, lower and higher rates favour to macroscopic crystal growth and continuous precipitation in reaction–diffusion systems.

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