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On Keller-Rubinow model for Liesegang structure formation

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ABSTRACT We consider a chemical process, the precipitate of which will be represented by a structure in the form of rings. The study and modeling of this process is relevant, since it becomes possible to form micro- and nanostructures based on this approach. We consider the version of the one-dimensional model of Keller and Rubinow which describes the formation of Liesegang rings due to the Ostwald supersaturation. The dependencies of the results obtained on the initial conditions and the model parameters were studied numerically.

KEYWORDS nanostructures, Liesegang rings, Keller-Rubinow model, chemical reaction modeling.

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1. Introduction

In 1896, colloid chemist R. E. Liesegang observed a striking regular patterns of reactions with the formation of a precipitate, which are called are formed by bands or Liesegang rings, depending on their shape [1]. The Liesegang phenomenon is a spontaneous pattern formation, which is a periodic distribution of the precipitate discovered in diffusion-limited systems. Over the past century, it has been experimentally attempted to control the periodicity of patterns and structures of precipitates by varying the concentration of the hydrogel or electrolytes, adding organic or inorganic impurities, and applying an electric or pH field [2–7].

These precipitate-forming reactions are briefly described as follows: created electrolyte (e.g., $\mathrm{Pb}\left(\mathrm{NO}_3\right)_2$) at a relatively low concentration Traces are placed in a test tube filled with gel. Then the second is added electrolyte (e.g., KI) in high concentration on top of the gel so that the I-ions diffuse into the gel and react with $\mathrm{Pb}+$ ions, forming created by $\mathrm{PbI2}$. Then layers of $\mathrm{PbI2}$ precipitate appear parallel to the surface diffusion layer. The self-organized structure of Liesegang rings can be attributed to the periodic colloidal structures. Such rings can also be seen on self-organization of bilirubin and protein in cholelithiasis, fungal howling colony on an apple. Self-assembly is the autonomous organization of components into patterns or structures without human intervention. Self-assembling processes are common throughout nature and technology. They involve components from the molecular (crystals) to the planetary (weather systems) scale and many different kinds of interactions [8].

2. Formation of Liesegang rings

The layers of sediment that precipitate in a chemical reaction exhibit several scaling properties. If we denote by X_n the distance from the nth strip to the first one, then it is surprising to observe that $X_{n+1} = \sigma X_n$ for some positive constant σ . This phenomenon is the so-called law of intervals. In addition, it was noticed that there is a positive constant α such that $X_n = \alpha\sqrt{t_n}$, where t_n- is the growth time of the n-th stripe. This relationship is commonly referred to as the law of time. Finally, if $\boldsymbol{w}_n$ denotes the thickness of the nth layer, then it turns out that the ratio w_{n+1}/w_n is approximately constant: this is the so-called width law [9–11]. Fig. 1 shows a sketch of possible configuration; however, this figure does not represent a real experiment but is the result of numerical simulations.

A number of scientific studies have been carried out, both from an experimental and theoretical point of view. Based on the study of these processes, two major theories have been developed.

- The first one is the prenucleation theory, which is based on the ideas of supersaturation: this theory uses the diffusion reaction model proposed by Keller and Rubinow. Numerical calculations clearly show the fulfillment of the width law for one-dimensional Liesegang rings [12–14].
- The second theory is the theory of postnucleation, which is based on the process of maturation of colloidal particles according to Ostwald [15,16].

Let us consider the existence of discrete precipitates bands that appear in experiments. To do this, we choose a one-dimensional model based on the ideas of Keller and Rubinow. Let a, b and c be the concentrations of the monomers $\mathcal{A}, \mathcal{B}$ and the resulting substance $\mathcal{C}$ during the reaction $\mathcal{A} + \mathcal{B} \rightarrow \mathcal{C}$ and let d be the concentration of the substance formed

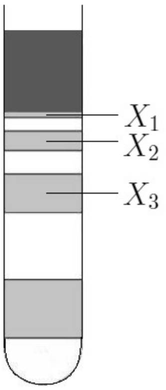


FIG. 1. Liesegang bands in vitro

as a result of precipitation of $\mathcal{C} \to \mathcal{D}$. Then the diffusion reaction process under consideration can be described by the following system:

$$\begin{cases} a_t = D_a a_{xx} - kab, \\ b_t = D_b b_{xx} - kab, \\ c_t = D_c c_{xx} + kab - P(c,d), \\ d_t = P(c,d). \end{cases}$$

Here D_a, D_b and D_c are the diffusion coefficients for A, B and C, respectively. $P(c,d)$ is a precipitate that includes the supersaturation effect. It can be given by the following expression:

$$P(c,d) = \begin{cases} 0 & \text{if } c < C_s \text{ and } d = 0, \\ \lambda\,(c - c^*)^+ & \text{if } c \geq C_s \text{ or } d > 0, \end{cases}$$

where C_s and c^* $(C_s > c^*)$ are the concentrations of supersaturation and saturation, respectively; λ is the settling rate constant $\mathcal{C} \to \mathcal{D}$. The superscript $^+$ denotes the non-negative parts of the corresponding function. We simplify our system under the following assumptions:

(i) The diffusion rate D_b is much less than the diffusion rate D_a,

(ii) The reaction rate k is very fast,

(iii) $c^* = 0$.

Assumption (i) allows us to perform a number of explicit calculations. Without this assumption, we can formally perform similar calculations, but we have no proof of their validity. Assumption (ii) is realistic from the chemical point of view. This leads to a simplification of the system:

$$\begin{cases} a_t = D_a a_{xx} - kab, & 0 < x < \infty,\ t > 0, \\ b_t = -kab, & 0 < x < \infty,\ t > 0, \\ c_t = D_c c_{xx} + kab - P(c,d), & 0 < x < \infty,\ t > 0, \\ d_t = P(c,d), & 0 < x < \infty,\ t > 0. \end{cases}$$

Here we assume that k is very large [10]. Initial and boundary conditions are as follows

$$\begin{cases} a(x,0) = c(x,0) = d(x,0) = 0, \quad b(x,0) = b_0, \quad 0 < x < \infty, \\ a(0,t) = a_0, \quad c_x(0,t) = 0, \quad t > 0, \end{cases}$$

where a_0 and b_0 are positive constants. In experiments, a_0 is much larger than b_0. Let's run numerical simulations where we assume (iii) $c^* > 0$. Note that there have been several precipitation events; these events are characterized by peaks in the function d and the corresponding discontinuities in the spatial derivative of the function c.

Let's start by rewriting the problems taking into account our assumption that $c^* = 0$

$$(\mathrm{P}_k^*)\begin{cases} a_t = D_a a_{xx} - kab, & 0 < x < \infty,\ t > 0,\\ b_t = -kab, & 0 < x < \infty,\ t > 0,\\ c_t = Dc_{xx} + kab - \lambda c\tilde{H}\left((c - C_s)^+ + d\right), & 0 < x < \infty,\ t > 0\\ d_t = \lambda c\tilde{H}\left((c - C_s)^+ + d\right), & 0 < x < \infty,\ t > 0,\\ a(0,t) = a_0 > 0, & t > 0,\\ c_x(0,t) = 0, & t > 0,\\ a(x,0) = c(x,0) = d(x,0) = 0; \quad b(x,0) = b_0 > 0 & 0 < x < \infty. \end{cases}$$

Here D_c is now replaced by D and $\tilde{H}$ is the Heaviside function.

$$\tilde{H}(y) = \begin{cases} 0 & \text{if } y \leq 0,\\ 1 & \text{if } y > 0. \end{cases}$$

The equations for c and d (in the P_k^* problem) were formulated to express the chemical assumption that $d_t = \lambda c$ if $c > C_s$ or if $d > 0$, otherwise $d_t = 0$. The above formulation introduces a non-uniqueness problem, which can be avoided if we choose a different formulation. On the one hand, the equations for c and d are not continuous. It is for this reason that we cannot be sure that the solution is unique, even if $c - C_s \leq 0$ is everywhere. The chemical arguments imply that $d(x,t)$ can be positive if and only if its growth was caused by a positive value of $c(x,\tau) - C_s$ for some $\tau\ leqt$. This leads us to find a solution such that $d(x,t) = 0$ if $c(x,\tau) \leq C_s$ for all $\tau < t$. Let us then reformulate our problem P_k^* in a slightly different way, more precisely, from the chemical point of view, since this excludes any possibility of spontaneous growth of d. Let's try to assume that c is continuous, then we introduce the function

$$w(x,t) = \int_0^t (c(x,s) - C_s)^+ \, ds.$$

We claim that $w(x,t) > 0$ if and only if $(c(x,t) - C_s)^+ + d(x,t) > 0$. Indeed, let's first assume that $w(\bar{x},\bar{t}) > 0$. Then there exists $t_1 < t_2 \leq \bar{t}$ such that $c(x,t) > C_s$ for all $t_1 < t < t_2$. The differential equation for d implies that $d(\bar{x},\bar{t}) > 0$, which in turn means that $(c(\bar{x},\bar{t}) - C_s)^+ + d(\bar{x},\bar{t}) > 0$. Conversely, if $w(x,t) = 0$, then it is clear that $c(x,\tau) \leq C_s$ for all $\tau \leq t$. Due to the chemical arguments discussed above, we assume that $d(x,t) = 0$. Therefore, it is quite reasonable to replace the argument $(c - C_s)^+ + d$ from $\tilde{H}$ with the new argument w. Note that with such a change in the arguments, any reference to d can be completely excluded from the P_k^* problem. Let's continue consideration of problem P_k^*:

$$(\mathrm{P}_k^*)\begin{cases} a_t = D_a a_{xx} - kab, & 0 < x < \infty,\ t > 0,\\ b_t = -kab, & 0 < x < \infty,\ t > 0,\\ c_t = Dc_{xx} + kab - \lambda c\tilde{H}\left(\int_0^t (c(x,\tau) - C_s)^+ \, d\tau\right), & 0 < x < \infty,\ t > 0,\\ a(0,t) = a_0 > 0, & t > 0,\\ c_x(0,t) = 0, & t > 0,\\ a(x,0) = c(x,0) = 0; \quad b(x,0) = b_0 > 0, & 0 < x < \infty. \end{cases}$$

Let's consider the P_k^* problem for very large values of k, or, in other words, to study its asymptotic behavior as k tends to infinity. In this problem, we will use the notation a_k, b_k, c_k to solve P_k^*. Let's solve a_k and b_k first, then calculate ka_kb_k and use this expression as the given source in the equation for c_k. In particular, we will be interested in the rationale for this approach, since k tends to infinity. The behavior of a_k and b_k was considered in [10, 11]. Namely, it was shown that $a := \lim\limits_{k\to\infty} a_k$ is the solution of the single-phase Stefan problem with the melting boundary $\zeta(t) = \alpha\sqrt{t}$ for some positive constant α.

$$(\mathrm{P}_k)\begin{cases} c_{kt} = Dc_{kxx} + ka_kb_k - \lambda c_k\tilde{H}\left(\int_0^t \left(c_k(x,\tau) - C_s\right)^+ \right) d\tau\Bigg), & 0 < x < \infty,\ t > 0,\\ c_{kx}(0,t) = 0, & t > 0,\\ c_k(x,0) = 0, & x > 0. \end{cases}$$

3. Modeling

To simulate these rings, let's try to reproduce the Liesegang phenomenon numerically. To simulate the chemical process described in the previous chapter, we will simulate the process of diffusion of two monomers $\mathcal{A}$, $\mathcal{B}$ and the substance $\mathcal{A}+\mathcal{B}$ obtained in the course of a chemical reaction $\to \mathcal{C}$. As a result of calculations, we obtain the concentration of the precipitate $\mathcal{D}$, which precipitates from the reaction product. We will model the reactions on the segment $X = [0, 1]$.

We inherit the initial conditions for our substances, as well as the initial conditions of the process. Since the considered chemical reaction is described by differential equations, therefore, the time step δt must be chosen according to the Courant-Friedrichs-Levy criterion, which is necessary for the stability of our model.

Let us consider the process of diffusion of the substance $\mathcal{A}$. The distribution of the substance concentration $\mathcal{A}$ on X is shown in Fig. 2 for two time moments $t_1 = 0, t_2 = 600$ (we use δt as a time unit. The distribution of the $\mathcal{B}$ substance will proceed in a similar way to the spread of the $\mathcal{A}$ substance considered above, only with a different diffusion rate, until these substances react and some product $\mathcal{C}$ is formed. The chemical reaction product $\mathcal{C}$ will also begin to diffuse through the test tube. The distribution of the concentration $\mathcal{C}$ over the test tube on the graph is shown in Fig. 3. As you can see on the graph, the diffusion of $\mathcal{C}$ starts at some point in the tube where the chemical reaction started after the diffusing substances $\mathcal{A}$ and $\mathcal{B}$ entered into a chemical reaction.

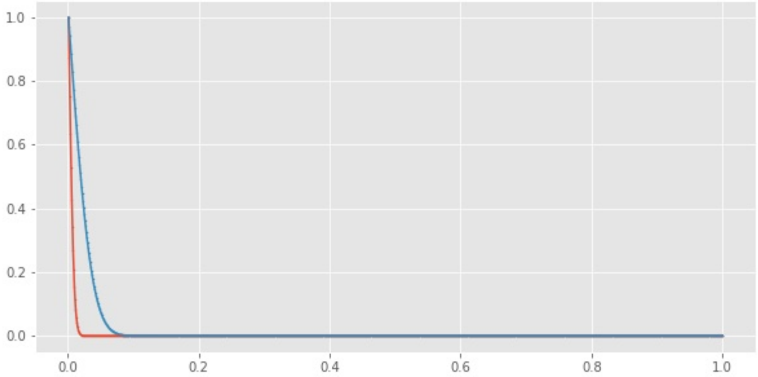
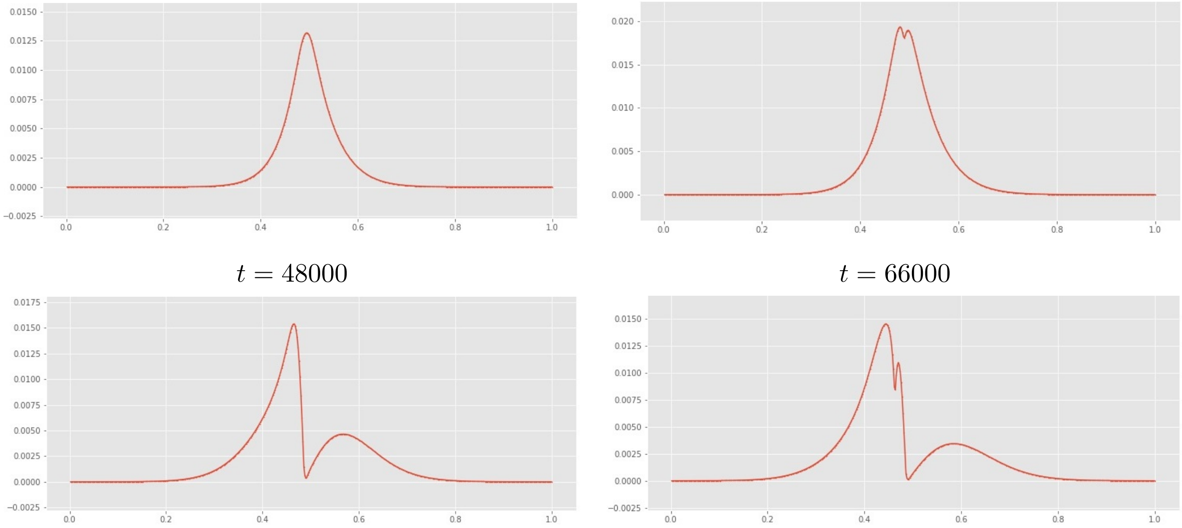


FIG. 2. Graph of dependence of substance concentration $\mathcal{A}$ on X. Where, the red line on the graph is the concentration of substance $\mathcal{A}$ at $t_1 = 0$, and the blue line on the graph shows the concentration of substance $\mathcal{A}$ at $t_2 = 600$ (arbitrary units)



$t = 48000$

$t = 66000$

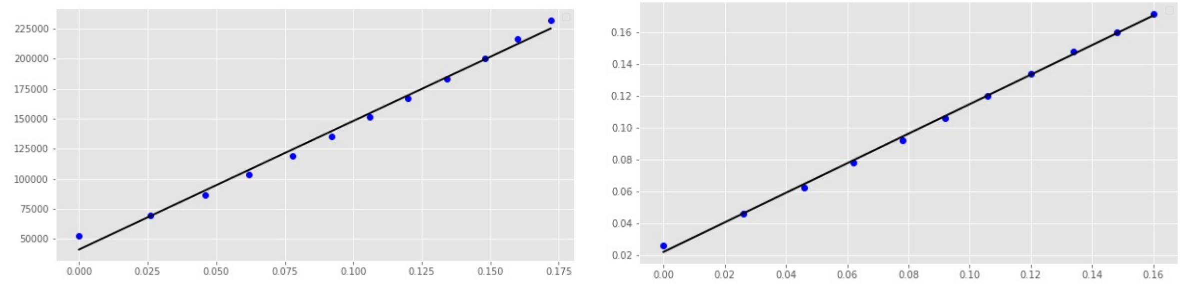
$t = 70000$

$t = 86000$

FIG. 3. Plot of $\mathcal{C}$ product concentration versus X over time

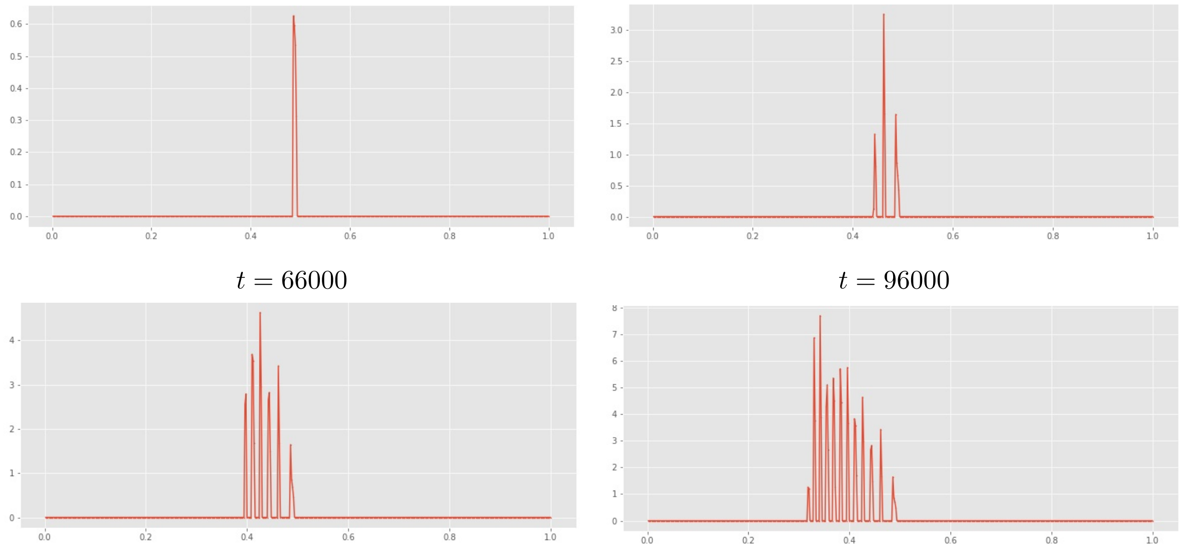
We can observe the refraction of the graph of the concentration of the substance $\mathcal{C}$ at some point in time. At this time moment, $\mathcal{C} \to \mathcal{D}$ will precipitate. We will be interested in the $\mathcal{D}$ precipitate, since rings will form when it is isolated. Let's look at the graphs of the concentration of the substance $\mathcal{D}$, which will fall out over time. It can be noted that the refraction of the $\mathcal{C}$ concentration graph corresponds to the beginning of $\mathcal{C}$ precipitation. It is at these moments in time that Liesegang rings will appear or grow.

Let's make sure on the graphs that our model will satisfy the law of time and distance, respectively. It is shown in Fig. 4.



(A) (B)

FIG. 4. (A)Time low. Graph of square root of formation time versus distance between the first and N-th rings. (B)Distance low. Graph of the distance between the first and rings and the first and $(N+1)$-th rings N-th



$t = 66000$ $t = 96000$

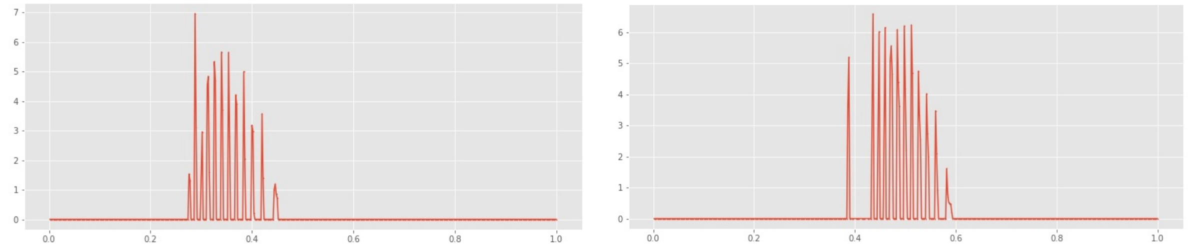
$t = 150000$ $t = 240000$

FIG. 5. Graph of the distribution of the sediment concentration $\mathcal{D}$ on X over time

Formation of Liesegang bands, i.e. the distribution of the sediment concentration $\mathcal{D}$ on X for different time moments is shown in Fig. 5.

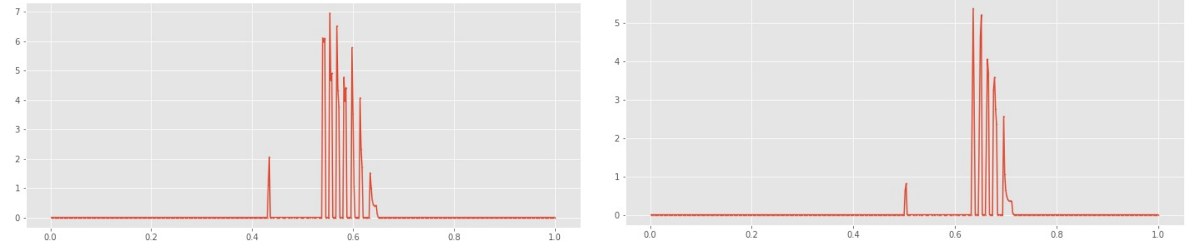
Let us study the dependence of the ring structure on the diffusion rate parameter. The simulation of the chemical process showed that over time, a different amount of $\mathcal{D}$ precipitate appears. The required amount of sediment for further study was obtained at the time moment $t = 260000$ (arbitrary unit). All further simulations were performed with this value of t.

One can observe an interesting behavior of our model when the diffusion rate parameter $\dashv D_a$ changes. When studying the chemical model, we used the tabular value of the parameter $D_a = 4e-7$. We performed calculations by increasing the value of the parameter D_a. When this parameter was changed, we began to observe a different arrangement of the formed Liesegang rings (see Fig. 6). When the value of this parameter increases to $D_a = 8e-7$, a shift is observed on the graph of the distribution of the sediment concentration $\mathcal{D}$ on X, the general group of Liesegang rings to the right. It can also be seen that one of the peaks of the distribution of the sediment concentration $\mathcal{D}$ on X budded from the general group of peaks, thereby violating the linearity of the distance law. One can see that the following increase of D_a confirm this tendency. Another interesting peculiarity is that the total number of rings decreased.



$D_a = 3e - 7$

$D_a = 8e - 7$



$D_a = 12e - 7$

$D_a = 20e - 7$

FIG. 6. Graphs of the dependence of the sediment concentration $\mathcal{D}$ on X, for different values of the diffusion rate parameter D_a

4. Conclusion

The aim of this work was to provide a working model simulating the chemical process of growing Liesegang rings. To construct such a model, theoretical provisions were studied, and systems of differential equations were described that characterize the diffusion process. We implemented the one-dimensional model of Keller and Rubinow, used in their analysis of the Ostwald supersaturation theory, to grow Liesegang rings. For numerical analysis, we used the `C++` [19] programming language and the `Armadillo` [17] library for linear algebra and scientific computing. The programming language `Python` [20, 21] and the package for data processing and analysis `Pandas` [18] were used for data analysis. To test this model for correctness, we checked the laws of time and distance. It showed satisfactory results.

The resulting model for simulating the growth of Liesegang rings gives us the opportunity to study the chemical process under various initial conditions and parameters. The beginning of the formation of the reaction product $\mathcal{C}$ is shown on the graph of the distribution of the concentration of $\mathcal{C}$ on X, which corresponds to the beginning of the chemical reaction between substances $\mathcal{A}$ and $\mathcal{B}$. A plot of $\mathcal{C}$ concentration versus X over time shows an interesting behavior, namely its refraction. Also, the product $\mathcal{C}$, in turn, precipitates $\mathcal{C} \to \mathcal{D}$. We have considered in detail the dependence of the formation of the precipitate and the rings themselves, respectively, on the diffusion propagation of $\mathcal{C}$. We managed to understand the dependence of $\mathcal{C}$ on its sediment $\mathcal{D}$. Namely, we learned that the moment of time when the precipitate begins to fall out is equal to the moment of the beginning of refraction of the graph of the dependence of the concentration $\mathcal{C}$ on X. And also that each subsequent refraction of the graph of the distribution of the concentration of $\mathcal{C}$ on X will tell us about the growth of Liesegang rings, or an increase in the number of Liesegang rings.

We also simulated the growth of Liesegang rings for other values of the parameter D_a, which is responsible for the rate of diffusion propagation. When changing the values of this parameter, we observed a shift in the location of the rings. There is a certain relationship between an increase in the value of the parameter D_a and a shift of the Liesegang rings on the graph of the distribution of the concentration $\mathcal{D}$ on X to the right. There is also some budding of one of the rings from the general group of rings.

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Conflict of interest: the authors declare no conflict of interest.