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ORIGINAL CONTRIBUTION

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Liesegang patterns: Estimation of diffusion coefficient and a plausible justification for colloid explanation

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Abstract The Liesegang phenomenon is interpreted as a moving boundary problem. The existing time law, spacing law, and width law are revisited and reformulated on the basis of the new scenario. A better understanding of the basic facts associated with pattern formation is made possible with the new concept. The phenomenon is explained on the basis of colloidal kinetics. Diffusion coefficients of the outer electrolyte in the gel for various experiments in the literature are calculated. The diffusion coefficients so calculated range from 1.792–5.996×10^{-10} m^2 s^{-1}. It is suggested that such values confirm the fast colloidal dynamics during the process of periodic precipitation pattern formation.

Keywords Liesegang rings · Periodic precipitation · Moving boundary · Colloid diffusion · Diffusion coefficient

Introduction

Pattern formation occurs in systems where chemical reactions are coupled with diffusion under specific physiochemical conditions. Among the reaction diffusion controlled systems one of the most interesting cases occurs when an electrolyte (outer electrolyte) diffuses and reacts with another electrolyte (inner electrolyte) that is contained in a gel. The chemical reactions between the two diffusing electrolytes lead to an insoluble product that precipitates rhythmically in bands or rings (depending upon the dimensionality of the experimental set up) perpendicular to the direction of diffusion. This mechanism called Liesegang phenomenon [1], has been widely studied because it offers a model to explain a great variety of formations in nature, ranging from agate rocks and gold veins to the growth of bacterial rings in agar and gallstones.

Liesegang pattern on macroscopic scale is visible to the naked eye. The presence of gel is not absolutely necessary for pattern formation. The role of the gel matrix is to prevent sedimentation of the precipitate or convection of solutions. In general, these Liesegang structures appear to follow three laws.

The position x_n (measured from the gel surface) of the n^{th} band is related to the time t_n of its formation [2]:

$$x_n^2 \sim t_n \tag{1}$$

This relation, which is often called the time law, is a direct consequence of the diffusive nature of the reactants and its dynamics is in fact a straight-forward approximation of the famous Einstein–Smoluchowski relation [3].

Jablczynski law or spacing law [4] is a more intricate property of the bands. The spatially ordered patterns follow a geometric series:

$$x_{n+1}/x_n = (1+p) \tag{2}$$

with $0.05 < p < 0.4$ [5]. The quantity $(1+p)$ is referred to as the spacing coefficient.

It is also generally observed that the width w_n of the band increases with their position according to the relation (width law) [6, 7]:

$$w_n \sim x_n \tag{3}$$

Careful observations with a large number of bands Droz et al. [8] framed a more accurate behavior and according to them

$$w_n \sim x_n^{\varphi} \tag{4}$$

where the width exponent φ depends on C_{A0} and C_{B0}, the initial concentrations of the outer and inner electrolytes A and B, respectively and ranges from 0.9 to 0.99. Since the boundaries of the bands are not sharply defined, the errors in the determination of the width of the bands are large and the width law is usually ignored.

Although there are a large number of interesting observations about Liesegang phenomena in particular systems, the above three points appear to be the only ones which describe quantifiable results and carry some generality.

Existing theories

Several competing theories have been developed for explaining the mechanism of Liesegang phenomenon [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Of the various explanations that have been proposed, Ostwald's supersaturation theory [9] is by far the simplest and long standing. According to this theory, the diffusion of electrolyte A into a gel impregnated with electrolyte B forms a layer of supersaturated solution near the initial boundary between the two. Precipitation of the reaction product is assumed to occur once a critical degree of supersaturation is exceeded. By serving as active sites for further precipitation, the band of crystals robs ions from the neighborhood by diffusion. Consequently, no precipitation occurs in the depleted layers of solution next to the first band. As the electrolyte A continues to diffuse deeper into the gel containing the electrolyte B, however, a second layer of supersaturated solution forms beyond the first band. From this, a second band of crystals precipitates, and so on. Supersaturation theory is classified as a 'pre nucleation' theory because the underlying pattern formation is assumed to be generated prior to the nucleation stage.

In recent years 'post nucleation' theories of periodic precipitation have been developed based on the autocatalytic competitive growth of colloid particles [7, 19, 20, 21]. The other frequently used model is based on the sol coagulation theory [18]. In this, the precipitation has no kinetic barrier but produces a sol that is protected by gel matrix. The zones consist of coagulated precipitate, which is produced when the concentration of the outer electrolyte reaches the critical coagulation concentration. It is supposed that the sol particles are able to diffuse despite their large size. Shinohara [18] developed a variant of this mechanism that does not require this latter assumption.

Other theories of periodic precipitation are based on colloidal coagulation, semi permeable membranes, or coulombic repulsion [16]. There are many experimental findings which are consistent with the colloid explanation [11, 12, 13, 14] but appear to be incompatible with the supersaturation one. Evidence has accumulated over many years that the initial form of the precipitate is colloidal [19], which demonstrated that the appearance of a visible ring is preceded by a continuous distribution of colloidal material, whose front travels out from the previous ring according to the simple Fickian diffusion law $x^2/t = \text{constant}$. In spite of the powerful conclusions drawn on the basis of colloidal explanations, there is an apparent difficulty for an explanation involving colloids; namely, the diffusion coefficients of the colloid particles (particle size ranging from 20–200 nm) are too low to account for the development of Liesegang structures within the time limit of the experiment [16]. However, with the moving boundary model discussed below, the findings seem to be consistent with the colloid explanation.

The moving boundary model

It is important to note that in all theoretical approaches and studies proposed [2, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36], the interface of the reagents is considered to be stationary and all distances are measured from the gel solution interface. We report a new scenario here where the formation of the periodic ring system is treated as a moving boundary problem. Accordingly, we shall assume that the boundary, which separates the outer ions and inner electrolyte, virtually migrates into the positive direction of the advancement of the A-type ions. Initially the boundary which separates A and B ions was the gel solution interface. When the first precipitation zone (ring) was formed, A-type ions occupy up to this region and its concentration reaches the reservoir concentration C_{A0}. This implies that the boundary of A-type ions has been shifted to the region of the precipitation front. This assumption holds good as the reservoir concentration C_{A0} of the A-type ions is sufficiently large compared with the initial concentration C_{B0} of the B-type ions. This will repeat in time and the boundary region moves from one ring to the other. For a one-dimensional system the concentration levels of A species at the boundary are:

$$C_A(x,t) = C_{A0};\ \text{at } t \le t_n \text{ and } x_0 \le x \le x_n \tag{5}$$

where n denotes the number of the ring. The initial value x_0 corresponds to the position of the gel solution interface and x_1, x_2, etc. are the positions of the first, second, etc. rings.

Till the boundary advances to a new ring position, a steady state condition is assumed to be established within the region. Statistical fluctuations and thermal instabilities within this range are assumed to be minimum. The collective motion of the precipitants from one ring to the other is more or less uniform and therefore it is noteworthy to assume that the boundary layer shifts from one ring to the next with uniform velocity v_n (Fig. 1).

In a similar situation, to account for the quantity of isotopes diffusing into a medium having moving boundary, Lothar Senf [37] assumed a cubical concentration profile for the isotopes. According to the authors, an exponential profile is found to be more appropriate for the diffusant to describe the Liesegang phenomenon. Peterlin [38], while studying moving boundary problems, observed that the concentration within the first medium is declining because of the mass transfer across the boundary. Hence, according to him, the amplitude of the concentration profile of the diffusant within the second media declines as a function of time. However, for the present calculations, we assume an exponential profile with constant pre-exponential factor.

When a new ring is established at $x_n(t)$, the concentration profile of A-type ions in the gel medium is assumed to be:

$$C_A(x,t) = C_{A0} \exp\left\{-\beta \frac{x - x_n(t)}{\xi_{n+1}}\right\}; \quad x_n \le x \le x_{n+1} \tag{6}$$

where β is regarded as a constant for a system, called the concentration profile index, which can be easily calculated and ξ_{n+1} is the separation between the n^{th} and $(n+1)^{\text{th}}$ rings.

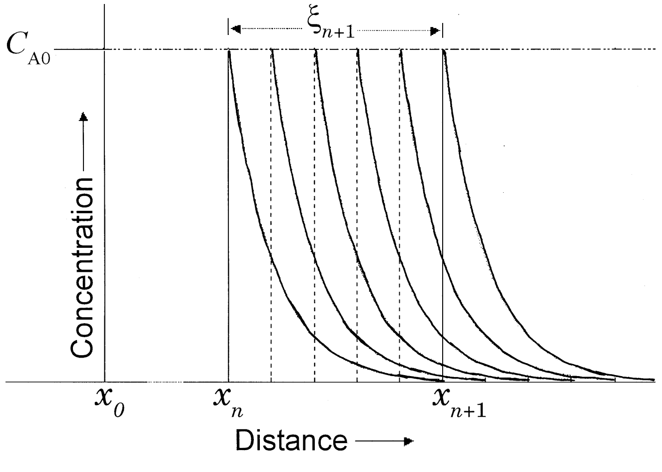

Fig. 1 Concentration distribution with moving boundary. The gel solution interface is denoted by x_0. The position of the n^{th} and $(n+1)^{\text{th}}$ rings are x_n and x_{n+1}, respectively

For an infinitesimal boundary layer advancing into the positive x-direction, the equilibrium condition for the amount of diffusant exchanged per unit area per unit time is:

$$vC_A(x^+,t) + D_A \frac{\partial}{\partial x} C_A(x^+,t) = D_A \frac{\partial}{\partial x} C_A left(x^-,t) \tag{7}$$

where D_A is the diffusion coefficient of the diffusant A. For A-type ions, only unidirectional diffusion is considered and hence

$$D_A \frac{\partial}{\partial x} C_A(x^-,t) = 0 \tag{8}$$

Thus, the amount of substance diffusing in the x-direction follows the concentration gradient of the system and the simplified balance equation is

$$vC_A(x^+,t) + D_A \frac{\partial}{\partial x} C_A(x^+,t) = 0 \tag{9}$$

Substituting Eq. 6 in Eq. 9 and applying the above boundary condition we get,

$$v_n = \beta D_A / \xi_{n+1} \tag{10}$$

As the effective diffusion coefficient of A-type ions D_A in the gel medium is constant, one easily finds

$$v_n \xi_{n+1} = \text{constant}; \tag{11}$$

which is the characteristic equation for boundary migration. If τ_n is the time taken by the boundary to travel from the $(n\text{–}1)^{\text{th}}$ ring position to the n^{th} ring position, then

$$v_n = \frac{\xi_n}{\tau_n} \tag{12}$$

Substituting this in Eq. 11,

$$\xi_n \xi_{n+1} \sim \tau_n \tag{13}$$

This is in fact a better relation than the time law $x_n^2 \sim t_n$. As stated above, in all the existing theories, the distances were measured from the gel solution interface. The concentration of the outer ions gradually builds up in the gel column and attains the maximum value C_{A0} up to the ring position and, hence, it may not be proper to take the distance from the gel solution interface, once the ring is formed. The formation of a ring is enough to conclude that the boundary of A-type ions has been advanced into the gel medium up to the ring position. Hence, ξ_n is a better choice of distance than x_n and therefore the modified time law (Eq. 13) is more meaningful. Also, the theoretical analysis is based on Brownian motion where we consider the 'random walk' at the molecular level and the transitions are between closely neighboring states. This implies that the distance measurement cannot be made from the initial surface if one really wants to assume Einstein's solution to the problem. This conclusion leads to two more relations.

As the boundary layer shifts from one ring position to the next with uniform velocity, from Eq. 11 it is also evident that

$$v_n \xi_{n+1} = v_{n-1}\ \xi_n \tag{14}$$

$$\xi_{n+1}/\xi_n = \frac{v_{n-1}}{v_n} = (1 + p') \tag{15}$$

the new spacing constant, which is expected to be little different from Eq. 2.

For regular Liesegang pattern

$$\xi_{n+1} = \xi_n + \Delta\xi_n \tag{16}$$

Substituting this in Eq. 15,

$$\Delta\xi_n \sim \xi_n \tag{17}$$

This relation seems to be in a better position when compared with the width law $w_n \sim x_n$. It should be noticed that the elemental increment accounted for ξ_n is not exactly the width of the ring w_n. Combining Eqs. 15 and 17 we have

$$\Delta\xi_{n+1}/\Delta\xi_n = (1 + p') \tag{18}$$

The modified time law (Eq. 13), spacing law (Eq. 15), and the width law (Eq. 17) represent the picturization of the characteristic Eq. 11 for boundary migration.

Estimation of diffusion coefficient

A method for estimation of the effective diffusion coefficient of A ions in the gel medium can be formulated based on this theory. Incorporating Eq. 12 in Eq. 10 we get

$$D_A = \frac{1}{\beta}\frac{\xi_n \xi_{n+1}}{\tau_n} \tag{19}$$

According to Einstein's law of one dimensional Brownian motion [3]

$$D_A = x_n^2/2t_n \tag{20}$$

In a recent publication, Young [39], analyzing the results of the 22 sets of experiments performed by Morse and Pierce [2], argued that the distance x_n in Eq. 20 must be the distance of the n^{th} band from the $(n\text{–}1)^{\text{th}}$ band and t_n the time of formation of n^{th} band after the previous band is formed. Using the moving boundary model, Young's suggestion can be fully interpreted. As the theoretical interpretation discussed above almost coincides with the idea put forward by Young, Eq. 20 can be rewritten in terms of the nomenclature discussed here as

$$D_A = \xi_n^2/2\tau_n \tag{21}$$

From Eqs. 19, 21, and 15 one can conclude that

$$\beta = 2(1 + p') \tag{22}$$

Detailed investigation of the experimental data obtained from Morse and Pierce [2], Pillai et al. [6], and Kurien et al. [40], showed that $(1 + p')$ lies between 1.04 and 1.5 and, hence, that the concentration profile index β lies between 2.08 and 3. For a given precipitation pattern β can be evaluated and, using Eq. 19, D_A can be obtained. The diffusion coefficient obtained from the data of Pillai et al. [6] concerning Liesegang bands formed by different electrolytes in different gels are calculated and tabulated in Table 1. The results show that the diffusion coefficients so calculated range from 1.792×10^{-10} –5.996×10^{-10} m^2 s^{-1}. These values are 10–100 times greater than the average values for spheres of colloid dimensions. However, this in itself doesn't necessarily suggest the conclusion that the particles are smaller ions. A regular ring or band structure is obtained when the

Table 1

Details of gel medium	Outer electrolyte and concentration	Inner electrolyte and concentration	$\frac{\xi_{n+1}}{\xi_n}$	p	$D_A \times 10^{10}$ m^2 s^{-1} (mean ± standard error)
Silica density 1.03 g cm^{-3}, pH~7	$Pb(CH_3COO)_2$ 0.2 M	$(NH_4)_2CO_3$ 0.1 M	1.261	2.522	1.792 ± 0.299 (4)[a]
Silica density 1.03 g cm^{-3}, pH~7.15	$Pb(NO_3)_2$ 0.2 M	$(NH_4)_2CO_3$ 0.1 M	1.389	2.778	2.805 ± 0.262 (3)
Agar Agar concentration 1.5%	$(NH_4)_2CO_3$ 2 M	$CaCl_2$ 0.1 M	1.113	2.226	5.996 (2)
Agar Agar concentration 1.5%	$(NH_4)_2CO_3$ 0.5 M	$CaCl_2$ 0.1 M	1.258	2.517	3.638 ± 0.097 (3)
Gelatin	K_2CrO_4 2.997 N	$AgNO_3$ 0.00991 N	1.185	2.371	2.998 ± 0.101 (9)
Gelatin	Ag NO_3 1 N	K_2CrO_4 0.01333 N	1.066	2.132	3.512 ± 0.262 (13)

[a] Number of trials for the calculation of D_A

concentration of the outer electrolyte is much larger than that of inner electrolyte. In Liesegang experiments one typically has $0.005 \leq C_{B0}/C_{A0} \leq 0.1$ [5]. According to the moving boundary concept, when a precipitation zone (ring) was formed, A-type ions occupy up to that region and its concentration reaches the reservoir concentration C_{A0} or we say the boundary of the A-type ions has been migrated to the region of the precipitation front. The number of ions moving in the forward direction will be very large compared to the number of ions moving in the reverse direction. This hails Young's conclusion [39] that the particle diffuses without much molecular bombardment. This is of course an essential axiom of the moving boundary model. As the particles are diffusing without much molecular collision the colloidal particles will move a given distance in fewer steps and hence in shorter time. This may be the reason for its fast diffusion and the observed higher values of diffusion coefficients.

Evidence available supports the argument that the initial form of the precipitate is colloidal [12, 13, 19, 20]. The colloidal coagulation plays a vital role during the early stages of ring formation. Flicker and Ross [19] describe the mechanism of chemical instability as a reason for periodic pattern formation and the ring formation is considered as a post nucleation phenomenon. The auto-catalytic growth of particles and their nonlinear dynamics brings in the geometric pattern. According to Gerd Venzl [20], the process of Liesegang band formation is characterized by three distinct stages. The first stage is the production (nucleation) of a continuous, and essentially homogenous, colloid characterized by colloidal dynamics occurring within a well-localized region. Second is the coarsening of the colloid. Large particle flux into this homogenous colloid zone from outside generates spatial instabilities. Such instabilities can remove the stability of the system and its kinetics. Finally, the nonlinear dynamics of the colloid particles result in precipitation and pattern formation. For the macroscopic pattern generation, slow coarsening of colloid particles is very essential [20]. The particle size therefore grows at a slow pace only, resulting in considerably fast diffusion.

Conclusion

The authors have developed a mathematical model for the pattern formation in gelatinous media. The theory is very successful in explaining many features of the phenomenon. The one-dimensional model suggested above is based on the idea of a moving boundary inside a semi-solid medium. The virtual motion of the boundary as the system advances into the gel column can be paralleled to the random motion of Brownian particles. While the ring advances into the gel column, the boundary between the electrolytes migrates with the precipitation front. As a result of this, it may not be proper to take the distance from the gel solution interface once the ring is formed. The formation of a ring is enough to conclude that the boundary of the diffusant has been advanced into the gel medium up to the ring position. Existing empirical laws have been modified and a new method developed to estimate the diffusion coefficient of the outer electrolyte in the gel. The values of the diffusion coefficients obtained for various Liesegang systems in different gels suggest the fast colloidal dynamics during the process of periodic structure formation.

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