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# Formation of periodic precipitation patterns: a moving boundary problem

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### Abstract

A new scenario for the formation of Liesegang patterns is proposed. The periodic precipitation pattern formation in a gel column is interpreted as a moving boundary problem. The existing time law, space law, and width law are revisited and reformulated on the basis of a moving boundary assumption and more meaningful explanations are given. All the new equations suggested were found to be in good agreement with experimental observations. © 2002 Elsevier Science B.V. All rights reserved.

# 1. Introduction

The formation of rhythmic precipitation patterns in physical as well as biological systems is a subject of extensive research ever since its remarkable discovery by R.E. Liesegang in 1896 [1]. When anions diffuse into a gel medium impregnated with cations, the possible reaction product segregates into concentric rings or bands depending upon the geometry of the system. The phenomenon has since been examined by a large number of investigators and many theories have been suggested to explain the rhythmic structure. So far, no single theory of periodic precipitation seems to be able to account for all observed features, possibly because of the variety and complexity of the observed phenomena. The mechanisms responsible for these structures are still under discussion [2–6].

In a simple ring system, as one observed in a gel column inside a test tube, the species of A type ions diffuse from the outer electrolyte into the gel, having almost uniformly distributed B type ions, and the two co-precipitates react chemically resulting in the product C inside the gel medium. Precipitation occurs when the local product of the ion concentrations  $C_A C_B$  exceeds some threshold value  $K_{sp}$ , if the reaction is of the form  $A + B \rightarrow C$ [7]. Once the precipitation front is formed, the concentration of A type ions reaches its maximum value – the reservoir concentration  $C_{A0}$  – up to the region of the precipitation front. This assumption holds well provided the reservoir concentration  $C_{A0}$  of the A ions is sufficiently high compared with the concentration  $C_{B0}$  of the B type ions. The

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A type ions further penetrate into the gel medium and a new precipitation zone is formed at a later time, when the concentration condition is further achieved. As the diffusion advances into the gel, consecutive bands of precipitate are observed in the tube. Three laws, characterizing the Liesegang phenomenon were framed by phenomenological investigators. The first one is the so-called *time law* given by Morse and Pierce [8] which states that  $x_n^2 \sim t_n$  where  $x_n$  is the position of the *n*th band measured from the interface of the reagents and  $t_n$ is the time of its formation. This result is analogous to the well known Einstein-Smoluchowski relation for Brownian motion interpreted in terms of random walk in a homogeneous space [9]. Secondly, the positions of the rings follow a geometric progression,  $x_{n+1}/x_n \rightarrow (1+p)$  for large enough n, known as Jablczynski law [10] or spacing law, where (1 + p) being known as the spacing coefficient. Later it has been found that the spacing coefficient is a non-universal quantity depending, among other parameters, on the experimentally controllable initial electrolyte concentrations  $C_{A0}$ and  $C_{\rm B0}$ . This dependence was expressed further by Matalon and Packter [11] as

$$p = F(C_{\rm B0}) + \frac{G(C_{\rm B0})}{C_{\rm A0}},$$

where *F* and *G* are decreasing functions of their argument  $C_{B0}$ . Finally the width  $w_n$  of the band has been observed to increase with *n* and obey a simple linear relation  $w_n \sim x_n$  [12]. Based on detailed experimental observations with a large number of bands, a more accurate behavior was framed by Chopard et al. [13] and expressed by a new law,  $w_n \sim x_n^{\alpha}$ , where the constant parameter  $\alpha$  depends only on C<sub>A0</sub> and C<sub>B0</sub> whose value ranges from 0.49 to 0.61. Later Droz et al. [14] combining scaling properties of the density of precipitate in the bands, found that  $\alpha$  ranges from 0.90 to 0.99.

## 2. The moving boundary model

It is important to note that in all the theoretical approaches proposed [2,3,5–8,10–23], the interface of the reagents is considered to be stationary. In this letter, we report a new scenario where the

formation of periodic ring systems 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 gradually 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 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

$$C_{\rm A}(x,t) = C_{\rm A0}, \quad \text{at } t \leq t_n \text{ and } x_0 \leq x \leq x_n,$$
 (1)

where *n* denotes the number of the ring, which is a positive integer. The initial value  $x_0$  corresponds to 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 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



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

that the boundary layer shifts from one ring position to the next with uniform velocity  $v_n$ .

The concentration profile of the A type ions within the gel medium will establish an exponential distribution (Fig. 1). Peterlin [24], while studying moving boundary problems, observed that the amplitude of the concentration profile may also decline as a function of time. However, at least for the present calculations, we assume a profile with constant pre-exponential factor. This is, in fact not a realistic picture of the problem. However, this assumption is not much deviated from the actual situation, since the reservoir concentration  $C_{A0}$  of the A type ions is sufficiently high compared with the initial concentration  $C_{B0}$  of the B type ions. It has been known since the earliest experiments of Liesegang that optimum results for ring or band formation are obtained when the concentration of the outer electrolyte is much higher, preferably by several orders of magnitude than that of the inner electrolyte. In regular Liesegang experiments one typically has  $0.005 \leq C_{B0}/C_{A0} \leq 0.1$  [2]. In a similar situation, to account for the quantity of isotopes diffusing into a medium having a moving boundary, Lothar Senf [25] assumed a cubical concentration profile. According to the authors an exponential profile with index flexibility is found to be more appropriate to describe the Liesegang phenomenon.

After a new ring is established at  $x_n(t)$ , the concentration profile of A type ions at any point between *n*th and (n + 1)th ring is assumed to be

$$C_{\rm A}(x,t) = C_{\rm A0} \exp\left\{-\beta \frac{[x - x_n(t)]}{\xi_{n+1}}\right\}, \quad x_n \leqslant x \leqslant x_{n+1},$$
(2)

where  $\beta(>0)$  is regarded as a constant for a system, called the concentration profile index and  $\xi_{n+1}$  is the separation between the *n*th and (n + 1)th rings. The region between the *n*th and (n + 1)th rings is referred to as the  $\xi_{n+1}$ th zone. In studying the formation of precipitation band at  $x_n$ , we consider the diffusion of ions from the immediate neighboring zones only ( $\xi_n$ th and  $\xi_{n+1}$ th zones).

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 can be expressed as follows: the amount of substance diffusing into the boundary layer augmented by the amount of substance gathered by the advancement of the boundary layer is equal to the amount of substance diffusing out. In mathematical terms

$$D_{\mathcal{A}}\partial_{x}C_{\mathcal{A}}(x_{+},t) + vC_{\mathcal{A}}(x_{+},t) = D_{\mathcal{A}}\partial_{x}C_{\mathcal{A}}(x_{-},t).$$
(3)

The boundary migration velocity is denoted as v. Here only unidirectional diffusion is considered and hence the amount of substance diffusing in the positive x-direction follows the concentration gradient of the system and the simplified balance equation is

$$D_{\rm A}\partial_x C_{\rm A}(x_+, t) + v C_{\rm A}(x_+, t) = 0.$$
(4)

Substitution of (2) in (4) and applying the above boundary condition, we get

$$\xi_{n+1} = \beta D_{\mathcal{A}} / v_{n+1}. \tag{5}$$

This is a significant relation which connects the boundary migration velocity v with the ring separation  $\xi$ . Since the effective diffusion coefficient of A type ions  $D_A$  in the gel is a constant, one easily finds

$$v_{n+1}\xi_{n+1} = \text{constant},\tag{6}$$

which characterizes the nature of the boundary migration. If the boundary traverses inside a zone of length  $\xi$  within a time  $\tau$ , the velocity of migration

$$v = \xi/\tau. \tag{7}$$

Making a substitution for velocity in Eq. (5) one gets

$$\xi_n^2 \sim \tau_n. \tag{8}$$

This is in fact a better relation than the time law  $x_n^2 \sim t_n$ . In all the existing theories, the distances were measured from the gel solution interface. The concentration of the outer ions 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 measure the distance from the gel solution interface after the formation of a ring. 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. This implies that the distance measurement cannot be done from the initial interface, if one really wants to assume

Einstein's solution to the problem. Hence  $\xi_n$  is a better choice of distance than  $x_n$  and hence the modified relation (8) is more meaningful. This conclusion leads to two more relations.

As the boundary layer shifts from one ring position to the next with uniform velocity, from Eq. (6) it is also evident that

$$\xi_{n+1}/\xi_n = (1+p'),\tag{9}$$

which is the modified spacing law and (1 + p') is the new spacing constant. Writing  $\xi_{n+1} = \xi_n + \Delta \xi_n$ in Eq. (9) gives

$$\Delta \xi_n \sim \xi_n. \tag{10}$$

Even though Eq. (10) is not necessarily related to the width law  $w_n \sim x_n$ , the result obtained using this seems to be better. It is clearly evident from Eqs. (9) and (10) that the rings become more and more separated as it is away from the gel-solution interface. All the above modified relations picturize the fact that the precipitation pattern front obeys the characteristic equation for boundary migration.

#### 3. Experimental

The penetration of  $Ba(NO_3)_2$  into silica gel containing  $(NH_4)MoO_4$  results in a sharp boundary interface of  $BaMoO_4$  precipitate bands. In all the experiments we have obtained more than 15 bands. The time of formation  $t_n$  and distance of each ring from the gel solution interface  $x_n$  were recorded. The data were analyzed and the results are summarized in Figs. 2–4. The relatively large number of bands allowed a rather accurate determination of the constants involved in the modified relations (8)–(10).

Fig. 2 depicts the plot of  $\xi_n^2$  against  $\tau_n$ . The straight line shows the validity of the modified time law. To determine the value of the new spacing coefficient, we plotted  $\xi_{n+1}$  against  $\xi_n$  (Fig. 3). Note that the new spacing coefficient remains constant throughout the entire range of the band system as indicated by the slope and the value is found to be 1.077. The linear relationship  $\Delta \xi_n \sim \xi_n$  is also verified (Fig. 4) and the value of p' so obtained is 0.0715. Slight deviations observed were



Fig. 2. Verification of the modified time law with Liesegang rings of BaMoO<sub>4</sub>. Experimental details: silica gel of density 1.03 g cm<sup>-3</sup>, pH ~ 6, outer electrolyte Ba(NO<sub>3</sub>)<sub>2</sub> – 0.25 M, inner electrolyte  $(NH_4)_2MOO_4 - 0.1$  M.



Fig. 3. Determination of the new spacing coefficient (1 + p') given by the slope of the curve  $\xi_{n+1}$  versus  $\xi_n$ . The value of (1 + p') is found to be 1.0704.

due to the experimental error in the judicious measurement of ring positions and the time of ring formation. Within the limits of error the results suggest that a virtual migration of boundary takes place from one ring to the other.

## 4. Conclusions

To study the Liesegang pattern formation in gelatinous media, we have developed a one dimensional model based on the moving boundary



Fig. 4. Plot of  $\Delta \xi_n$  versus  $\xi_n$ . The experimental details are same as those given in Fig. 2.

concept. As the ring advances into the positive direction of the gel column, the boundary between ionic species 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. This leads to the modifications of the existing laws and positive conclusions. The modified time law and spacing law illuminate the fact that the formation of Liesegang pattern can be treated as a moving boundary problem. In this study the amplitude of the concentration profile of the external diffusant is treated as a constant. This is, in fact not a realistic picture of the problem. A study with varying amplitude for concentration is also in progress. The moving boundary model actually yields zero width for the bands. This is due to the absence of any precipitation reaction terms in the kinetics. The boundary itself has zero width as well. Surpassing the width law, one gets a better linear relationship, which predicts the geometrical positioning of the rings using this model.

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