

Rhythmic pattern formations in gels and Matalon–Packter law: A fresh perspective

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Abstract. The periodic precipitation pattern formation in gelatinous media is interpreted as a moving boundary problem. The time law, spacing law and width law are revisited on the basis of the new scenario. The explicit dependence of the geometric structure on the initial concentrations of the reactants is derived. Matalon–Packter law, which relates the spacing coefficient with the initial concentrations is reformulated removing many ambiguities and impractical parameters. Experimental results are discussed to establish the significance of moving boundary concept in the diffusion controlled pattern forming systems.

Keywords. Liesegang rings; periodic precipitation; moving boundary; Matalon–Packter law.

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1. Introduction

Pattern formations are widespread in nature and can be found in structures ranging from agate rocks and gold veins to the growth of bacterial rings in agar and gallstones. A specific example discussed below is the Liesegang ring structure, known ever since its discovery in 1896 [1].

Liesegang pattern is a stratification of parallel precipitation bands obtained when anions diffuse into a gel impregnated with cations. As a result of chemical reactions between electrolytes and physical mechanisms such as nucleation, aggregation, coagulation or flocculation, opaque or coloured zones are generated. A variety of systems yielding sparingly soluble salts exhibits this fascinating phenomenon. The dynamics of Liesegang banding is very complex, involving the coupling of diffusion and precipitation processes in non-equilibrium regime. Despite its complexity, the band formation is studied extensively because it offers a model to explain the naturally occurring patterns and also due to the importance of related practical problems such as crystallization in gels. Although the patterns have been investigated in different ways over a period of a century, there remains

many unresolved facts. The mechanism responsible for these structures is, therefore, still under discussion [2–10].

It is quite easy to produce the patterns in the laboratory. The simplest and usual way to perform a Liesegang experiment is to fill a tube with an inert semi-solid medium which contains one of the reactants B called the inner electrolyte. The other reactant A referred to as the outer electrolyte is taken over the gel column at one extremity of the tube. Usually the concentration level of the outer electrolyte is maintained high to minimize the possible loss of ions due to evaporation and other such transport mechanisms during the experimental processes. The role of gel in this experiment is essentially passive, to prevent convection of solutions and sedimentation of the precipitate.

The well-known Liesegang patterns are stationary in the sense that the bands are ‘locked’ in their positions once they are formed. A small category of Liesegang systems is, however, dynamic, displaying a propagation of the whole pattern behind the diffusing electrolyte [4].

The regular and ordered precipitation zones usually exhibit a few well-defined features and appear to follow simple relations.

1.1 Time law

The position of the ring and its time of formation are interestingly related by a simple equation often called time law [11]. According to Morse and Pierce [11] who first noticed this relationship, the position x_n (measured from the gel surface) of the n th band is related to the time t_n of its formation:

$$x_n^2 \sim t_n. \quad (1)$$

This law follows evidently from the diffusive nature of the reaction-diffusion front which is in fact a straightforward approximation of the well-known Einstein-Smoluchowski relation [12].

1.2 Spacing law

Jablczynski law or spacing law [13] is a more intricate property of the bands. The patterns follow a geometric series

$$x_n \sim (1 + p)^n \quad (2)$$

implying that the ratio between the positions of the adjacent bands x_{n+1}/x_n tends to be a constant for large n :

$$\frac{x_{n+1}}{x_n} \xrightarrow{n \text{ large}} (1 + p). \quad (3)$$

The quantity $(1 + p)$ is referred to as the spacing coefficient. It has been determined for a wide range of systems by many investigators who have concluded that the p values lie between 0.05 and 0.4 [14]. The spacing between the bands normally increases as x_n increases. Sometimes situations just opposite to this have also been observed and it is referred to as ‘revert spacing’ phenomenon [15,16].

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A rigorous understanding of the spacing law was made possible by Matalon and Packter [17]. They observed that the spacing coefficient is a non-universal quantity depending upon the experimentally controllable parameters C_{A0} and C_{B0} , the uniform initial concentrations of the reacting species A and B and a few less controllable material parameters. This dependence is expressed by

$$p = F(C_{B0}) + \frac{G(C_{B0})}{C_{A0}}, \quad (4)$$

where F and G are decreasing functions of their arguments. For different systems, Matalon and Packter [17] have noticed that $F(C_{B0}) \sim C_{B0}^{-\delta}$ with $0.2 \leq \delta \leq 2.7$. The dependence of G on C_{B0} is less known but it is generally observed that G decreases as C_{B0} increases.

1.3 Width law

The width of the bands w_n grows with the distance and obeys a simple relation [18,19].

$$w_n \sim x_n. \quad (5)$$

By careful observations with a large number of bands, obtained with Boltzmann cellular automata simulations including fluctuations, a more accurate behavior was framed by Chopard, Luthi and Droz [20] and they expressed it as a new law:

$$w_n \sim \varphi_n \quad (6)$$

where the width exponent φ depends on C_{A0} and C_{B0} . They have obtained the band patterns, which exhibited a width exponent varying between $\varphi = 0.49$ to 0.61 . Later Droz *et al* [5] combined scaling properties of the density of precipitates in the bands and found that φ ranges from 0.90 to 0.99 . In an experimentalists view, the width law is problematic since fluctuations in the width appear to be large and the boundaries of the bands are not sharply defined. As the error in the determination of width of rings are large, no serious attention was paid to this relation.

All the three laws mentioned above are quantifiable results and possess some kind of generality. The spacing law is found to be more significant than the other two laws, since error factor in experimental observations is below the permitted limits. Measurements of the time of formation and width of the rings are difficult and the error bars are large. The quantitative experimental observations concern mainly the spacing law.

1.4 Existing theories

Several competing theories have been developed for explaining the mechanism of Liesegang phenomenon [2–11,13–30]. Most of the theories perform well in deriving the time law and the spacing law but are not equivalent when applied to derive Matalon–Packter relation. All the theories share the assumption that the precipitate appears as the system passes through some nucleation or coagulation thresholds. However, they differ on pre- or post-nucleation assumptions.

The simplest and the first developed theory is based on the concept of supersaturation of ion-product [29] and has been developed by many researchers [21]. According to the promoters of this theory, the outer reactant A and the inner reactant B turn directly into a precipitate and the nucleation of the precipitate occurs when the local product of the ion concentration $C_A C_B$ reaches some threshold C^* . Another variant is the nucleation and growth theory [20]. According to this theory, A and B react to produce an intermediate compound, which may either be a molecule or a colloidal particle. These models are characterized by two thresholds, one for nucleation and other for droplet growth. In the induced sol-coagulation theory [30] it is assumed that A and B react to produce a sol which coagulates if two conditions are satisfied. First its concentration should exceed a supersaturation threshold and secondly the local concentration of the outer electrolyte must be above the critical coagulation concentration threshold.

The time and spacing laws follow from the above theories. Various attempts have been made by a large number of researchers to calculate the functional form of $p(C_{A0}, C_{B0})$ using these theories. The dependence of p on C_{A0} , obtained by Wagner [21], is of the form

$$p \sim C_{A0}^{-2/3} \quad (7)$$

in contrast to the Matalon–Packter prediction [17], $p \sim 1/C_{A0}$. However, we should notice that the range of p , where $p \sim C_{A0}^{-2/3}$ holds is certainly much smaller than the experimentally observed values $0.05 < p < 0.4$. The first successful attempt to derive the Matalon–Packter law was made by Antal *et al* [14]. With the ion product supersaturation theory Matalon–Packter relation was obtained with $F(C_{B0}) = 0.12$ and $G(C_{B0}) \sim 1/C_{B0}$. However, in experiments $F(C_{B0})$ is not a universal constant, it depends on C_{B0} [17]. Further more the experimentally observed $G(C_{B0})$ is more varied than being just $G(C_{B0}) \sim 1/C_{B0}$. Nucleation and droplet growth theory also provide Matalon–Packter law with $F(C_{B0}) \sim 1/C_{B0}$ and $G(C_{B0}) = \text{constant}$ [14]. The results are similar to the ion product results, but with the roles of F and G interchanged. With the induced sol-coagulation theory they obtained $F(C_{B0}) \sim 1/C_{B0}^2$ and $G(C_{B0}) \sim (k + k' C_{B0})/C_{B0}^2$ where k and k' are constants [14], confirming the decreasing character of these functions.

Although it is possible to derive Matalon–Packter relation from these theories, the resulting function $F(C_{B0})$ and $G(C_{B0})$ appear to be too rigid to accommodate the experimental findings. The problem with all these theories is that they employ a large number of parameters and some of these parameters are not easy to grasp theoretically and impossible to control experimentally. The mechanisms involved in the explanation are too detailed and complicated and an exhaustive numerical study is cumbersome due to a large number of parameters involved in the problem.

This article aims at describing the mechanism of band formation in simple systems without employing unrealistic terms but at the same time, keeping the true spirit of diffusion and by reducing the number of indeterminable terms. Once the basic mechanism of pattern formation is established, it is easy to show the existence of the time law, spacing law and width law (in a rather modified way). In attempting to derive Matalon–Packter law, the intention is to keep the formulas and calculations simple so that the explicit dependence of C_{A0} and C_{B0} could be displayed.

2. The moving boundary model

It is important to note that in all theoretical approaches and studies proposed [2–11,13–37], the interface of the reagents is considered to be stationary. We report a new scenario where the formation of the 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 located at $(x = 0, y, z)$ plane.

We believe that the important features of the original problem are not lost after making the following simplifying assumptions.

1. The initial concentration of the outer electrolyte C_{A0} is assumed to be much larger than that of the inner electrolyte C_{B0} and it is also assumed that $C_A(x = 0, t)$ is kept fixed at C_{A0} . In experiments, one typically has $0.005 \leq C_{B0}/C_{A0} \leq 0.1$.
2. Initially, i.e. at $t = 0$ the boundary which separates the outer and inner electrolytes (gel–solution interface) is located at the $(x = 0, y, z)$ plane. Also the B type ions are assumed to be uniformly distributed inside the gel medium and all the A type ions are on the negative side of the boundary. In terms of ion concentrations, this means that

$$\begin{aligned} C_A(x < 0, t = 0) = C_{A0} \quad \text{and} \quad C_B(x < 0, t = 0) = 0 \quad \text{while} \\ C_A(x > 0, t = 0) = 0 \quad \text{and} \quad C_B(x > 0, t = 0) = C_{B0}, \\ \left. \frac{\partial}{\partial x} C_A(x, t) \right|_{x < 0} = 0 \quad \text{and} \quad \left. \frac{\partial}{\partial x} C_B(x, t) \right|_{x > 0} = 0. \end{aligned} \quad (8)$$

With these initial conditions the system becomes effectively one-dimensional, since the concentrations depend only on x at all times. Hence the experimental set up can be described by one-dimensional reaction-diffusion equations.

3. All concentration profiles can be approximated by exponential curves in the neighborhood of the reaction zones and precipitation bands.
4. Precipitation bands are much narrower than the diffusion length.
5. A small fraction of the inner electrolyte can penetrate the existing precipitation band. If the reaction and aggregation rates are sufficiently large, the existing precipitation band acts as a sink for the inner electrolyte.
6. Since A and B particles react in pairs, the difference in their numbers is conserved.

The ion-product supersaturation theory incorporating moving boundary model of diffusion is sufficient to account for the Matalon–Packter law. In this theory the diffusive reagents A and B turn into the precipitate C without any intermediate steps and the process is denoted as $A + B \rightarrow C$. The basic assumption made here is that the precipitation occurs at time t and at a site x if the product of the ion concentration $C_A(x, t)C_B(x, t)$ exceeds a critical value

$$C_A(x, t)C_B(x, t) \geq C^*. \quad (9)$$

This occurs only at $x_n, x_{n+1} \dots$, and not at any intermediate points. The equations describing this reaction-diffusion process are given by

$$\begin{aligned} \frac{\partial C_A}{\partial t} &= D_A \frac{\partial^2 C_A}{\partial x^2} - K\Theta(C_A C_B - C^*) - RC_A C_B C_C, \\ \frac{\partial C_B}{\partial t} &= D_B \frac{\partial^2 C_B}{\partial x^2} - K\Theta(C_A C_B - C^*) - RC_A C_B C_C, \\ \frac{\partial C_C}{\partial t} &= K\Theta(C_A C_B - C^*) + RC_A C_B C_C, \end{aligned} \quad (10)$$

where D_A and D_B are the diffusion coefficients of A and B and Θ is the Heaviside step function describing a sharp threshold for precipitation with K being the rate constant. The last terms on the right hand sides represent the aggregation on to the existing precipitate of concentration $C_C(x, t)$ and R is the aggregation rate constant.

These equations were solved by the method of finite differences for the initial conditions described in eq. (8) by several workers [37,38]. Many have successfully developed one-dimensional models based on reaction-diffusion differential equations to simulate Liesegang pattern formation [9,33].

In attempting to derive Matalon–Packter law, our basic assumption is that the formation of periodic ring systems can be 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. The boundary denotes a plane ($y-z$) where concentration level of A type ions is homogeneous and maximum. Initially the boundary which separates A and B ions was the gel–solution interface in the $y-z$ plane. When the first precipitation zone (ring) was formed, the concentration level of A type ions reaches the reservoir concentration C_{A0} up to that zone. 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 to the initial concentration C_{B0} of the B type ions. This process will repeat in time and the boundary region moves from one ring to the other (figure 1). Hence the concentration level of A species after a ring is formed at x_n are

$$C_A(0 \leq x \leq x_n, t \leq t_n) = C_{A0}, \quad (11)$$

where n denotes the number of rings. The distances x_1, x_2, \dots are the positions of the first ring, second ring, and so on.

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

In a similar situation, to account for the quantity of isotopes diffusing into a medium having moving boundary, Lothar Senf [39,40] assumed a cubical concentration profile. According to the authors an exponential profile is found to be more appropriate to describe the Liesegang phenomenon. Peterlin [41], 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 an exponential profile with constant pre-exponential factor.

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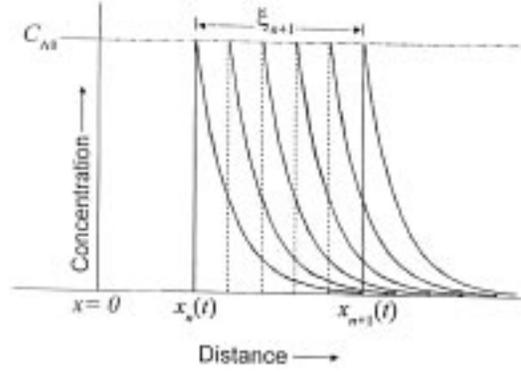


Figure 1. Concentration distribution with moving boundary. The gel solution interface is denoted by $x = 0$. The positions of the n th and $(n + 1)$ th rings are $x_n(t)$ and $x_{n+1}(t)$ respectively.

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

$$C_A(x, t) = C_{A0} \exp \left\{ -\beta \frac{[x - x_n(t)]}{\xi_{n+1}} \right\}; \quad x_n \leq x \leq x_{n+1}, \quad (12)$$

where $\beta (> 0)$ is a constant for a given system, called concentration profile index and ξ_{n+1} is the separation between the n th and $(n + 1)$ th rings.

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

$$D_A \frac{\partial}{\partial x} C_A(x^+, t) + v C_A(x^+, t) = D_A \frac{\partial}{\partial x} C_A(x^-, t), \quad (13)$$

where D_A is the coefficient of diffusion for the ionic species A . For A type ions, 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

$$D_A \frac{\partial}{\partial x} C_A(x^+, t) + v C_A(x^+, t) = 0. \quad (14)$$

Substituting (12) in (14) and applying the above boundary condition we get

$$v_n = \beta D_A / \xi_{n+1}. \quad (15)$$

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

$$v_n \xi_{n+1} = \text{constant}; \quad (16)$$

which characterizes the nature of the boundary migration. If τ_n is the time taken by the boundary to travel from the $(n - 1)$ th ring position to the n th ring position, then

$$v_n = \xi_n / \tau_n. \quad (17)$$

Substituting this in (16),

$$\xi_n \xi_{n+1} \sim \tau_n. \quad (18)$$

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 gradually builds up in the gel column and attains a 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 (x_n) 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 hence the modified time law (18) is more meaningful. Also the theoretical analysis is based on Brownian motion where we consider the ‘random walk’ at the molecular level and the transition are ‘between closely neighboring’ states. This implies that the distance measurement cannot be done 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 (16) it is also evident that

$$v_{n-1} \xi_n = v_n \xi_{n+1}, \quad (19)$$

$$\frac{\xi_{n+1}}{\xi_n} = \frac{v_{n-1}}{v_n}. \quad (20)$$

Since

$$\frac{\xi_{n+1}}{\xi_n} = \frac{x_{n+1} - x_n}{x_n - x_{n-1}} = \frac{x_{n+1}}{x_n}, \quad (21)$$

$$\frac{\xi_{n+1}}{\xi_n} = (1 + p), \quad (22)$$

the spacing constant, which is expected to be the same as eq. (3). For regular Liesegang pattern,

$$\xi_{n+1} = \xi_n + \Delta \xi_n. \quad (23)$$

Substituting this in (22)

$$\frac{\Delta \xi_n}{\xi_n} = p, \quad (24)$$

$$\Delta \xi_n \sim \xi_n. \quad (25)$$

This relation seems to be in a better position when compared to the width law $w_n \sim x_n$. It is to be noticed that the elemental increment accounted for ξ is not exactly the width of the ring w_n . All the above modified relations (18), (22) and (25) picturize the fact that the precipitation pattern front obeys the characteristic equation (16) for boundary migration.

3. Derivation of Matalon–Packter law

While A type ions move into the positive direction inside the gel medium, eq. (12) is sufficient to represent the concentration profile of A species near the ring position. For B type ions, the homogeneity of its concentration profile inside the gel column has been disturbed by the reaction process and the subsequent formation of the ring system. Hence a concentration profile of the type

$$C_B(x,t) = \eta C_{B0} \exp \left\{ -\gamma \frac{[x_n(t) - x]}{\xi_n} \right\} + C_{B0} \left[1 - \eta' \exp \left\{ -\gamma \frac{[x - x_n(t)]}{\xi_{n+1}} \right\} \right] \quad (26)$$

is appropriate to the situation. Here $\gamma (> 0)$ is a constant, called the concentration profile index for the system. The first term on the right hand side of eq. (26) represents those components of B which have successfully penetrated the ring in the negative x -direction. As this fraction is very small, the coefficient η will be a very small positive quantity. The coefficient η' appearing in the second term signifies the factor of C_{B0} which had been eliminated from its initial level due to the formation of the reaction product C . We can apply the condition of ring formation by considering the immediate neighboring zones of the n th ring (ξ_n th and ξ_{n+1} th zones). On the left side, the concentration of B reduces to zero very fast since the precipitation zone acts as a sink for B type ions whereas, on the positive side of x , the concentration level of B is maximum within a short range from the ξ_n th zone. The characteristic picture exhibiting the concentration profiles as well as the ion-product profile in the neighborhood of ξ_n is shown in figure 2. We can now apply the conditions for ring formation as stipulated in the ion product theory, viz.,

$$C_A(x,t)C_B(x,t)|_{x_n,t_n} = C^*, \quad (27)$$

$$\frac{\partial}{\partial x} \{C_A(x,t)C_B(x,t)\}|_{x_n,t_n} = 0. \quad (28)$$

Upon substitution of $C_A(x,t)$ and $C_B(x,t)$, eqs (27) and (28) reduce to

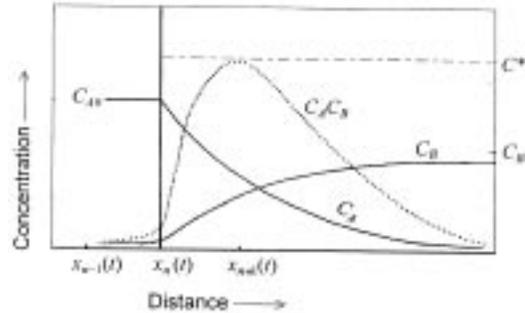


Figure 2. Concentration profiles of A type and B type species and the ion-product profile in the neighborhood of a ring position at $x_n(t)$. For better visibility the ion-product $C_A C_B$ and its critical value C^* are magnified 25 times.

$$(\eta - \eta' + 1)C_{A0}C_{B0} = C^*, \quad (29)$$

$$\eta' \left(\frac{\beta}{\gamma} + 1 \right) = \frac{\beta}{\gamma} + \eta \left(\frac{\beta}{\gamma} - \frac{\xi_{n+1}}{\xi_n} \right). \quad (30)$$

Writing $\beta/\gamma = \alpha$, and using (22) one obtains

$$\eta\{\alpha - (1 + p)\} + \alpha = \eta'(\alpha + 1) \quad (31)$$

which allows us to eliminate η' from (29) and the following equation for p is obtained

$$\begin{aligned} p &= \frac{\kappa C^*}{\eta C_{B0}^2} + \frac{\kappa \alpha C^* - (1 + 2\eta)C_{B0}^2}{C_{A0}(\kappa \eta C_{B0})} \\ &= F(C_{B0}) + \frac{G(C_{B0})}{C_{A0}}, \end{aligned} \quad (32)$$

where $\kappa = C_{B0}/C_{A0}$ is the dimensionless ratio of the initial concentrations, an easily known parameter. One can see from (32) that

$$F(C_{B0}) \sim 1/C_{B0}^2, \quad G(C_{B0}) \sim (\lambda - \lambda' C_{B0}^2)/C_{B0}, \quad (33)$$

where λ and λ' are constants. The power law form $F(C_{B0}) \sim C_{B0}^{-2}$ is very much close to what has been observed by Matalon and Packter [17] and the fact that $G(C_{B0})$ is a decreasing function of C_{B0} is also in accordance with the experimental observations. In the limit, $C^*/C_{A0} \rightarrow 1$, $F(C_{B0}) \sim C_{B0}^{-1}$. Assuming that the crossover between C_{B0}^{-2} and C_{B0}^{-1} behaviors is smooth, one should be able to find regimes where $F(C_{B0}) \sim C_{B0}^{-\delta}$ with $1 \leq \delta \leq 2$. Since this covers a major portion of the experimentally observed range $0.2 \leq \delta \leq 2.7$, we conclude that the ion product supersaturation theory incorporating the moving boundary model of diffusion provides one of the best descriptions of pattern formations in gelatinous media.

An exhaustive numerical study has been made with the analytical expression (32) derived for $p(C_{A0}, C_{B0})$. We have studied the dependence of the spacing coefficient $(1 + p)$ on $C^*/(C_{A0}C_{B0})$ for $\alpha = 1$ and for various η values. The linear dependence of $(1 + p)$ on $C^*/(C_{A0}C_{B0})$ clearly establishes the above derivation of Matalon–Packter law. Typical results are displayed in figure 3. As η increases it is seen that the value of $C^*/(C_{A0}C_{B0})$ also increases satisfying eq. (32). In all cases studied, $(1 + p)$ lies between 1 and 1.5 which agrees closely with experimental results.

4. Experimental

The penetration of $\text{Ba}(\text{NO}_3)_2$ into silica gel containing $(\text{NH}_4)_2\text{MoO}_4$ results in a sharp boundary interface of BaMoO_4 precipitate bands. A good set of about 15 rings were formed when 0.25 M of the outer electrolyte, 0.1 M of inner electrolyte and a gel of pH value 6 were used. The time of formation t_n and the distance of each ring x_n were recorded. The data were analyzed and the results are summarized in figures 4–6. A relatively large

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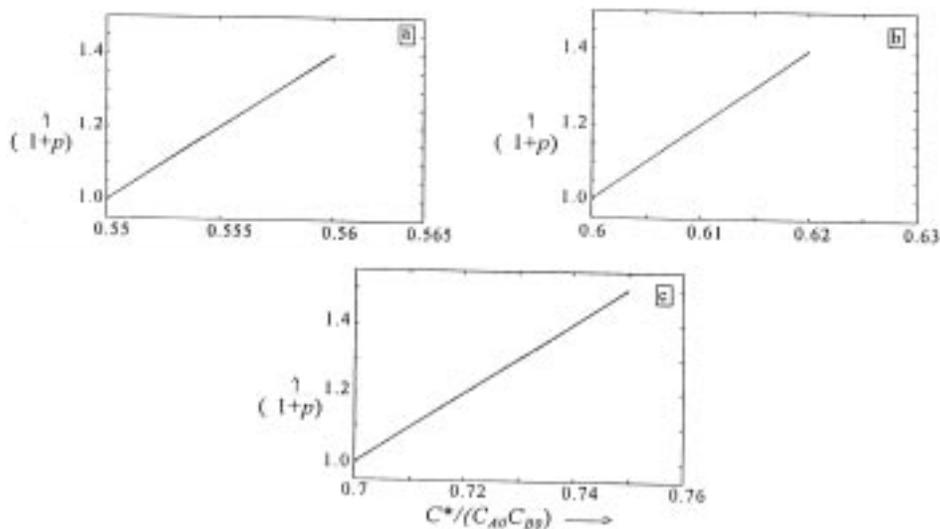


Figure 3. Dependence of the spacing coefficient $(1+p)$ on $C^*/(C_{A0}C_{B0})$ as given by ion product supersaturation moving boundary model for $\alpha = (\beta/\gamma) = 1$. (a) $\eta = 0.5$, (b) $\eta = 0.1$, (c) $\eta = 0.2$. The linear dependence of $(1+p)$ on $C^*/(C_{A0}C_{B0})$ is clearly established, which demonstrates Matalon–Packter law. In all cases $(1+p)$ lies between 1 and 1.5 which agrees closely with experimental results.

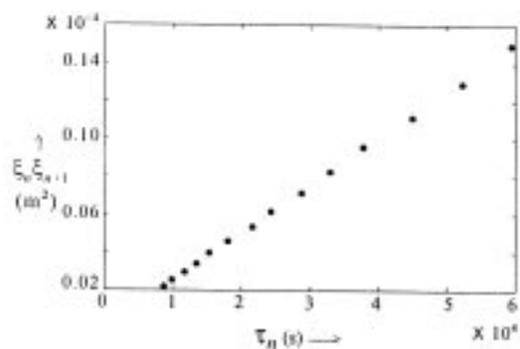


Figure 4. Verification of the modified time law with Liesegang rings of BaMoO_4 . Experimental details: silica gel of density 1.03 g cm^{-3} , $\text{pH} \sim 6$, outer electrolyte $\text{Ba}(\text{NO}_3)_2$: 0.25 M, inner electrolyte $(\text{NH}_4)_2\text{MoO}_4$: 0.1 M.

number of bands allowed a rather accurate determination of the constants involved in the modified relations (18), (22) and (25).

Figure 4 depicts the plot of $\xi_n \xi_{n+1}$ against τ_n . The straight line shows the validity of the modified time law. To determine the value of the spacing coefficient, we plotted ξ_{n+1} against ξ_n (figure 5). Note that the spacing coefficient $(1+p)$ remains constant throughout the entire range of the band system and the value is found to be 1.077. The linear relationship $\Delta \xi_n \sim \xi_n$ is also verified (figure 6) and the value of p so obtained is 0.0715. Slight deviations observed were due to experimental error in the judicious measurement of ring

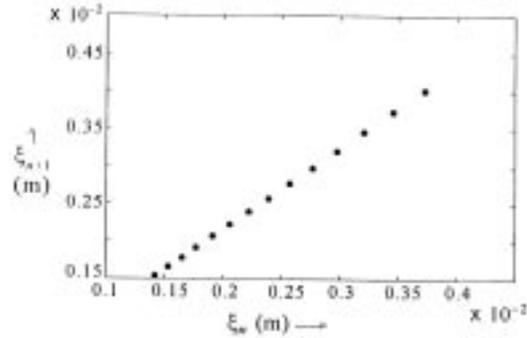


Figure 5. Determination of the new spacing coefficient $(1 + p)$ given by the slope of the curve ξ_{n+1} versus ξ_n . The value of $(1 + p)$ is found to be 1.077. Experimental details are the same as in figure 4.

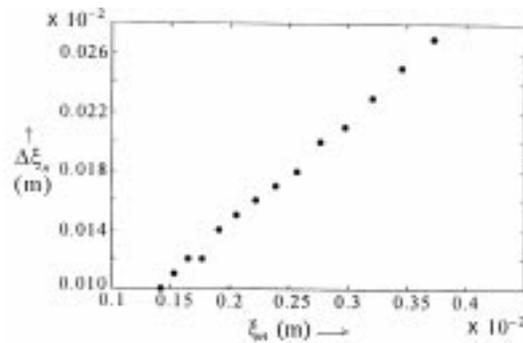


Figure 6. Plot of $\Delta\xi_n$ versus ξ_n . The experimental details are the same as those given in figure 4.

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.

5. Conclusions

To study the Liesegang pattern formation, we have developed a one-dimensional model based on the ion product supersaturation theory incorporating moving boundary concept. The main results are summarized in eqs (18), (22), (25) and (32). The modified time law, spacing law and width law illuminate the fact that the formation of Liesegang pattern can be treated as a moving boundary problem. The relationship between the most frequently studied parameters, the initial concentrations of the electrolytes and the spacing coefficient, as suggested by Matalon and Packter has been obtained by us. A number of parameters of the Matalon–Packter law derived by us is less compared with those obtained from other theories. So a better understanding of the basic facts of pattern forming processes is made possible.

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