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Role of colloid dynamics in the formation of Liesegang rings in multi-component systems

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Pattern formation in reaction diffusion systems is a widely discussed topic in these days. Though it was discovered more than a century ago [1], the mechanism of this nonlinear phenomenon of self-formation of patterns in systems is not yet fully understood. R. E. Liesegang made the remarkable discovery of this phenomenon in 1896 and since then many phenomenological investigators have suggested different theories to explain their rhythmic structure. Owing to the complexity of the structure and its dependence on a wide range of physical parameters, all the experimental results could not satisfactorily be explained by the suggested theories. Hence the mechanisms responsible for these structures are still under discussion [2–4]. Recently the role of fast colloid dynamics in the formation of Liesegang phenomenon has gathered attention. Stern's review [5] summarizes the important experimental results of banded precipitation and provides critical comments on the various theories of periodic precipitation. Survey of the literature shows some more excellent and fascinating reviews on this subject published recently [6, 7].

The formation of patterns is due to the diffusion of the electrolyte (A) into a gelatinous medium impregnated with another electrolyte (B) and the subsequent chemical reaction. A striking feature is that these patterns obey simple generic laws. After a transient time, these bands appear at some positions x_{i} and times t_{i} and have a width w_{i}. It is first observed that the position x_{n} (measured from the initial interface of the reagents) of the nth band is related to the time t_{n} of its formation through the so-called time law $x_{\mathrm{n}} \sim t_{\mathrm{n}}^{1/2}$. Second, the ratio between the positions of the adjacent bands $x_{\mathrm{n}+1}/x_{\mathrm{n}}$ approaches a constant value slightly above unity, called spacing coefficient. Reverse banding also has been observed in some systems where the ratio $0 \leq x_{\mathrm{n}+1}/x_{\mathrm{n}} \leq 1$. This experimental observation is usually referred to as the spacing law. Finally, the width of the bands w_{n} varies linearly with the distance, $w_{\mathrm{n}} \sim x_{\mathrm{n}}$.

In general, explanations of the Liesegang phenomenon can be classified as either pre-nucleation or post-nucleation processes. The former suggests that the product of the reactants directly turn into a precipitate, where the local concentration product reaches some threshold. One can symbolize this process by the reaction scheme $A + B \rightarrow D$ where D stands for the precipitate state. According to the second scenario, the two species A and B react to produce a new species C, which represents a colloidal state. When the local concentration of C reaches some threshold value, nucleation occurs: the C particles precipitate and become D particles at rest. Such processes can be tagged with the following symbolic reaction scheme: $A + B \rightarrow C \rightarrow D$.

Several authors have investigated the role of diffusion in the process of periodic precipitation, by calculating the diffusion coefficients of the A ions in the gel medium [8–10], based on the simple mathematical model suggested by Kirov [11]. The third author together with Ittyachen and Joseph has extended the said theory to multi-component systems and the values of the effective diffusion coefficients were estimated [12].

We have recently developed a simple model of band formation [13, 14], termed as moving boundary model, based on the assumption that the boundary which separates the outer ions and the inner electrolyte virtually migrate into the positive direction of the advancement of the A type ions. It has been known since the earliest experiments of Liesegang [1] that optimum results for ring or band formation are obtained when the initial concentration C_{A0} of the outer electrolyte is much higher, preferably by several orders of magnitude greater than that of the initial concentration C_{B0} of the inner electrolyte. In regular Liesegang experiments one typically has $10\ C_{\mathrm{B0}} \leq C_{\mathrm{A0}} \leq 200\ C_{\mathrm{B0}}$ [6]. Initially the boundary which separates A and B ions was the gel solution interface which is chosen at $x = 0$ in the y-z plane. When the first precipitation zone (ring) was formed, the concentration of the outer ions gradually builds up in the gel column and attains its maximum value C_{A0} up to that zone. This assumption suggests that the boundary of A type ions has been shifted up to the new ring. The reservoir concentration C_{A0} of the A type ions is sufficiently large, and presumably the boundary migrates. This process will repeat in time and the boundary region moves from one ring to the other. As a result the concentration level of A species after a ring is formed at any position x_{n} is

$$C_{\mathrm{A}}(0 \leq x \leq x_{\mathrm{n}}, t \leq t_{\mathrm{n}}) = C_{\mathrm{A0}} \tag{1}$$

where the suffix n denotes the ring number. The time law in fact turns out from the Einstein-Smoluchowski

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solution for the random walk problem [15]. Theoretical investigations based on Brownian motion consider the "random walk" at the molecular level and the transitions between closely neighboring states. The distance measurement from the gel solution interface therefore could not be sufficient to fit in the random walk conditions. Based on the above assumptions, we have modified the conventional time law, spacing law and the width law by considering the separation between the rings as prime parameter in distance measurements [13] as:

$$\xi_{\mathrm{n}} \sim \tau_{\mathrm{n}}^{1/2} \tag{2}$$

$$\xi_{\mathrm{n+1}}/\xi_{\mathrm{n}} = (1 + p') \tag{3}$$

$$w_{\mathrm{n}} \sim \xi_{\mathrm{n}} \tag{4}$$

where ξ_{n} is the inter ring spacing; here it may be read as the spacing between the $(n - 1)$th and nth rings and τ_{n} is the time taken for the appearance of the nth ring after the $(n - 1)$th ring is formed.

The moving boundary model also enables us to determine the diffusion coefficients of the advancing electrolytes in the gelatinous medium. With a reasonable approximation that the boundary virtually migrates into the medium with uniform velocity from one ring to the other, one can deduce an expression for diffusion coefficients [16] as:

$$D_{\mathrm{A}} = \xi_{\mathrm{n}}^2/2\tau_{\mathrm{n}} \tag{5}$$

This distance measurement as the authors have suggested in our recent communications [13, 14] is commensurate with the distance measured from the gel-solution interface in other theories. With the values of the diffusion coefficients estimated for various systems in different gels, we have concluded that fast colloidal dynamics play a pivotal role in the formation of these periodic structures [16]. In this letter, we focus on to the multi-component systems and draw the principles of colloidal dynamics associated with the patterning.

During the crystallization of mixed rare earth oxalates in gel medium, two kinds of ring systems were observed with lanthanum and copper as cations [17]. These experiments were performed in single glass tubes containing a vertical column of sodium meta silicate gel, uniformly charged with oxalic acid. Measured volumes of lanthanum nitrate (LN) and copper nitrate (CN) solutions were poured over the gel as the source of cations. Well-defined periodic ring systems in the form of micro crystals were visible after a few hours. When the cations from the upper solution diffuse into the gel and meet the oxalate ions, they combine to form mixed oxalate crystals at discrete places separated by a distance dictated by the growth conditions of the system. Since the two-component upper electrolyte system behaves similar to a single component system [17], diffusion coefficients of the upper ions can be estimated using Equation 4. From the observed rate of movement of the advancing boundary, the diffusion coefficients for the outer ions are estimated (Table I). The new spacing coefficient $\xi_{\mathrm{n+1}}/\xi_{\mathrm{n}} = (1 + p')$ is also calculated for each set of rings. Diffusion coefficients calculated ranges from 4.981×10^{-11} to 8.905×10^{-11} m^2 s^{-1}. Calculations based on Einstein's diffusion equation for colloidal particles of diameter 20 nm in water at 20 °C yield a value of diffusion coefficient equal to 2.15×10^{-11} m^2 s^{-1} and 6.5 h for average Brownian displacement in one direction by 1 mm [18]. The values obtained by us are in fact 2–4 times greater than those quoted for 20 nm size colloidal particles.

TABLE I Estimation of the diffusion coefficients of the outer electrolytes: Inner electrolyte: 0.5 M oxalic acid, silica gel density: 1.03 g cm^{-3}, pH $\sim$ 6.6

Outer electrolytes and concentrations (M)	Type of species	$(1 + p')$	$D_{\mathrm{A}} \times 10^{11}$ (m^2 s^{-1})
0.4 CN and 0.5 LN	I	1.143	7.828
	II	1.126	8.905
0.6 CN and 0.5 LN	I	1.130	4.981
	II	1.128	7.286
0.5 CN and 0.2 LN	I	1.120	5.850
	II	1.117	6.451

Once a precipitation zone (ring) was established, upper ions may occupy up to that region and their concentrations reach their original level. It is to be noted that a regular ring or band is formed when the concentration of the outer electrolyte is much larger than that of the inner electrolyte [6]. Hence the number of particles moving in the forward direction will be large compared to the number of particles moving in the reverse direction. This in fact supports Young's conclusion [19] that the particles diffuse without much molecular bombardment. As the particles are not much encountering with other particles inside the medium, they cross 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. Slow coarsening of colloid particles is very essential for the macroscopic pattern generation [20]. The particle size therefore grows at a slow pace only, which also results in considerably fast diffusion.

Thus the values of diffusion coefficients obtained for various multi-component Liesegang systems are suggestive of the fast colloidal dynamics during the process of periodic structure formation.

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