Introduction

In 1896 Liesegang, a chemist engaged in photographic research, observed that when a drop of a concentrated solution of silver nitrate was placed on a layer of gelatin containing a dilute solution of potassium dichromate the resulting dark-red precipitate of silver dichromate did not develop uniformly, as would be anticipated, but as clearly defined concentric rings of ever-increasing separation centred on the source of the silver ions [1–3].

Every precipitation reaction so far investigated has, in the right conditions, yielded rings (or in tubes, bands) of precipitate. In solution, most work has involved the presence of gels (e.g. gelatin and agar) in the precipitating phase; but the gel’s role is essentially passive, i.e. it prevents sedimentation and convection currents interfering with the results of diffusion. There are two quantitative relations found for Liesegang rings, namely the spacing law [4, 5] and the time law [6]. The former is the logarithmic relation governing the spacing of the rings, which develop at progressively greater distances (x) from the initial interface of the two reactants and from one another. Thus, for two adjacent precipitates, the nth and (n + 1)th rings,

\[ x_{n+1} = K_1(x_n) \].  

The time law relates the time \( t_n \) for the formation of the nth ring with its distance (x) from the initial interface, such that

\[ x_n^2 = K_2 \ t_n \],  

where \( t_n \) is the time measured from the start of the experiment.

In general, explanations of the Liesegang phenomenon can be classed as either prenucleation or postnucleation processes. The former is represented by the proposal of Ostwald [7, 8], published within a year of Liesegang’s observations, that the product of the reaction is not immediately precipitated, but remains in a supersaturated solution. When nucleation finally occurs, the nuclei grow, not only at the expense of supersaturation in their immediate neighbourhood, but also by material diffusing from the adjacent zone in

Abstract The persuasive evidence for the role of colloid in the formation of Liesegang rings is nullified by the low diffusion constants (less than \( 2 \times 10^{-11} \) m\(^2\) s\(^{-1}\)) of sol particles; however, those values were obtained for sols suspended in otherwise homogeneous solutions. The essential randomness of Brownian motion in such situations is absent in Liesegang experiments, where the large excess of outer electrolyte diffusing into the gel creates a bias in molecular bombardment resulting in sol particles moving a given distance in fewer steps, hence in a shorter time. From Einstein’s equation \( D = x^2 / 2t \) values for D of \( 2-4 \times 10^{-10} \) m\(^2\) s\(^{-1}\) have been calculated for Liesegang experiments in the literature. It is suggested that such values could well pertain to sol particles diffusing in the heterogeneous conditions existing in those experiments.

Key words Liesegang rings · Diffusion of colloid · Colloid diffusion · Brownian motion · Periodic precipitation
Evidence for the colloid explanation

There are at least seven experimental findings which are consistent with the colloid explanation but appear to be incompatible with the supersaturation one.

1. Initial dispersal of crystalline product throughout the inner electrolyte in either the presence of gel [14] or, more significantly, in its absence [15] does not prevent formation of periodic structures.

2. When equivalent quantities of the reactants are mixed in the gel solution to give a colloidal product, subsequent passage of a strong solution of the diffusing reagent through the gel produces flocculation and band formation. If the colloidal product (e.g. PbI$_2$) is dispersed as a sol in the gel solution in the absence of other electrolytes, the use of solutions of Pb(NO$_3$)$_2$, of KI or even of unrelated salts (e.g. AgNO$_3$ or Na$_2$CO$_3$) as the diffusing reagent will yield band systems [16].

3. Bands are obtained in nongelatinous media when nonreacting electrolytes diffuse into colloidal solutions of insoluble metal hydroxides and salts peptized with electrolytes [17, 18]; they are also obtained in gelatinous media when nonreacting electrolytes diffuse into sols of Fe(OH)$_3$ or As$_2$S$_3$ [16].

4. The dependence of ring formation on the type and purity of the gel used is not explicable on the basis of supersaturation theory, but is readily accounted for by the influence of such conditions on sol formation and flocculation [19].

5. Substances which can be peptized in the presence of gelatin also form rings; those which cannot be peptized form no rings [9].

6. Evidence has accumulated over many years that the initial form of the precipitate is colloidal [10]; this culminated in experiments [20] 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 diffusion law $x^2 = kt$.

7. The ring locations were influenced by gravity, indicating the presence of colloidal particles of at least 250 Å radius for a substantial fraction of the time required for the formation of a visible structure.

The difficulty for the colloid explanation

Despite the persuasiveness of this evidence, there is an apparently insuperable difficulty for an explanation involving colloid; namely, that diffusion coefficients ($D$) of colloidal particles are too low to account for development of Liesegang structures within the time limit of the experiment [21]. This can be shown by comparison of the experimental rates of development of Liesegang structures with the rates of diffusion for colloidal particles (e.g. radius 0.01–0.1 μm) derived from theoretical calculations based on Einstein’s diffusion equation [22]. Such calculations for spherical particles of radius 0.1 μm in water at 20 °C yield a value of $D = 2.15 \times 10^{-12}$ m$^2$ s$^{-1}$ and a calculated time of 2.7 days for average Brownian displacement in one direction by 1 mm [22]. The corresponding values for particles of radius 0.01 μm are $2.15 \times 10^{-11}$ m$^2$ s$^{-1}$ and 6.5 h. In contrast, the values for spheres of radii of small ions are $2.15 \times 10^{-9}$ m$^2$ s$^{-1}$ and 1 mm in 4 min.

This difficulty is particularly perplexing with regard to the experiments of Gore [17, 18] mentioned earlier, where Liesegang bands were formed in the absence of gel by developing sols of peptized, insoluble metal hydroxides and salts by nonreacting, outer electrolytes. Since formation of the bands did not involve the stages of nucleation and initial precipitation, genesis of the phenomenon is limited to the question of how colloid particles can migrate to form the bands. Either the colloidal compound is sufficiently soluble to permit its transference between particles, which should be detectable by isotopic labelling and dialysis, or diffusion of sol particles must be adequate. Is it possible that diffusion velocities of sol particles in these experiments could be much greater than the values derived from theoretical calculations?

Reassessment of colloid diffusion

Diffusion of colloid particles is manifested as Brownian movement, a continuous and haphazard motion (Fig. 1), which results from the difference in the sum of simultaneous impacts received from molecules hitting the particle from different sides. The smaller the particle the less probable it is that molecular bombardment will be exactly balanced and hence the more intense will be the Brownian movement. The number of such “unbalanced” collisions is probably greater than $10^{10}$ s$^{-1}$, with each producing a change in both direction of motion and velocity. The randomness of the motion reflects the