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SHORT COMMUNICATION

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Justification for the colloid explanation of Liesegang ring formation

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Abstract The persuasive evidence for the role of colloid in the formation of Liesegang rings is nullified by the low diffusion constants (less than 2×10^{-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

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,

$$x_{n+1} = K_1(x_n) \ . \tag{1}$$

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

$$x_n^2 = K_2 \ t_n \ , \tag{2}$$

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 front. This depletion of product produces a zone free of precipitate. Representative of the second process is the proposal that interaction of the reactants initially produces a sol, which might yield periodic precipitation by either diffusion or by one of various suggested mechanisms [9–13].

Over the course of the twentieth century, although each explanation had its periods of ascendancy, the supersaturation one was usually the more favoured, as is presently the case. This is despite most experimental evidence supporting the colloid explanation.

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_2CO_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_2S_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 colloid 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 colloid 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 2.15×10^{-11} m^2 s^{-1} and 6.5 h. In contrast, the values for spheres of radii of small ions are 2.15×10^{-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 homogeneity of the solution in which the colloid is suspended. However, in Gore's Liesegang experiments the medium in which the sol particles are suspended was far from homogeneous because of the large excess of ions of the outer electrolyte diffusing into it. 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. Thus, in the experiments of Morse and Pierce [6] detailed later there would be for group A (Table 1), initially, 100 times as many ions colliding with a sol particle on one side as on the other. In these conditions, the bias in molecular bombardment will result in colloidal particles having a less random motion, thus moving a given distance in fewer steps and hence in a shorter time, i.e. a higher diffusion constant. This is evident from Einstein's law of one-dimensional Brownian motion, expressed by the equation

$$D = \langle x^2 \rangle / 2t \tag{3}$$

where D is the diffusion constant and x is the average displacement of the particle in time t. The diffusion constant is thus directly related to the average time required to cover any given distance by Brownian motion. It is because Brownian motion is random that it results in transport of matter from regions of higher to those of lower concentration [22]. However, in the circumstances where I suggest it is not random, the reverse holds; the precipitate is not distributed uniformly, but is concentrated into rings or bands, separated by regions void of the material.

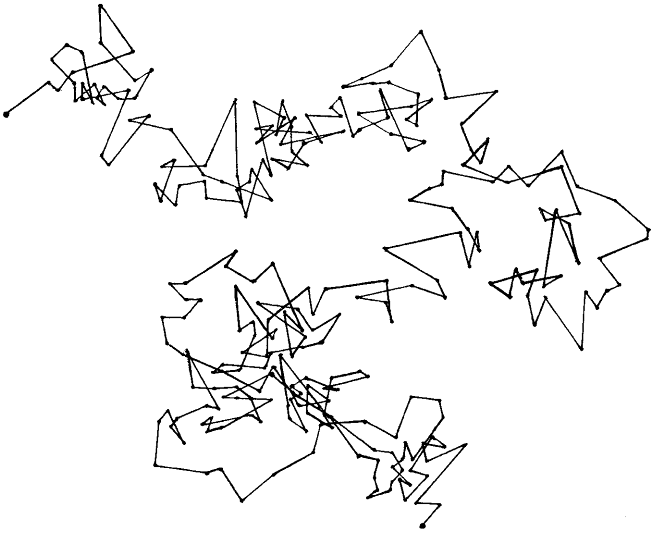

Fig. 1 Observed path of a gamboge particle exhibiting Brownian motion. Each straight line segment would, if the time intervals were 100 times shorter, be replaced by a pattern as complicated as the whole figure, and so on indefinitely. (From Ref. [23].)

There are two significant objections to this explanation.

1. The bombardment of the colloid particle by the excess ions of the outer electrolyte on one side would be exactly balanced by that of a corresponding excess of water molecules on the more dilute side.
2. The concentration gradient of the ions of the outer electrolyte causing the increased diffusion of the sol particles would, because of the much higher diffusion coefficient of those ions compared with that of the colloid, rapidly pass beyond those particles, thereby relieving the biased bombardment.

However, the first objection can be countered by the fact that water is highly associated, so that the effective number of its molecules is always much less than would otherwise be expected; as a consequence, the excess of water present on the more dilute side would not necessarily balance the increase in collision frequency due to the outer electrolyte. Regarding objection 2, the influence of the concentration gradient would not be annulled on its passing the sol particle; for as ions of the outer electrolyte diffuse further into the inner medium (e.g. in a tube) they are replaced by a net diffusion of ions along the tube from the reservoir. Thus, at every point there must always be more ions moving forward than in the reverse direction.

This interpretation is supported by the findings of Ghosh [15], who, studying the Liesegang phenomenon under the microscope, observed in every case a very marked Brownian movement in the initial stage of precipitation and by the fact that reducing the concentration of the outer electrolyte increases the time of ring

Table 1 Data for the formation of Liesegang bands in five groups of experiments of Morse and Pierce [6] (see text for details) have been used to calculate the value of the diffusion constant, D, for successive bands after the first, using Einstein's equation ($D = x^2/2t$)

Group	Number of experiments per group	Outer concentration	Inner concentration	Relative ion concentration	$10^{10} \times D$ ($\mathrm{m^2\ s^{-1}}$) (mean ± standard error)
A	7	1N	1/150N	100:1	3.908 ± 0.60 (7)
B	4	1N	1/75N	50:1	3.471 ± 0.068 (4)
C	4	2N	1/75N	100:1	3.670 ± 0.048 (4)
D	2	0.5N	1/75N	25:1	2.839 (2)
E	5	0.5N	1/150N	50:1	3.951 ± 0.044 (5)

formation at a particular distance, as does increasing the concentration of the inner electrolyte [21]. In this regard, a linear relation has been shown between the logarithm of the outer electrolyte concentration and x^2/t, where x is the distance of a ring from the gel boundary and t is the time of its formation [24].

If Liesegang rings are the result of diffusion of colloid particles, greatly enhanced by the concentration gradient of the outer electrolyte and impeded by the concentration of the inner electrolyte, the resulting diffusion constant of the particles could be determined from Einstein's law of Brownian motion (Eq. 3). Using this equation, I have calculated D for the formation of Liesegang bands from the data, for example, of Morse and Pierce [6]. Those authors investigated periodic precipitation as bands formed when a concentrated solution of silver nitrate rose up a capillary tube filled with a gel of dilute potassium chromate in gelatin. The first band of silver chromate precipitate started at the gel boundary and constituted atypically 39–66% of the final banded structure (22 experiments). The distance of each band after the first was measured from the gel boundary; the time interval for the formation of each of those bands was from the start of the experiment. They found the ratio $x/\sqrt{t}$ to be a constant, both within experiments and within each group of experiments (A to E, as in Table 1), but not between groups. The mean value of the constant $x/\sqrt{t}$ for group A was 0.01465, yielding a value for D (Eq. 3) of 1.073×10^{-9} m^2 s^{-1}; this would seem to bear out the verdict that the formation of Liesegang structures is far too rapid to be explained by colloid diffusion.

However, a very different solution is obtained if D is calculated for each successive band after the first. In each case the distance between successive bands is x and the time of formation of the band is t. The results are given in the table for the five groups and show that the diffusion constant so calculated is about 3.8×10^{-10} m^2 s^{-1} when the relative ion concentration of the outer and inner electrolytes is 100:1 (group A). This value is 1–2 orders of magnitude greater than the values quoted earlier for spheres of colloidal dimensions (0.01–0.1 μm) [21] and an order of magnitude smaller than the average value for small ions. The latter may be reduced, however, in gel media ([25], for 14 different ions in agar a median reduction of 30%).

Comparison of the values of D for the various groups (A–E) in the table shows that D is related to the relative ion concentration of the outer and inner electrolytes (A > B > D); however, apparently, it is affected more strongly by the absolute concentration of the inner electrolyte (A = E > B = C > D, with differences statistically significant, $P < 0.01$ and $P < 0.05$, respectively, in the Mann–Witney U test [26] based on mean values for each experiment). All these results are compatible with the above colloid interpretation of periodic precipitation, i.e. that the diffusion constant reflects the diffusion of sol particles to the point where flocculation takes place.

A similar value for the diffusion constant was obtained from data of Pillari et al. [24] concerning Liesegang bands formed by K_2CrO_4 (3N) diffusing into gelatin containing dilute $AgNO_3$ (0.01N); the mean value for 11 successive bands was $(2.6 \pm 0.3) \times 10^{-10}$ m^2 s^{-1}.

In 1970 Shinohara [27] published a mathematical analysis of Liesegang band formation by sol diffusion which predicted both the spacing and time laws; however, it failed to find favour, not unexpectedly, since it assumed sol particles diffuse as fast as small ions. But if the case made here for colloid particles having very much higher diffusion constants in Liesegang experiments is acceptable, then Shinohara's analysis would be appropriate.

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