Revert Banding in One-Dimensional Periodic Precipitation of the (AgNO₃ + KBr) System in Agar Gel

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ABSTRACT: A periodically precipitating system wherein interband distance successively decreases is known as revert Liesegang banding. The phenomenon is rare, and the underlying mechanism is implicit. In the present paper, the Liesegang system comprising of AgNO₃ and KBr as the outer and inner electrolyte pair showing revert banding in agar gel by employing a 1D experimental setup is studied under varying concentrations of participating species. Revert banding was observed under all the experimental conditions. The concentrations of inner and outer electrolytes were found to play a major role in reverting since they build the ionic strength inside Liesegang tubes. We hypothesize that the band reverting is the interplay of van der Waals and electrical double-layer interactions, and hence classical DLVO (Derjaguin–Landau–Verwey–Overbeek) theory can be applied to interpret reverting. We propose that revert deposition of precipitates is the outcome of flocculation and peptization of sols, which is the manifestation of balancing attractive and repulsive interactions acting on colloidal particles responsible for band formation.

INTRODUCTION

Self-assembled (SA) patterns are widely distributed in the living and nonliving world. Many of these phenomena are periodic in nature. Some of the examples of periodic formation are concentric orbits of the planets in the solar system (physical), protein crystallization (biological), stratification of minerals in rocks (geological), and periodic self-assembly of nanomaterials (chemical). The underlying mechanism of many of these formations is explicit, although many of them still remain a mystery. One of the most fascinating SA patterns that can be easily exhibited in a laboratory is the periodic precipitation in gels called Liesegang banding. The Liesegang pattern is a spontaneous self-assembly of precipitates in the form of discs or bands at regular spaces in gel due to Brownian motion of the diffusing species. The bands are formed as a result of reaction—diffusion interactions at the interface. The patterns appear as concentric rings in a circular (2D) geometry and bands in a linear geometry (1D). One-dimensional (1D) Liesegang patterns can be obtained by immobilizing one of the reactants (inner electrolyte) in the gel supported in a glass tube of appropriate dimensions held in a vertical position. The other reactant, namely, the outer electrolyte, is poured from the top of the glass tube and is allowed to diffuse through the gel. As the diffusion front proceeds, the precipitate is deposited in the form of bands at specific distances. A large number of Liesegang systems consisting of hydroxides, sulfides, chromates and dichromates, and phosphates are reported.

It has been explicitly shown that Liesegang patterns obey few generic spatio-temporal laws related to interband spacing, widths of the bands, and time of their formation. The most common being the spacing law is given by \( \frac{x_{n+1}}{x_n} = (1 + p) \) where \( x \) is the distance of the band from the gel—outer electrolyte interface, \( n \) is the band number, and \( p \) is the spacing coefficient. It has been observed that, under a given set of experimental conditions, the spacing coefficient is the function of the initial concentrations of the inner and outer electrolytes \( (a_0 \) and \( b_0 \) respectively) as shown by the Matalon–Packter law given by \( p = F(b_0) + G(b_0) \) where \( F \) and \( G \) are the decreasing functions of the initial concentrations. It is observed that two types of Liesegang patterns are experimentally observed: (1) direct ring formation in which the gap between

Supporting Information

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two successive bands go on increasing and (2) revert or inverse banding wherein the gap between two successive bands would decrease in the downward direction of diffusion. While the experimental and theoretical studies on the former are overwhelming, comparatively much less attention has been given to the latter as reverse patterns are rarely observed.

Liesegang systems consisting of precipitates of Ag₃CrO₄, AgI, CuS, HgS, and PbCrO₄ have been reported to exhibit revert banding.

There are three prominent theories to explain the Liesegang phenomenon, namely, the supersaturation theory, the adsorption theory, and the coagulation theory. 

A few theories based on adsorption of precipitating ions on the precipitate itself were proposed to explain revert banding. In order to explain revert patterns, it was thought that the diffusion electrolyte renders a high peptizing influence or dissolves the precipitate formed as a result of a reaction between the two participating ions. The decrease in the concentration of the peptizing ion along with the diffusion path results in “reverting” the system of rings. 

Kanniah et al. obtained the revert patterns followed by a direct one in a single experiment using various concentrations of KI and AgNO₃ as inner and outer electrolytes, respectively. They proposed that Ag⁺ ions are adsorbed on AgI creating a positively charged sol, Ag⁺@AgI. This leads to the formation of an electrical double layer implicating that the Ag⁺ ions peptize the sol. The peptizing capacity is directly proportional to the concentration of Ag⁺ ions. As the diffusion progresses in the downward direction, the peptizing ability decreases the sol leading to reverting of the system of bands. Molnar et al. provided the theoretical model and corresponding simulation for the adsorption theory of reverting.

The Liesegang system consisting of chromates of lead and copper showed the revert banding due to a photochemical process. Authors of this study proposed that exposure to electromagnetic radiation led to photoactivation of Ag₃CrO₄ resulting in a high degree of ionization. The charged atmosphere inside the Liesegang tube was responsible for high nucleation rates and hence revert banding.

It was thought that an autocatalytic process due to adsorption of diffusing ions of the outer electrolyte can lead to a revert periodic precipitation of lyophilic CdS.

The most intriguing consequence of revert banding is the challenge for universal applicability of the Matalon–Pacter law to Liesegang banding. It is understood that the spacing coefficients obtained in revert banding systems do not follow the Matalon–Pacter law, which has emphasis on the dependence of on decreasing functions of the initial concentrations of outer and inner electrolytes. Hence, there is a need for a new type of spacing law that can be applied to both types of patterning. It was observed that the critical coagulation concentration (CCC) or the flocculation value of each band in the KI–AgNO₃ system decreases with the band number leading to reverting. However, it was noted that, from a particular band, the CCC value started to increase. The region of reversal of the potential is an isoelectric region. It was pointed out that, from this region onward, a direct pattern formation is observed.

A few experimental studies were also performed to propose the mechanism of revert spacing in a PbCrO₄ system. It was concluded that adsorption of diffusing CrO₄⁻ ions on the precipitate of PbCrO₄ is responsible for reverting. It was observed that the extent of adsorption increases with the band number while it decreases in the direct type of the Liesegang system.

Therefore, essentially, almost all the available reports on the revert periodically precipitating systems support the mechanism of specific ionic adsorption of diffusing ions on the sol/precipitate leading to a decrease in the band gap. However, the following facts remain to be explained: (1) the layered/continuous adsorption of the ions on the precipitate should lead to thickening of the band as there is extra precipitate deposition thereby changing the morphology (bandwidths) of the system irrespective of the concentration of ions in the band. No reports are available on the width law of the revert banding system. (2) The most common systems, namely, those of AgI and PbCrO₄, form negative and positive sol, respectively; therefore, the adsorption of diffusing Ag⁺ and CrO₄⁻ on AgI and PbCrO₄, respectively, is predicted. Such deposition leads to the formation of an electrical double layer around the precipitate, and as all the species taking part in the adsorption are charged, the electric double layer interaction should influence banding. (3) As early coagulation of the sol particles is responsible for revert banding, the attractive van der Waals (vdW) interactions may also be playing a role in the sol stability. VdW interactions are not considered in the adsorption mechanism, and (4) the role of the gel in the reverting is not considered; however, it is realized that its concentration changes the band gaps.

In view of this, it is important to understand the role of operating interactions among the sol particles in band reverting. If attractive vdW interactions are dominant over repulsive double-layer interactions, then there will be coagulation, and the result is a continuous band formation inside the tube rather than stratification. Also, if repulsive forces are dominant over attractive forces, then the molecules of the precipitating substance do not form sol particles. In the case of dominant repulsive interactions, the molecular species formed as an outcome of a chemical reaction between inner and outer electrolytes also diffuses in the downward direction along with the ions of the outer electrolyte. If their concentration reaches the threshold, then there is a formation of direct bands as predicted by ion-product supersaturation theories, which propose that the supersaturation of diffusing ions triggers nucleation. Therefore, it is reasonable to assume that revert banding is the outcome of the balancing of these two types of interactions. The individual interactions can be determined on the basis of DLVO theory. In the present paper, we report detailed experimental investigations on the Liesegang system consisting of AgNO₃ and KBr as the outer–inner electrolyte pair. To our knowledge, no studies have been performed on this system exhibiting revert banding. An attempt is made to unravel the mechanism of reverting on the basis of attractive and repulsive interactions among the sol particles.

## RESULTS AND DISCUSSION

**Evidence for Revert Spacing in the AgNO₃ + KBr System. Effect of Outer Electrolyte Concentration.** Concentrations of outer and inner electrolytes were carefully chosen for the experiments as it is known that excessive ionic strength will lead to continuous precipitation and, with lower concentrations, band formation is difficult. Therefore, we have chosen the inner and outer electrolyte concentrations in such a way that the ionic strength inside the diffusion tube remains in the range of 0.20 to 0.60 M. The concentrations
were below the critical coagulation concentration, CCC (0.900 to 1.000 mol L\(^{-1}\)) as determined by using DLVO theory neglecting the contribution due to gel counterions if any, and with the above CCC, the continuous precipitation is expected. The CCC will be determined later.

Figure 1a shows the photographs of revert bands of AgBr when the concentration of the outer electrolyte is varied in the range of 0.30 to 0.50 M. It can be seen from Figure 1a that the bands are curved up in the top and curved down in the bottom portion of the tube as the CCD camera was placed near the tube while the photograph was being taken. However, this does not affect the “distance analysis” as the traveling microscope was focused on the band center while locating the band.

The concentrations of the inner electrolyte (KBr) and the gel were 0.01 M and 1.00% w/v, respectively. The AgBr bands are gray in color due to photochemical decomposition of AgBr to Ag\(^0\) as shown in the following reaction: \(2\text{AgBr}\rightarrow\text{h}\nu\ 2\text{Ag}^0 + \text{Br}_2\). Figure 1b–d shows the interband distance and a new parameter defined as \(U = (\Delta x + W)/2\) where \(\Delta x\) is the interband distance and \(W\) is the band width, plotted against the number of rings showing a decreasing trend confirming revert periodic precipitation. However, it should be noted that the confirmation of revert banding based on \(U\) and \(\Delta x\) values may be erroneous as determination of the exact band width is often difficult due to diffused band boundaries.

Effect of Inner Electrolyte Concentration. Figure 2a shows the photographs of Liesegang bands obtained by varying the concentration of KBr in the range of 0.005 to 0.015 M. The concentrations of AgNO\(_3\) and the gel were 0.500 M and 1.000%, respectively. Figure 2b–d shows the interband distance and \(U\) as defined earlier and interband distance (\(\Delta x\)) versus band number plots indicating the revert banding under this condition also.

Effect of Gel Concentration. Figure S1 (Supporting Information) shows the photographs of the bands by varying the concentration of the agar gel in the range of 0.50 to 1.50% (w/v). The concentrations of outer and inner electrolytes were 0.50 and 0.05 mol L\(^{-1}\), respectively. Previously, it was observed experimentally that the gel concentration has a considerable effect on revert spacing as it offers obstruction for the diffusion of the outer electrolyte. This process causes the bands to precipitate further away from the preceding one. In present studies, the gel plays no role in the reverting of the bands unlike as observed by Sultan et al. in their system of revert banding. It is known that ionic strength directly affects the pore size distribution of the agar gel. We have calculated that the mean ionic strength in our experiments lies in the range of 0.30 to 0.60 M, indicating the average gel pore size of 500 to 700 nm. The diameters of Ag\(^+\) and NO\(_3\)\(^-\) ions are 230 and 330 pm, respectively. With the gel concentration in the range of 0.5 to 2.0%, the gel pore size remains in the same range; hence, as far as our system is concerned, it has a very small effect on band location. However, it should be noted that, with larger ionic sizes, the gel obstruction effect may play a significant role in band location. It is also possible that gel counterions also play a role. The small variation observed in the spacing pattern with the gel concentration needs further mechanistic investigations, which is being studied in our laboratory.

Effect of Light on the Banding Pattern. As silver halides are photosensitive, a control experiment, which was performed in the absence of light, also showed revert banding, but the color of the bands was different from that observed in the experiments performed in the presence of light due to a photochemical process (see the Supporting Information, Figure S2). Das et al. found that photoactivation of chromate ions is essential for the reaction to take place and further band formation; however, in the present study, the reactor ions are not photosensitive, but the product is. Hence, revert bands are formed first followed by photodecomposition to Ag\(^0\). Hence, it
can be inferred that revert banding is observed in the presence as well as in the absence of light.

It can be observed from Figures 1 and 2 and Figure S1 that revert banding is obtained under all experimental conditions; however, a number of bands formed depended on the concentration of participating species. The bands formed in all the systems were well resolved. The reaction mechanism for band formation involves the following steps according to Ostwald’s sol-coagulation theory.\(^{16,26,31}\) The floc formed in the final step deposits in the tube as bands.

\[
\text{Primary reaction: } \text{AgNO}_3 + \text{KBr} \rightarrow \text{AgBr}_{aq} + \text{KNO}_2
\]

\[
\text{Nucleation: } \text{AgBr}_{aq} \rightarrow \text{AgBr}_{sol}
\]

\[
\text{Flocculation: } \text{AgBr}_{sol} \rightarrow \text{AgBr}_{floc}
\]

Step 1, shown in the above reaction sequence, is instantaneous as AgBr\(_{aq}\) is formed when the concentration product of \(\text{Ag}^+\) and \(\text{Br}^-\) exceeds their solubility product. However, steps 2 and 3 are comparatively slow; hence, deposition of the precipitate as bands depends on the ionic strength inside the column.\(^7\)\(^{42}\) All the steps leading to Liesegang bands, such as sol formation, their flocculation to deposit as bands, and the distance between bands, should be discussed in the view of interactions among the precipitated colloidal particles. In the present work, we have determined values of the attractive van der Waals (\(E_{vdW}\)) and repulsive electrical double layer (\(E_{DL}\)) energies under the premises of classical DLVO theory to explain stability (or instability) of the sols responsible for resultant reverting of the Liesegang bands.

**van der Waals Interaction Energy (\(E_{vdW}\)).** Unceasing movement of charges associated with atoms, molecules, and bulk materials give rise to van der Waals forces. Being attractive in nature, they are considered to be responsible for flocculation of colloidal particles. In the present system, the AgBr colloid is assumed to be spherical in nature. Therefore, it can be imagined that two colloidal spheres interact with each other with nonretarding van der Waals forces. The interaction energy, \(E_{vdW}\), is given by

\[
E_{vdW} = \frac{-AH}{6} \left[ \frac{2R1R2}{h(h + 2R1 + 2R2)} + \frac{2R1R2}{(h + 2R1) + (h + 2R2)} + \ln \frac{h(h + 2R1 + 2R2)}{(h + 2R1) + (h + 2R2)} \right]
\]

where \(AH\) \((\approx 30 \times 10^{-20} \text{ J for silver})\) is called the Hamaker constant, \(R1\) and \(R2\) \((= 5 \times 10^{-9} \text{ m})\) are the radii of colloidal particles, and \(h\) is the distance between the two interacting particles.\(^{43,44}\) The \(h\) values were taken in the range of 0.10 to 2.00 nm. The effect of \(h\) on \(E_{vdW}\) is shown in Figure 3.

**Electrical Double Layer Interaction Energy (\(E_{DL}\)).** It is known that the AgBr sol particles are negatively charged; hence, positive ions available in the vicinity, that is, \(\text{Ag}^+\) and \(\text{K}^+\), would adsorb on the sol surface. This gives rise to electrical double layer interactions (\(E_{DL}\)). These interactions are repulsive or attractive depending on the nature of the surface potential. The value of \(E_{DL}\) depends on the properties of the surrounding medium such as ionic strength, pH, type of metal ions, etc. It should be noted that the movement and concentration of charged particles can be very influential during colloidal flocculation and peptization. The \(E_{DL}\) in the present work is calculated using the equation\(^49\)

\[
E_{DL} = 4\pi D_{el} R^{2} \psi_{f}^{2} \left[ \frac{R}{2R + h} \ln \left( 1 + \frac{Re^{-eh}}{R + h} \right) \right]
\]
where \( \varepsilon_0 \) is the relative permittivity of the medium, \( R \) is the radius of the colloidal particle (= 5 nm), \( \psi_s \) is the surface charge, and \( \kappa \) is the Debye screening length. In the present work, the value of the surface potential, \( \psi_s \), was taken to be 50 mV,\(^{35,46}\) and \( \kappa \) for the 1:1 symmetric electrolyte (AgNO\(_3\), in the present case) is calculated using the equation

\[
k^{-1} = \sqrt{\frac{\varepsilon_0 e k_B T}{2 [I] e^2}} = \left[ \frac{0.304}{[I]} \right] \text{nm}
\]  

(6)

where \([I]\) is the ionic strength in the medium.\(^{39,40}\)

According to classical DLVO theory, the net interaction energy \( (E_D) \) among the colloidal particles is given by

\[
E_D = E_{vdW} + E_{DL}
\]  

(7)

Figure 3 shows the \( E_D \), \( E_{vdW} \), and \( E_{DL} \) as functions of interparticle distance. It can be seen that the primary minima is observed at smaller \( h \) values (0.10 to 0.12 nm). At \( h \) values beyond 0.70 nm, \( E_{vdW} \) saturates around \(-1 \times 10^{-20}\) J. Values of \( E_{DL} \) are calculated using the ionic strengths for the electrolyte concentration values in the range of 0.3 to 2.0 M. Using the surface potential of 50 mV, it can be seen that the double layer energy values decrease monotonically with interparticle distance and also decrease with the increase in the electrolyte concentration. The net interaction energy, \( E_D \), peaks at 0.30 to 0.40 nm. It can be observed that the critical coagulation concentration (the electrolyte concentration at which the peak barrier has \( E_D = 0 \) and also \( dE_D/dh = 0 \)) is in the range of 0.90 to 1.00 mol L\(^{-1}\) electrolyte. In our studies, the chosen electrolyte concentrations were in the range of 0.30 to 0.60 mol L\(^{-1}\), which is less than that of theoretically determined CCC (which is 0.90 to 1.00 mol L\(^{-1}\)); hence, spontaneous coagulation of the precipitate to form a continuous band is not possible. The energy barrier value for the lowest electrolyte concentration is \( 1.05 \times 10^{-20} \) J at 0.30 nm corresponding to 2.56 kT.

It is established that coagulation and peptization behavior of an aggregate can be explained within the DLVO framework. According to this theory, coagulation of the sol and its peptization can be understood from the viewpoint of competition between \( E_{vdW} \) forces that are attractive in nature and \( E_{DL} \) forces among the sols that are repulsive in nature. If the \( E_{vdW} \) exceeds the \( E_{DL} \), the sol coagulation takes place, and if the \( E_{DL} \) exceeds \( E_{vdW} \), peptization is triggered. For smaller inter-sol particle distances, the aggregates experience more \( E_{vdW} \) forces; however, when the aggregate becomes larger and deposits in the medium as a band, the \( E_{DL} \) forces due to the presence of ionic strength inside the medium lead to a large surface charge density triggering peptization. This process makes the diffusing ions thermalize and cross the Stern barrier.

**Mechanism of Band Reverting in the AgBr System.** The underlying mechanism of revert Liesegang banding has been under intense research for many years.\(^{18–22}\) The earliest explanation is on the basis of the zeta potential (\( \zeta \)). It is known that if the \( \zeta \)-potential is lowered below a certain critical value, agglomeration of colloidal particles is triggered. Distortion of the electrical double layer formed around sol by altering the medium condition such as adsorption of diffusing ions can lead to lowering of the \( \zeta \)-potential. Although \( \zeta \)-potential is inversely correlated with coagulation, it does not represent the surface potential (\( \psi_s \)) as shown in eq 5. According to Mathur and Ghosh,\(^{38}\) the decreased concentration of diffusion ions responsible for rendering peptization along with the diffusion front leads to band reverting. However, the mechanism of peptization was not clearly discussed. In the present study, we assume that the flocculation and peptization is the outcome of interactions among the sol particles, which depend on surface charges. Hence, DLVO theory is appropriate to explain the band patterns of the AgBr system. We propose the following mechanism for the revert system of bands.

Let us consider experiment employing varying concentrations of AgNO\(_3\). At the interface of the gel—outer electrolyte
present in the system such as K+, Br−, formed nearer the previous one due to the decrease in the distance between the sol particles corresponds to that of the spacing coefficient. The decrease in the concentration is directly proportional to electrolyte interface. If the distance between them is approximately equal to the first minimum shown in Figure 3, then attractive van der Waals forces start operating between AgBr molecules. We have calculated the net DLVO energy and van der Waals energy at this stage in the range of −2.34 to −1.70 × 10⁻²⁰ J using eq 4. These attractive forces enable AgBr molecules to flocculate triggering the formation of AgBr sol. The flocculation process continues, and the aggregate deposits at a specific position. In this way, the first band of the AgBr floc is deposited. As the AgBr floc formed in first band is negatively charged, Ag⁺ ions get adsorbed on its surface. Adjacent sol particles also having net positive charges repel each other, and if the distance between them becomes equal to that corresponding to the energy barrier as shown in Figure 3, Ag⁺ peptizes the sol. The peptizing Ag⁺ start to diffuse in the downward direction but with a smaller number density.

The DLVO theory predicts that the number density of ions (i.e., concentration) is directly proportional to the fourth power of the surface potential. Hence, as the surface potential decreases, the repulsion between two sol particles decreases leading to the band formation, which is nearer the previous one. The above process continues, and the distance between successive bands decreases with the decrease in concentration of diffusing Ag⁺ ions leading to revert banding. This ion number density or concentration after each band formation should correspond to a critical coagulation concentration.

Therefore, we propose that the first band is the irreversible deposition of sol due to van der Waals forces where the distance between the sol particles corresponds to that of the first minimum shown in Figure 6. The successive bands are formed nearer the previous one due to the decrease in the concentration of peptizing Ag⁺ ions leading to a negative value of the spacing coefficient. It is observed that the values of the spacing coefficient are directly proportional to electrolyte concentration. Therefore, obviously, if the concentration of Ag⁺ is low, then the number density of peptizing (and diffusing) ions is smaller, and the band formation would take place closer to the previous one. We have observed the same trend in all the experiments performed in the present work. It should also be noted that the effect due to the inner electrolyte will not affect the revert band trend as its concentration is the same for all the experiments, and we have assumed that the K⁺ and Br− ions are uniformly distributed inside the diffusion medium.

It is mentioned previously that the role of counterions present in the system such as K⁺, Br⁻ (before reaction), NO₃⁻, and that originating from whatever small dissociation of agar gel is negligible. It is known that the role of any ion that is responsible for flocculation should be seen from the viewpoint of the Hofmeister series.22,23 According to this series, the coagulating power of cations varies as Al³⁺ > Ca²⁺ > Ni³⁺ > Zn²⁺ > Co²⁺ > Mg²⁺ > K⁺ = Na⁺. Therefore, obviously, K⁺ ions have a minimum coagulation capacity, and in addition to that, as an inner electrolyte, their concentration is negligible compared to Ag⁺. Therefore, in the present study, we have neglected the role of counterions in reverting; however, at high concentrations, they may play an important role in pattern formation.

In the present work, we have attempted to apply DLVO theory to understand the mechanism of revert bands of the AgBr system. We have proposed the reaction mechanism of the AgBr floc formation and its deposition as bands through series of reactions including the primary reaction followed by nucleation and finally coagulation of the precipitate. The coagulation and peptization can be the interplay of van der Waals and electrical double layer energies based on where revert banding can be explained; however, explaining direct bands on the basis of DLVO theory (coagulation theory) needs to be explored. If the band formation (revert or direct) is believed to be the outcome of supersaturation or adsorption (and not of nucleation followed by coagulation) of participating ions at specific locations where the solubility product or electrostatic interactions are responsible for band formation, then DLVO explanation needs further investigations.

**CONCLUSIONS**

We have studied one of the most intriguing self-assembles of periodic precipitation where the precipitate of AgBr is deposited in a revert fashion using a 1D experimental setup. We observed that, under all three experimental conditions described in the study, the system preserves revert banding. Theoretical calculations of interacting energies based on classical DLVO theory could successfully explain the underlying mechanism of the reverting system. We found that $E_{vdW}$ dominates at the start of band formation (coagulation), whereas $E_{DL}$ is responsible for the formation of a new band nearer the previous one due to the peptizing effect of diffusing ions of the outer electrolyte. This led to the reverting of system morphology as the threshold concentration (CCC) required for the next band is reached early. The increase in the spacing coefficient value is attributed to the ion strength inside the experimental tube created by the reactants themselves. However, whether the same morphology is retained by externally provided ion strength needs to be explored.
**EXPERIMENTAL SECTION**

An experimental assembly to obtain Liesegang patterns consists of a glass tube of known dimensions containing a gel, an outer electrolyte, and an inner electrolyte. In the present studies, agar gel with a known weight-per-volume concentration along with AgNO₃ and KBr as the outer and inner electrolyte pair with predetermined concentrations was used. All the chemicals were of analytical grade and used without further purification. Three sets of experiments were performed in a sequential manner by varying concentrations of the outer electrolyte, inner electrolyte, or gel. The experimental conditions are summarized in Table 1.

Typically, the agar gel was prepared by slow addition of 2 g of agar powder into 200 mL of boiling water. The required amount of KBr (as the inner electrolyte) was added to boiling agar solution so that its final concentration is in the desired range. The boiling liquid was immediately poured into hard glass tubes with sealed bottoms having an inner diameter of 7.5 mm and length of 150 mm. Two-thirds of the glass tube was filled with agar solution. The tube was allowed to stand vertically overnight at 297.0 ± 0.2 K in a water bath for gel formation. Next day, after ensuring gel formation, a solution of AgNO₃ (as an outer electrolyte) of known concentration was poured from the top to fill the remaining one-third of the glass tube. The open top of the tube was covered with aluminum foil to avoid concentration change due to solvent evaporation. After pouring AgNO₃, a yellow-colored line, which on exposure to light turned gray, appeared at the gel.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00937.

Cover page, photographs of revert Liesegang patterns showing effect of gel concentration, photographs of the control experiment showing revert banding in the AgBr system by varying the concentration of the outer electrolyte. It should be noted that band boundaries are diffused with only few bands (PDF)

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Notes

The authors declare no competing financial interest.

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