Chapter 5

Experimental Verification of the New Model in Different Systems

A series of experiments on Liesegang band formation is presented. The time of formation, width and separation of the bands were determined by visual observations and by measurements with a microscope. With the developed lead fluoride, copper chromate and lead carbonate bands in agar agar gel and copper chromate, calcium phosphate, strontium fluoride and barium molybdate bands in silica gel, the characteristic laws of banding predicted on the basis of the moving boundary model have been verified. The verification of the modified width law confirms the idea of formation of intermediate colloidal haze prior to patterning.

5.1 Introduction

Quantitative characterization of Liesegang patterns based on different theories is abundantly found in literature [1-15], notably in the work of Ross and his group [16-18]. This chapter includes a report of the systematic study on a series of Liesegang patterns developed in different gelatinous media. The interesting features and characteristic laws of banding were investigated on the basis of the moving boundary model described in chapter 3.
Experiments were performed on different Liesegang systems in which

1. patterns are manifested with relatively sharp, well-defined band boundaries and distinct band spacing.

2. the time scale of appearance of the patterns is convenient.

3. patterns are suitable for prolonged visual observation: the core bands maintain their visual features for a long period of time (~ 60 days or more) without being damaged.

4. patterns are reproducible to a large extent.

These properties of the systems made them suitable for the investigations.

All sparingly soluble substances can be periodically precipitated under suitable conditions. The most simple and general way to perform the experiment is to use a gel cylinder. One of the two reacting electrolytes was uniformly dissolved in the gel matrix before it was solidified. After the gel had set, a thoroughly mixed solution of the other electrolyte was poured onto the top of the solid gel surface. To minimize evaporation the tubes were properly sealed. In some experiments a two-gel system was used. The second electrolyte was also dissolved in a gel forming mixture before it was poured on to the inner set gel. Downward diffusion of the outer electrolyte occurs and a beautiful stratification of parallel discs of the reaction products separated by clear spaces were formed inside the gelatinous medium. These bands become thicker and more widely spaced in a regular way as we go down from the junction of the electrolytes, an observation
consistent with the normal trend of the ring spacing. Occasionally helical precipitate was formed instead of discrete discs. In such cases the pitch of the helix increases as the precipitate develops downwards and eventually breaks away to form regular bands.

The experimental conditions for obtaining the periodic precipitation of lead fluoride, copper chromate, lead carbonate in agar-agar gel and copper chromate, calcium phosphate, strontium fluoride, barium molybdate in silica gel are reported here. The optimum conditions under which regular rhythmic precipitation patterns are formed were investigated for each system. Most of the existing studies pertaining to Liesegang systems [1-15] were conducted in test tubes of diameter 2-4 cm and length 15-20 cm in which 5-25 bands were only reported. Systems in glass tubes of diameter 0.4-2 cm and length 20-100 cm were also developed. All the experiments were carried out at room temperature. For thin and long tubes, a large number of well-separated bands sufficient for establishing the conclusions of the moving boundary model were obtained. Each system was analyzed and the results are summarized below. Following table (Table 5.1) gives the summary of the observations made on the patterns developed in the laboratory.
Table 5.1: Summary of the observations made on Liesegang patterns in different systems

<table>
<thead>
<tr>
<th>Inner electrolyte</th>
<th>Outer electrolyte</th>
<th>Diameter and length of tube (cm)</th>
<th>No. of bands</th>
<th>Time of formation of the pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead Fluoride bands</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>KF, 0.06 M (in 1% agar agar gel)</td>
<td>Pb(NO$_3$)$_2$, 0.3M (in 1% agar agar gel)</td>
<td>0.4, 50 0.7, 50 0.8, 50 1.2, 80 1.8, 15</td>
<td>15-20 regular 4-5 spiral + 12-14 regular 4-5 spiral + 11-13 regular 10-14 spiral + 5-6 regular 4-6 spiral + 8-12 regular</td>
<td>12-14 days</td>
</tr>
<tr>
<td>KF, 0.05 M (in 1% agar agar gel)</td>
<td></td>
<td>0.4, 50 0.7, 50 0.8, 50</td>
<td>15-25 regular 20-22 regular 12-16 regular</td>
<td>13-15 days</td>
</tr>
<tr>
<td>Copper Chromate bands</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$, 0.02 M (in 1.5% agar agar gel)</td>
<td>K$_2$Cr$_2$O$_7$, 0.15 M</td>
<td>0.4, 50 0.4, 30 0.8, 50 1.8, 15</td>
<td>45-50 regular 34-28 regular 32-36 regular 20-24 irregular</td>
<td>18-20 days</td>
</tr>
<tr>
<td></td>
<td>K$_2$Cr$_2$O$_7$, 0.2 M</td>
<td>0.4, 50 0.8, 50</td>
<td>84-86 regular 15-18 regular + 25-30 irregular</td>
<td>20-22 days</td>
</tr>
<tr>
<td></td>
<td>K$_2$Cr$_2$O$_7$, 0.25 M</td>
<td>0.4, 50</td>
<td>80-90 regular</td>
<td>33-35 days</td>
</tr>
<tr>
<td></td>
<td>K$_2$Cr$_2$O$_7$, 0.35 M</td>
<td>0.7, 50 0.8, 50 0.4, 100</td>
<td>32 irregular+10-12 regular 35 irregular + 3-4 regular 110-120 regular</td>
<td>56-60 days</td>
</tr>
<tr>
<td></td>
<td>K$_2$Cr$_2$O$_7$, 0.1 N (in silica gel of relative density 1.06 and pH~6)</td>
<td>Cu(SO$_4$)$_2$, 0.5 M</td>
<td>1.6, 50 1.8, 15 2.0, 15</td>
<td>10 irregular + 9-10 regular 15-16 regular 8 irregular + 6-8 regular</td>
</tr>
<tr>
<td>Lead Carbonate bands</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Na$_2$CO$_3$, 0.05 M (in 1% agar agar gel)</td>
<td>Pb(CH$_3$COO)$_2$, 0.3 M</td>
<td>0.4, 15 0.4, 50 0.8, 50 1.8, 15 2.0, 15</td>
<td>18-22 regular 28-32 regular 18-20 regular irregular irregular</td>
<td>14-18 days</td>
</tr>
<tr>
<td></td>
<td>Pb(CH$_3$COO)$_2$, 1M</td>
<td>0.4, 15 0.7, 50</td>
<td>60-65 regular 35-40 regular</td>
<td>18-20 days</td>
</tr>
</tbody>
</table>
## Experimental Verification of the New Model in Different Systems

<table>
<thead>
<tr>
<th>Inner electrolyte</th>
<th>Outer electrolyte</th>
<th>Diameter and length of tube (cm)</th>
<th>No. of bands</th>
<th>Time of formation of the pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calcium Phosphate bands</strong></td>
<td></td>
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</tr>
<tr>
<td>H₃PO₄, 0.8 M (in silica gel of relative density 1.06 and pH-6)</td>
<td>CaCl₂, 1.2 M</td>
<td>2.4, 18</td>
<td>18-20 regular</td>
<td>12-15 days</td>
</tr>
<tr>
<td><strong>Strontium Fluoride bands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF, 0.3 M</td>
<td>SrCl₂, 1 M</td>
<td>1.8, 15</td>
<td>10-12 regular, 8-10 regular, 8-9 regular</td>
<td>3 days</td>
</tr>
<tr>
<td>NaF, 0.36 M</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NaF, 0.4 M (in silica gel of relative density 1.04 and pH-6)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NaF, 0.4 M</td>
<td>1.6, 15</td>
<td>3-4 regular</td>
<td>3 days</td>
<td></td>
</tr>
<tr>
<td>NaF, 0.5 M</td>
<td>1.8, 15</td>
<td>4-5 regular</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF, 0.6 M (in silica gel of relative density 1.05 and pH-6)</td>
<td>1.8, 15</td>
<td>3-4 regular, irregular</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4, 15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Barium Molybdate bands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂MoO₄, 0.1 M (in silica gel of relative density 1.03 and pH-6)</td>
<td>Ba(NO₃)₂, 0.25 M</td>
<td>2.4, 15</td>
<td>14-15 regular</td>
<td>6-7 days</td>
</tr>
</tbody>
</table>
5.2 Precipitate bands in agar-agar gel

5.2.1 PbF$_2$ patterns

One gram of agar-agar powder of bacteriological grade was added to 100 ml of double distilled water and heated to boil for about 20 minutes so that all the particles were dissolved. To this a required amount (0.3486 g) of potassium fluoride was added and this solution was made up to 100 ml with hot distilled water and was well stirred with a magnetic stirrer (this gives 0.06 M concentration of potassium fluoride in the solution). Clear liquid was poured into long glass tubes of 0.4 cm diameter and 50 cm length until it became half full. The upper level of the gel in each tube was marked to indicate the interface between the co-precipitate solutions. The tubes were allowed to stand for 16-18 hours at room temperature for solidification. A gel solution of Pb(NO$_3$)$_2$ of desired concentration (1g of agar powder and 9.936 g of Pb(NO$_3$)$_2$ in 100 ml double distilled water to produce 0.3 M solution) was prepared in a similar manner and was poured over the top of the solidified gel in tubes.

The tubes were clamped vertically on stands and left to age for weeks. The penetration of Pb(NO$_3$)$_2$ into the agar gel containing KF resulted in 15-20 PbF$_2$ precipitate bands. Even though the bands started to appear within the first day, the whole pattern emerges out only in one to two weeks. The PbF$_2$ bands are produced by the chemical reaction

\[
Pb(NO_3)_2 + 2KF \rightarrow PbF_2 + 2KNO_3
\]

The experiment was repeated for different inner electrolyte concentrations. In order to study the effect of the tube dimensions, the experiment was conducted in glass tubes of dimensions 0.7 x 50 cm, 0.8 x 50 cm, 1.2 x 80 cm, 1.8 x 15 cm etc. For wider tubes a number of helical rings of
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precipitate is observed near the boundary followed by regular rings whereas for thin tubes only a few helical rings were formed. For tube of dimension 1.2 x 80 cm 10-14 helical rings followed by 5-6 regular rings were formed.

The time of formation of each band was measured during the evolution of the pattern. The width and separation of bands were obtained from the final precipitation pattern using a traveling microscope to the nearest 0.001 cm. The coordinate of the gel solution interface was first determined. Then, the positions of the \( N \) bands \( \{x_n\}_{n=1,2,\ldots,N} \) were measured. Here \( x_n \) stands for the position of the lower limit of the precipitate zone. The positions \( \{\bar{x}_n\}_{n=1,2,\ldots,N} \) of the upper boundaries of the precipitate layers were also measured. The difference of these two quantities provides the width of the \( n^{th} \) band

\[
W_n = \bar{x}_n - x_n
\]

If \( x_{n+1} \) and \( \bar{x}_{n+1} \) are the corresponding values for \((n+1)^{th}\) bands, the spacing between the \( n^{th} \) and the \((n+1)^{th}\) bands

\[
\xi_n = x_{n+1} - x_n
\]

As the boundaries of the developed precipitation regions was sharp, the uncertainties on width and spacing values were estimated to be very small. The value of \( \Delta \xi_n \) given by equation 3.18 is obtained as

\[
\Delta \xi_n = \xi_{n+1} - \xi_n
\]

In some situations where \( C_{A0} \gg C_{B0} \), as soon as the upper electrolyte is poured over the gel a thick precipitate is formed. In that case distances are measured from the lower edge of the precipitate and not from the interface. The photograph of the patterns (Figure 5.1-5.3) was recorded with a Nikon F65D S.L.R. camera. A close-up of the helical rings are also shown (Figure 5.4)
Figure 5.1: Liesegang structures of PbF$_2$ in agar-agar gel. Experimental details: inner electrolyte, 0.06 M KF in 1% agar-agar gel; outer electrolyte, 0.3 M Pb(NO$_3$)$_2$ in 1% agar-agar gel; diameter and length of the tubes: tube 1, 2 & 3: 0.4 x 50 cm, tube 4: 0.7 x 50 cm, tube 5: 0.8 x 50 cm. Time of evolution of bands: 12-14 days.

Figure 5.2: PbF$_2$ bands in agar-agar gel. Experimental details are same as those given in Figure 5.1. Diameter and length of the tubes: 1.8 x 15 cm. Time of evolution of bands: 12-14 days.
Figure 5.3: Liesegang bands of PbF$_2$ in agar-agar gel. Experimental details: inner electrolyte, 0.05 M KF in 1.5% agar-agar; outer electrolyte, 0.3 M Pb(NO$_3$)$_2$ in 1% agar-agar gel. Diameter and length of the tubes: tube 1: 0.4x50 cm, tube 2: 0.7x50 cm, tube 3: 0.8x50 cm. Time of evolution of bands: 13-15 days.

Figure 5.4: A closer look of helical rings of PbF$_2$ in a tube of diameter 1.2 cm and length 80 cm. Other experimental details are the same as in Figure 5.1.
5.2.2 CuCr₂O₇ bands

Banded precipitation of copper chromate in agar-agar gel was obtained with copper nitrate and potassium chromate as diffusing electrolytes. Copper nitrate solution of concentration 0.02 M was prepared in double distilled water containing 1.5% agar-agar at 85-90°C. The solution was thoroughly mixed with the help of a magnetic stirrer. Hot solution was then poured into tubes of inner diameters 0.4, 0.7, 0.8 cm and length 30-100 cm and into test tubes of inner diameter 1.8 cm and length 15 cm. They were allowed to cool at room temperature to solidify. After the solidification of the gel, an equal volume of aqueous solution of potassium chromate of 0.15 M concentration was added to the upper portion of the tube. The tube was then sealed at the top. The experiment was repeated with 0.2 M, 0.25 M and 0.35 M potassium chromate solutions. The chemical reaction governing the formation of CuCr₂O₇ bands is

\[
\text{Cu(NO}_3\text{)}_2 + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{CuCr}_2\text{O}_7 + 2\text{KNO}_3
\]

For a given tube it is seen that the number of bands and the time of formation of the bands increase as the concentration of K₂Cr₂O₇ increases. As the diameter of the tube increases the bands near the interface becomes irregular or helical.

Even though experiments were carried out in both wide and thin tubes, all measurements were done for thin tubes, as large number of precipitate bands with sharply defined boundaries was obtained for thin tubes. In one experiment, with 0.02 M copper nitrate and 0.2 M potassium chromate in tubes of inner diameter 0.4 cm, pattern with 86 bands were obtained. In another set, with 0.2 M copper nitrate and 0.35 M potassium chromate in tubes of same diameter, a pattern having 120 bands was
obtained. Since the bands were very close together near the interface, the identification of the bands was extremely difficult during the early times of the experiment (the first four or five days) and hence there is every possibility of a sizable error in the measurements made for that region. As time advances, however, the spacing between the bands increases thus reducing the size of the uncertainty. Hence the measurements of time, space and width were confined only to the lower portion of the pattern, which was enough to establish the conclusions. Photographs of the pattern were also taken (Figure 5.5-5.9).

Figure 5.5: CuCr₂O₇ bands in 1.5% agar-agar gel. Experimental details: inner electrolyte - 0.02 M Cu(NO₃)₂, outer electrolyte - 0.15 M K₂Cr₂O₇ in tubes of dimensions 0.4x50 cm, 0.4x30 cm, 0.8x50 cm and 1.8x15 cm. Time of formation of the pattern: 18-20 days.
Figure 5.6: Copper chromate bands in 1.5% agar-agar gel. Inner electrolyte: 0.02 M Cu(NO$_3$)$_2$, outer electrolyte: 0.2 M K$_2$Cr$_2$O$_7$. Diameter and length of tubes: tube 1: 0.4 x 50 cm, tube 2: 0.8 x 50 cm. The time of formation of the bands: 20-22 days.

Figure 5.7: Copper chromate bands in 1.5% agar-agar gel with inner electrolyte 0.02 M Cu(NO$_3$)$_2$ and outer electrolyte: K$_2$Cr$_2$O$_7$ of different concentration, tube 1: 0.15 M, tube 2: 0.2 M, tube 3: 0.25 M (diameter and length of the tubes: 0.4 x 50 cm).
Figure 5.8: Copper chromate bands formed in 1.5% agar-agar gel in tubes of diameter 0.4 cm, length 100 cm. Inner electrolyte: 0.02 M Cu(NO₃)₂, outer electrolyte 0.35 M K₂Cr₂O₇. 110-120 bands are formed within 56-60 days.

Figure 5.9: Copper chromate patterns in 1.5% agar-agar gel. Inner electrolyte: 0.02 M Cu(NO₃)₂; Tube 1 & 2: diameter 0.8 cm and length 50 cm containing outer electrolyte K₂Cr₂O₇ of concentration 0.2 M and 0.35 M respectively, Tube 3: diameter 0.7 cm and length 50 cm containing same outer electrolyte of same concentration.
5.2.3 \( \text{PbCO}_3 \) bands

The penetration of lead acetate into the agar-agar gel (1 mass %) containing sodium carbonate resulted in well defined closely packed lead carbonate precipitate bands.

\[
Pb(CH_3COO)_2 + Na_2CO_3 \rightarrow PbCO_3 + 2NaCH_3COO
\]

With 0.05 M of sodium carbonate and 0.3 M of lead acetate in a tube of diameter 0.4 cm a pattern of 28-32 bands were obtained in 2-3 weeks. For 0.1 M sodium carbonate and 1 M lead acetate, the total number of precipitation bands increases to about 65. The time of formation of the set of

*Figure 5.10:* Lead carbonate bands in 1% agar-agar gel. Tubes 1 & 2 of diameter and length 0.4x50 and 0.8x50 cm respectively; Experimental details: Inner electrolyte 0.05 M \( \text{Na}_2\text{CO}_3 \), outer electrolyte 0.3 M \( \text{Pb}(\text{CH}_3\text{COO})_2 \). Tube 3 of diameter and length 0.7x50 cm, inner electrolyte 0.1 M \( \text{Na}_2\text{CO}_3 \), outer electrolyte 1 M \( \text{Pb}(\text{CH}_3\text{COO})_2 \).
bands is also increased to 20 days. Same trend is obtained for bands in tubes of diameter 0.8 cm. For test tubes of diameter 1.8 cm and 2 cm, almost all the rings formed are found to be irregular. Measurements were taken as discussed above. The pattern is depicted in Figure 5.10 and 5.11. The irregular patterns formed in test tubes are also shown (Figure 5.12).
5.3 Precipitate bands in silica gel

5.3.1 CuCr₂O₇ bands

Silica gel was prepared by mixing equal volumes of sodium meta silicate solution (density 1.06 g/ml) and N/2 acetic acid. The desired amount of inner electrolyte, K₂Cr₂O₇ was dissolved in the acid prior to mixing. The sodium meta silicate solution is added to the acid, stirring quickly and vigorously using a magnetic stirrer. The pH is adjusted to be ~ 6. The mixture was poured into wide glass tubes of dimensions 1.6 x 50, 1.8 x 15 and 2 x 15 cm and allowed to set. After setting, equal volumes of 0.5 N copper sulphate solution was poured on the gel as outer electrolyte.

Figure 5.13: Copper chromate bands in silica gel (relative density 1.06, pH ~ 6); inner electrolyte 0.1 N K₂Cr₂O₇, outer electrolyte 0.5 N Cu(SO₄)₂; tube 1: diameter 1.8 cm and length 15 cm, tube 2: diameter 2.0 cm and length 15 cm
Figure 5.14: Copper chromate bands in silica gel of relative density 1.03 and pH ~ 6 in long tubes of diameter 1.6 cm and length 50 cm. Inner electrolyte 0.1 N K₂Cr₂O₇ and outer electrolyte 0.5 N Cu(SO₄)₂. About 10 helical rings are formed near the interface.

With 0.1 N potassium chromate as the inner electrolyte, 15-16 copper chromate precipitate bands were produced in 12-14 days in tubes of diameter 1.8 cm by chemical reaction:

\[ K₂Cr₂O₇ + CuSO₄ → CuCr₂O₇ + K₂SO₄ \]

In tubes of diameter 2 cm, the first 8 bands were found to be helical in nature. About 22 bands were formed in long tubes out of which about 10 were helical. The position, width and time of formation of the bands were measured for the lower bands of the pattern as explained in section 5.2.1. Photographs of the patterns are shown in Figure 5.13 and 5.14. A view of the helical bands can be seen in Figure 5.14.
5.3.2 \( \text{Ca}(PO_4)_2 \) bands

Sodium meta silicate solution of relative density 1.06 was used to form the gel. \( \text{H}_3\text{PO}_4 \) of concentration 0.8 M is mixed with sodium meta silicate solution in such an amount that a pH of 6.0 could be set for the mixtures. After gelation took place, calcium chloride solution of molarity 1.2 M was gently poured on the set gel. About 20 well-defined good quality Liesegang bands of calcium phosphates were formed in each test tube within a period of 15 days.

\[
3\text{CaCl}_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\text{HCl}
\]

Figure 5.15: Liesegang structures of \( \text{Ca}_3(\text{PO}_4)_2 \) in silica gel. Experimental details: inner electrolyte, 0.8 M \( \text{H}_3\text{PO}_4 \) in silica gel of relative density 1.06, pH ~ 6; outer electrolyte: 1.2 M \( \text{CaCl}_2 \). Time of evolution of the bands: 12 – 15 days.
The width of the bands as well as the spacing between the consecutive bands was measured. The photograph was also recorded (Figure 5.15). When silica gel of relative density 1.03 of pH 6 - 6.5 was used with H₃PO₄ of 1.2 M and CaCl₂ solution of 1.2 M were used, dynamic triplet Liesegang patterns of Ca₃(PO₄)₂ was formed in thin tubes. An explanation of this amazing triplet pattern formation is given in chapter 7.

5.3.3. \( \text{SrF}_2 \) bands

Sodium meta silicate solution of density 1.04 g/ml and sodium fluoride solution of concentrations 0.3, 0.36, 0.4, 0.5 and 0.6 M were mixed in such a way that a pH of \( \sim 6.0 \) was obtained for the mixtures. The pH was adjusted by adding mineral acid like HCl. After gelation, the supernatant solutions of strontium chloride of molarity 1 M were poured on the set gels. Precipitation bands of strontium fluoride were formed in three days.

\[
\text{2NaF} + \text{SrCl}_2 \rightarrow \text{SrF}_2 + 2\text{NaCl}
\]

Figure 5.16: Strontium Fluoride bands in silica gel
The experiment was repeated with gel of density 1.05 g/ml. The spacing, width and time of formation of the bands were measured. Photograph was also taken (Figure 5.16 and 5.17).

![Figure 5.17: Strontium fluoride bands in silica gel of relative density 1.04 and pH~6. Experimental details: outer electrolyte 0.3 M NaF, inner electrolyte 1 M SrCl₂. Diameter and length of the tube 1.8x15 cm.](image)

5.3.4 BaMoO₄ bands

\((\text{NH}_4)_2\text{MoO}_4\) impregnated in silica gel of relative density 1.03 serves as the inner electrolyte. Dilute HNO₃ was used to adjust the pH of the gel medium. A set of the test tubes (2.4 x 15 cm) with gelling mixtures of pH value 6.0 was prepared. After the gels were properly set, the outer electrolyte Ba(NO₃)₂ of 0.25 M concentration was poured gently into the
test tube. As soon as the outer electrolyte was poured a thick precipitation band was formed below the interface, below which Liesegang bands of BaMoO₄ were formed.

The chemical reaction governing the formation of BaMoO₄ bands is:

\[(\text{NH}_4)_2\text{MoO}_4 + \text{Ba(NO}_3)_2 \rightarrow \text{BaMoO}_4 + 2\text{NH}_4\text{NO}_3\]

In all tubes, pattern containing more than 15 bands were obtained within a time span of 6-7 days. The time of formation and the spacing and width of each ring were recorded.

5.4 Verification of the laws of patterning

5.4.1 Modified time law

If \(\xi_n\) represents the spacing between the \((n-1)\)th and \(n\)th bands and \(\tau_n\) is the time taken for the appearance of the \(n\)th band after the \((n-1)\)th band is formed, then according to the modified time law given by equation 3.12

\[\xi_n^2 \sim \tau_n\]

Figure 5.18 - 5.22 depicts the plot of \(\xi_n^2\) against \(\tau_n\) for various Liesegang systems developed. The linear dependence between these quantities can be clearly seen. There is a good accordance with the theoretical and experimental observations. Slight deviations observed were due to experimental error in the measurement of band positions and the time of band formation.
Figure 5.18: Verification of the modified time law with Liesegang rings of copper chromate in 1.5% agar agar gel in glass tube of 0.4 cm diameter and 50 cm length. Outer electrolyte $K_2Cr_2O_7$ - 0.2 M, inner electrolyte $Cu(NO_3)_2$ - 0.02 M.

Figure 5.19: Verification of the modified time law for copper chromate bands in 1.5% agar agar gel in glass tube of 0.4 cm diameter and 1 m length. Outer electrolyte $K_2Cr_2O_7$ - 0.35 M, inner electrolyte $Cu(NO_3)_2$ - 0.02 M.
Figure 5.20: Verification of the modified time law with Liesegang bands of lead carbonate in 1 % agar agar gel in glass tube of 0.4 cm diameter and 15 cm length. Outer electrolyte Pb(CH\textsubscript{3}COO\textsubscript{2})\textsubscript{2} - 0.3 M, inner electrolyte Na\textsubscript{2}CO\textsubscript{3} - 0.05 M.

Figure 5.21: Verification of the modified time law with Strontium Fluoride bands in silica gel of relative density 1.04 and pH ~ 6 in test tubes of 1.8 cm diameter and 15 cm length. Outer electrolyte: SrCl\textsubscript{2} - 1 M, inner electrolyte: NaF - 0.3 M.
Figure 5.22: Verification of the modified time law with Liesegang rings of BaMoO$_4$. Experimental details: Silica gel of relative density 1.03 and pH= 6 in test tubes of 2.4 cm diameter and 15 cm length. Outer electrolyte Ba(NO$_3$)$_2$ - 0.25 M, inner electrolyte (NH$_4$)$_2$MoO$_4$ - 0.1 M.

5.4.2 Modified spacing law and determination of new spacing coefficient

The modified spacing law

$$\frac{\xi_{n+1}}{\xi_n} = (1 + p')$$

given by equation 3.15 was verified experimentally for the different precipitation systems developed. The $\xi_{n+1}$ values were plotted against $\xi_n$ values for all the cases and the plots (Figure 5.23 - 5.30) were proved to be explicitly linear. The straight line also implies that the new spacing coefficient remains constant throughout the entire range of the band system. The spacing coefficient obtained for different systems are given in the following table (Table 5.2).
Table: 5.2: Spacing coefficients obtained for various systems with different plots.

<table>
<thead>
<tr>
<th>Inner electrolyte</th>
<th>Outer electrolyte</th>
<th>Band details</th>
<th>((1+p')<em>{\xi_n-\xi</em>{n+1}}) plot.</th>
<th>((1+p')<em>{w_n-w</em>{n+1}}) plot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF, 0.06 M (in 1% agar agar gel)</td>
<td>Pb(NO\textsubscript{3})\textsubscript{2}, 0.3M (in 1% agar agar gel)</td>
<td>Lead fluoride bands</td>
<td>1.127</td>
<td>1.122</td>
</tr>
<tr>
<td>Cu(NO\textsubscript{3})\textsubscript{2}, 0.02 M (in 1.5% agar agar gel)</td>
<td>K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, 0.2 M</td>
<td>Copper chromate bands</td>
<td>1.019</td>
<td>1.014</td>
</tr>
<tr>
<td></td>
<td>K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, 0.35 M</td>
<td></td>
<td>1.026</td>
<td>1.028</td>
</tr>
<tr>
<td>K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, 0.1 N (in silica gel of relative density 1.06)</td>
<td>Cu(SO\textsubscript{4})\textsubscript{2}, 0.5 N</td>
<td></td>
<td>1.171</td>
<td>1.178</td>
</tr>
<tr>
<td>Na\textsubscript{2}CO\textsubscript{3}, 0.05 M (in 1% agar agar gel)</td>
<td>Pb(CH\textsubscript{3}COO)\textsubscript{2}, 0.3 M</td>
<td>Lead Carbonate bands</td>
<td>1.063</td>
<td>1.056</td>
</tr>
<tr>
<td>H\textsubscript{3}PO\textsubscript{4}, 0.8M (in silica gel of relative density 1.06, pH -6)</td>
<td>CaCl\textsubscript{2}, 1.2 M</td>
<td>Calcium Phosphate bands</td>
<td>1.153</td>
<td>1.149</td>
</tr>
<tr>
<td>NaF, 0.4 M (in silica gel of relative density 1.04, pH -6)</td>
<td>SrCl\textsubscript{2}, 1 M</td>
<td>Strontium Fluoride bands</td>
<td>1.252</td>
<td>1.265</td>
</tr>
<tr>
<td>(NH\textsubscript{4})\textsubscript{2}MoO\textsubscript{4}, 0.1M (in silica gel of relative density 1.03, pH -6)</td>
<td>Ba(NO\textsubscript{3})\textsubscript{2}, 0.25M</td>
<td>Barium Molybdate bands</td>
<td>1.076</td>
<td>1.071</td>
</tr>
</tbody>
</table>
Figure 5.23: Verification of the modified spacing law with Liesegang rings of lead fluoride in 1% agar agar gel in glass tube of 0.4 cm diameter and 50 cm length. Outer electrolyte Pb(NO₃)₂ - 0.3 M, inner electrolyte KF - 0.06 M.

Figure 5.24: Verification of the modified spacing law for copper chromate bands in tubes of diameter 0.4cm and length 50 cm. Inner electrolyte: 0.02 M Cu(NO₃)₂ in 1.5% agar-agar gel, outer electrolyte: 0.2 M K₂Cr₂O₇.
Figure 5.25: Verification of the modified spacing law for copper chromate bands in 1.5% agar agar gel in tubes of diameter 0.4 cm diameter and 1m length. Experimental details: Outer electrolyte: 0.35 M K₂Cr₂O₇, inner electrolyte: 0.02 M Cu(NO₃)₂.

Figure 5.26: Verification of modified spacing law with copper chromate bands in silica gel of relative density 1.06 and pH~6. Outer electrolyte Cu(SO₄)₂ - 0.5 N, Inner electrolyte K₂Cr₂O₇ - 0.1 N.
Figure 5.27: Verification of the modified spacing law for lead carbonate bands in 1% agar agar gel. Experimental details: inner electrolyte- 0.05 M sodium carbonate, outer electrolyte- 0.3 M lead acetate. Length and diameter of the tube: 0.4×15 cm.

Figure 5.28: Verification of modified spacing law with calcium phosphate bands in silica gel of relative density 1.06 and pH-6. Outer electrolyte: CaCl$_2$ - 1.2 M, inner electrolyte: H$_3$PO$_4$ - 0.8 M.
Figure 5.29: Verification of modified spacing law with strontium fluoride bands in silica gel of relative density 1.04 and pH-6 in test tubes of 1.8 cm diameter and 15 cm length. Outer electrolyte: \( \text{SrCl}_2 \) - 1 M, inner electrolyte: \( \text{NaF} \) - 0.4 M.

Figure 5.30: Verification of modified spacing law with barium molybdate bands in silica gel of relative density 1.03 and pH-6 in test tubes of 2.4 cm diameter and 15 cm length. Experimental details: Outer electrolyte \( \text{Ba(NO}_3\text{)}_2 \) - 0.25 M, inner electrolyte \( (\text{NH}_4)\text{MoO}_4 \) - 0.1 M.
5.4.3 $\xi_n - \Delta\xi_n$ plots and spacing coefficient

The linear relationship $\Delta\xi_n \sim \xi_n$ is verified graphically for different systems (Figure 5.31–5.34) and the values of $p'$ for each system is obtained. The spacing coefficient $(1 + p')$ obtained is tabulated (Table 5.3). Within the limits of error, the value of the spacing coefficient obtained from $\xi_n - \Delta\xi_n$ plots is in close agreement with the values obtained from $\xi_n - \xi_{n+1}$ plots. Slight deviations observed are due to the experimental error in the judicious measurements of band positions.

![Graph of $\Delta\xi_n$ versus $\xi_n$ for copper chromate bands. The experimental details are same as those given in Figure 5.26. The value of $p'$ obtained is 0.167.](image)

Figure 5.31: Plot of $\Delta\xi_n$ versus $\xi_n$ for copper chromate bands. The experimental details are same as those given in Figure 5.26. The value of $p'$ obtained is 0.167.
Figure 5.32: Plot of $\Delta \xi_n$ versus $\xi_n$ for lead carbonate bands. The experimental details are same as those given in Figure 5.27. The value of $p'$ obtained is 0.064.

Figure 5.33: Plot of $\Delta \xi_n$ versus $\xi_n$ for strontium fluoride bands. The experimental details are same as those given in Figure 5.29. The value of $p'$ obtained is 0.258
Figure 5.34: Plot of $\Delta \xi_n$ versus $\xi_n$ for barium molybdate bands. The experimental details are same as those given in Figure 5.30. The value of $p'$ obtained is 0.079.

Table 5.3: Spacing coefficients obtained from $\xi_n - \Delta \xi_n$ and $\xi_n - \xi_{n+1}$ plots.

<table>
<thead>
<tr>
<th>Inner electrolyte</th>
<th>Outer electrolyte</th>
<th>Band details</th>
<th>$(1+p')$ from $\xi_n - \Delta \xi_n$ plot</th>
<th>$(1+p')$ from $\xi_n - \xi_{n+1}$ plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$Cr$_2$O$_7$, 0.1 N</td>
<td>Cu(SO$_4$)$_2$, 0.5 N</td>
<td>Copper chromate bands</td>
<td>1.171</td>
<td>1.167</td>
</tr>
<tr>
<td>(in silica gel of relative density 1.06)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$CO$_3$, 0.05 M</td>
<td>Pb(CH$_3$COO)$_2$, 0.3 M</td>
<td>Lead Carbonate bands</td>
<td>1.063</td>
<td>1.064</td>
</tr>
<tr>
<td>(in 1% agar agar gel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF, 0.4 M</td>
<td>SrCl$_2$, 1 M</td>
<td>Strontium Fluoride bands</td>
<td>1.252</td>
<td>1.258</td>
</tr>
<tr>
<td>(in silica gel of relative density 1.04, pH ~ 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_2$MoO$_4$, 0.1 M</td>
<td>Ba(NO$_3$)$_2$, 0.25M</td>
<td>Barium Molybdate bands</td>
<td>1.076</td>
<td>1.079</td>
</tr>
<tr>
<td>(in silica gel of relative density 1.03, pH ~ 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.4.4 Modified Width law

The modified width law is verified by plotting $\xi_n$ against $w_n$ for the systems developed (Figure 5.35–5.42). The straight line proves the validity of the law. The new spacing coefficient is determined by depicting the plots of $w_{n+1}$ against $w_n$ (Figure 5.43–5.50). Equation (3.23) is verified and the results are tabulated (Table 5.2).

![Graph showing the verification of the modified width law](image)

**Figure 5.35:** Verification of the modified width law with Liesegang patterns of PbF$_2$. Experimental details same as in Figure 5.23
Figure 5.36: Verification of the modified width law with Liesegang patterns of CuCr$_2$O$_7$. Experimental details same as in Figure 5.24.

Figure 5.37: Modified width law verification with patterns of CuCr$_2$O$_7$. Experimental details same as in Figure 5.25.
Figure 5.38: Modified width law verification with patterns of CuCr$_2$O$_7$. Experimental details same as in Figure 5.26.

Figure 5.39: Modified width law verification with patterns of PbCO$_3$. Experimental details same as in Figure 5.27.
Figure 5.40: Modified width law verification with patterns of Ca₃(PO₄)₂. Experimental details same as in Figure 5.28.

Figure 5.41: Modified width law verification with patterns of SrF₂. Experimental details same as in Figure 5.29.
Figure 5.42: Verification of the modified width law with Liesegang patterns of BaMoO₄. Experimental details same as in Figure 5.30.

Figure 5.43: Determination of the new spacing coefficient $(1 + p')$ given by the slope of the $w_n$ versus $w_{n+1}$ plot for PbF₂ patterns. Experimental details same as in Figure 5.23. The value of $(1 + p')$ is found to be 1.122.
Figure 5.44: Determination of the new spacing coefficient \((1 + p')\) given by the slope of the \(w_n\) versus \(w_{n+1}\) plot for CuCr\(_2\)O\(_7\) patterns. Experimental details same as in Figure 5.24. The value of \((1 + p')\) is found to be 1.014.

Figure 5.45: Determination of the new spacing coefficient \((1 + p')\) given by the slope of the \(w_n\) versus \(w_{n+1}\) plot for CuCr\(_2\)O\(_7\) patterns. Experimental details same as in Figure 5.25. The value of \((1 + p')\) is found to be 1.028.
**Figure 5.46:** Determination of the new spacing coefficient \((1 + p')\) given by the slope of the \(w_n\) versus \(w_{n+1}\) plot for CuCr₂O₄ patterns. Experimental details same as in Figure 5.26. The value of \((1 + p')\) is found to be 1.178.

**Figure 5.47:** Determination of the new spacing coefficient \((1 + p')\) given by the slope of the \(w_n\) versus \(w_{n+1}\) plot for PbCO₃ patterns. Experimental details same as in Figure 5.27. The value of \((1 + p')\) is found to be 1.056.
Figure 5.48: Determination of the new spacing coefficient \((1 + p')\) given by the slope of the \(w_n\) versus \(w_{n+1}\) plot for \(\text{CuPO}_4\) patterns. Experimental details same as in Figure 5.28. The value of \((1 + p')\) is found to be 1.149.

Figure 4.49: Determination of the new spacing coefficient \((1 + p')\) given by the slope of the \(w_n\) versus \(w_{n+1}\) plot for \(\text{SrF}_2\) patterns. Experimental details same as in Figure 5.29. The value of \((1 + p')\) is found to be 1.265.
Experimental Verification of the New Model in Different Systems

5.5 Conclusions

The experiments done on various systems and the measurements taken thereon proved to be sufficient to establish the validity of the moving boundary model for pattern formation. The variety in structure obtained in this study reveals the rich though complex dynamics inherent in these Liesegang systems. These patterns are characterized in several ways and through measurements of various parameters. The main variables considered here are the spacing, width and the time of evolution of the bands.

With the developed patterns, the characteristic laws of banding predicted by the moving boundary model, are verified. Experimental verifications provide confirmatory support for the moving boundary model. The relatively large number of bands with sharply defined boundaries allowed a rather accurate determination of the new spacing coefficient.

Figure 5. 50: Determination of the new spacing coefficient \((1 + p')\) given by the slope of the \(w_n\) versus \(w_{n+1}\) plot for BaMoO₄ patterns. Experimental details same as in Figure 5. 30. The value of \((1 + p')\) is found to be 1.071.
References


