

LIESEGANG RING PHENOMENON STUDY IN GEL GROWN OXALATE CRYSTALS

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ABSTRACT

All sparingly soluble substances can be periodically precipitated under suitable condition. The study of Liesegang phenomenon is instructive in a general way, and it is its own importance. Liesegang rings in precipitation reactions are an example of pattern formation in chemical reaction-diffusion systems. Such patterns arise from the interplay between the reaction kinetics and the diffusion of chemical species. . The precipitation is continuous at the beginning and soon clear cut spaces in between are formed at the lower part of the tube. The periodic precipitation depends on various factors like the concentration of reactants, temperature, inherent properties of gel. For the different gel pH values in the optimized range 4.2 to 5.0, the position of ring (X) and its time of formation (t) for constant values of concentration of the outer electrolyte (0.5M - 2.0M) were noted for different rings. The linear relationship between them X and $t^{1/2}$ confirms that, the time law proposed by Morce and Pierce may be obeyed in our study. Different parameters such as pH, Concentration of cadmium chloride) affecting the space coefficient and velocity coefficient were studied.

Keywords: Gel growth, Liesegang ring, space coefficient, velocity coefficient, oxalate.

INTRODUCTION

Liesegang rings in precipitation reactions are an example of pattern formation in chemical reaction-diffusion systems. Such patterns arise from the interplay between the reaction kinetics and the diffusion of chemical species. Since particle size can affect colour, ring systems are sometimes multicolored. Hatschek¹⁰⁾ described such a case involving cadmium sulfide precipitates. The dependence of flocculation value on the sol concentration has been extensively studied by several colloid chemists like Sen and Dhar¹¹⁾, Mukherjee¹²⁾, Krut and van der Spek¹³⁾ and Burton and Bishop¹⁴⁾.

All sparingly soluble substances can be periodically precipitated under suitable condition. Generally the precipitates formed in tubes (or plates) are arranged in bands (or concentric rings). At first the precipitate is continuous, but later the bands are separated by relatively clear spaces. The positions of these rings are governed by a geometric progression law, proposed by Jablczynski¹⁷⁾, according to which the interspacing between successive rings

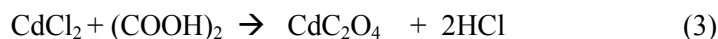
increased as the order of the ring from the gel boundary. This type of periodic precipitation is referred to in literature as the direct type Liesegang phenomenon. The direct type of periodic precipitation of silver iodide has been investigated by Roy¹⁸⁾ in starch and silica, and by Chatterji and Rastogi¹⁹⁾ in agar, by impregnating the gel with silver nitrate and taking potassium iodide over the set gel.

Several theories have been proposed to explain the nucleation and propagation of ring systems. Supersaturation theory of Wilhelm Ostwald²⁸⁾ which was the earliest of proposed theories got much acceptance²⁹⁻³³⁾ in spite of its many drawbacks^{34,35)}. The other theories are : (i) adsorption theory of Bradford³⁶⁾, (ii) coagulation theory of Dhar and Chatterji³⁷⁻⁴⁰⁾, (iii) Ostwald's diffusion wave theory⁴¹⁾, (iv) wave mechanical model⁴²⁾ and (v) flocculation theory of Shinohara⁴³⁾. But unfortunately, none of these proposed theories are able to explain all the observations both qualitatively and quantitatively, because all theories, in fact, demand a critical condition for the periodic precipitation to occur. For example, Ostwald's²⁸⁾ supersaturation theory is dependent on the metastable limit. Bradford³⁶⁾ assumes a critical concentration of the inner electrolyte. In the coagulation theory³⁷⁾, a definite yet critical concentration of electrolyte is required for coagulation. Ostwald⁴¹⁾ too specifies a critical concentration for the precipitation. Mobilization of the material is brought forth by diffusion in both the Ostwald's theories^{28,41)}, whereas adsorption does this function in Bradford's³⁶⁾ and Dhar's³⁷⁻⁴⁰⁾ theories. Hedges⁴⁴⁾ favors preferential diffusion to adsorption since the latter acts only over short distances, and it is concluded that the spacing of bands will depend on the difference in the rate of mobilization of reagents and products. The medium influences the threshold value of the critical condition and the speed of mobilization.

EXPERIMENTAL AND OBSERVATIONS

Experiments on the investigation of Liesegang rings in respect of cadmium oxalate crystals were conducted in 'corning' glass cylindrical test tubes of inner diameter 2.5 cm and length 25 cm. The chemicals used were: Commercial water glass solution, oxalic acid AR, cadmium chloride monohydrate RG.

In gel, the chemical reaction takes place as follows:



The gel was set by mixing water glass solution of specific gravity $1.04\text{g}\cdot\text{cm}^{-3}$ with requisite amount of aqueous solution of 0.5 M oxalic acid, resulting into pH 4.2, 4.4, 4.6, 4.8 and 5.0. The growth experiments were performed with cadmium chloride as supernatant solution of strength 0.5M, 1.0M, 1.5M and 2.0M. An amount of 20 ml of CdCl_2 solution was carefully poured along the walls of the tube and the time of feeding was exactly noted. Traveling microscope was used to measure the distance of each ring from the gel surface. When the feeding was complete, the reading corresponding to the interface was noted. Since a number of rings were formed in less than a minute, the induction period for the initiation of ring formation may be regarded as negligibly small. It was observed that the ring formation did not start right at the gel-solution interface; there was seemingly a continuous precipitate zone. Well spaced rings were nucleated after 10 to 12 minutes. The time of formation (t) and the distance of the rings (X) from the interface were noted for each ring. The Liesegang rings of cadmium oxalate formed in the acidic range are displayed in Fig.1 in which 10 rings can be seen over a depth of 5.2 cm in the tube.

It may be interesting to note that while working in the basic range of pH, cadmium chloride reacted with both sodium metasilicate and oxalic acid and a dense and continuous precipitation of 1 to 2 cm depth was observed embedded with some cadmium oxalate dendritic crystals, as evident from Fig2.

RESULTS AND DISCUSSION

It is evident that periodic precipitation of sparingly soluble substances can be obtained under suitable conditions, when a reactant is allowed to diffuse into the set gel containing another reactant in a test tube. The precipitation is continuous at the beginning and soon clear cut spaces in between are formed at the lower part of the tube. Such periodic precipitation normally, as one would expect, depends on various factors like the concentration of reactants, temperature, inherent properties of gel. The gel pH range, 4.2 to 5.0 is found, in the present case, suitable for Liesegang ring study because the position of ring as well as its time of formation can be noted accurately in this pH range. Above pH 5.0 the spacing of the rings is indeed too less to ascertain the position of the rings exactly differentiable one from the other. With the pH value less than 4.2, the time of formation increases enough large, entailing inaccuracy of time, and the crystal being larger the ring surfaces were not clear, hence inaccuracy in position of the ring.

A few results in respect of the ring formation which should be noted are as follows:

1. With lapse of time, Liesegang rings are formed invariably in all the tubes, provided pH is proper.
2. The distance between successive rings noticeably increases with the ring order, hence the direct type phenomenon.
3. The rings from the interface begin to dissolve with time with the supersaturated solution active, which is due to their slight solubility in the diffusing cadmium chloride solution and the reaction waste product, viz., hydrochloric acid.
4. The number of crystals in a latter, lower ring is only a fraction of that in the preceding, upper ring.
5. The latter, higher order rings are observed to be much wider than the previous ones, as clearly seen in the Fig.1. This implies that below the last ring, a ring will be nucleated containing just a few crystals which are spread in relatively larger volume. Since these nuclei are smaller in number, they grow relatively bigger crystals.

Occasionally it is observed that in some tubes the ring formation stopped abruptly, and single nucleus emerged below the last ring which grew faster on account of preferential deposition. The fact that this growing nucleus is not a part of the next ring can be judged from the nearness of the crystal to the last ring. This crystal, in the intermediate position, attracts towards it all the nutrients because of existing slight under saturation in its immediate vicinity, thereby hindering the nucleation of the next order rings.

Time and Space Laws

For the different gel pH values in the optimized range 4.2 to 5.0, the position of ring (X) and its time of formation (t) for constant values of concentration of the outer electrolyte (0.5M,

1.0M, 1.5M, 2.0M) were noted for different rings. The graph is plotted between the X_n and $t_n^{1/2}$ at constant concentration. We obtained linear relationship between them as shown in Fig 3. It implies that as mentioned in section 2, the time law proposed by Morce and Pierce²⁹⁾ is valid;

$$\frac{X_n}{t_n^{1/2}} = K \quad (4)$$

Where X_n is the position of n^{th} ring and t_n is the time of its formation and K is the velocity coefficient. The slope of the straight line gives the value of the velocity coefficient K (Table 1).

According to Shinohara⁴³⁾, the diffusion front is referred to as sol front, since the boundary moves forward leaving a sol region behind. The movement of the sol front can be expressed as

$$\frac{X_n}{t_n^{1/2}} = (kD_{oA})^{1/2} = K \quad (5)$$

Where k is known as the front constant and D_{oA} is the diffusion coefficient of the outer electrolyte. The above relation (5) suggests that the velocity coefficient is the product of front constant k and the diffusion coefficient D_{oA} . Hence, the effective diffusion coefficient of A ions is

$$D_{oA} = \frac{X^2/t}{4 \ln(C_{oA}/C_B)} \quad (7)$$

The values of C_{oA} for the outer electrolyte of strengths 0.5M, 1.0M, 1.5M and 2.0M are 0.425×10^{20} , 0.85×10^{20} , 1.275×10^{20} and 1.7×10^{20} ion cm^{-3} respectively, while C_B for the inner electrolyte concentration of strength 0.5M is 0.168×10^{20} ion cm^{-3} . The diffusion coefficient D_{oA} and the front constant k are thus calculated (Table 1 (a,b)). It is observed that diffusion coefficient D_{oA} is at variance with medium pH. From Table 1(b), it can be inferred that the front constant 'k' remains constant for constant value of the inner electrolyte at different pH value, whereas it increases with concentration of outer electrolyte.

Furthermore, using the data of the position of a ring and its order or the number of ring, the graphical plot of the spacing of ring (X_n) with different CdCl_2 concentration at constant medium pH (=5 in the present case) gives straight line as shown in Fig. 4. The linear variation of the distance of the ring (X_n) with the number of ring (n) verifies the validity of the space law given by Matalon and Packter⁵⁸⁾. Similar nature of curves is observed on X_n verses n graphs plotted using other pH values also. The slope gives values of the spacing coefficient S which are recorded for the media of different pH in Table2 (a). Thus the number of order of the ring (n) is related to its corresponding position (X_n) by the equation (1), whence the spacing coefficient can be expressed as

$$S = \frac{X_{n+1}}{X_n} \quad (8)$$

Dependence of Spacing Coefficient on Concentrations of the Outer Electrolytes

The spacing constant 'S' is found sensitive to the variation of concentration of the outer electrolyte. The dependence on the concentration change has been studied in some detail here. The values of 'S' as recorded in Table 2(a). Fig. 5(a) shows that the spacing coefficient at a given gel pH increases linearly with the increase in concentration of the outer electrolyte.

The average rate of increase of the spacing constant with the concentration $\left(\frac{dS}{dC_0}\right)$ is obtained as 0.01306, i.e about 1.3 %.

Such dependence has been studied by Wagner⁵⁷⁾ and Matalon and Packter⁵⁸⁾. Interestingly, the values of S and C₀ are found to be proportional to each other and so we can propose a relation as

$$(S - 1) = A + BC_0 \quad (9)$$

Where A and B are constants, B being similar to super saturation constant and hence it does not vary with concentration of the outer electrolyte. On plotting (S-1) verses C₀ (Fig.5 (b)), the values of the constants A and B can be obtained (Table. 5.2(b)). The fact that at higher concentration the spacing constant increases is possibly because the rate of diffusion of Cd²⁺ ions is enhanced by the increased concentration, although the inner electrolyte has a fixed concentration, and hence, the Cd²⁺ ions have to move greater depths to react with prevalent oxalate ions. This explains larger spacing between the rings at higher concentration of outer electrolyte, as observed.

Dependence of Spacing Coefficient on the GEL pH

The pH is a measure of acidity of the gel, it also indicates the concentration of inner electrolyte whose change may possibly alter the diffusion of both the reactants. The spacing constant 'S' is found sensitive to the variation of the gel pH as can be seen clearly from Table 3 and Fig. 6. The graph of Fig. 6 reveals that at a fixed concentration of the outer electrolyte, the spacing constant 'S' decreases with increasing gel pH. This may be because that at higher pH the gel is harder as the pore size is reduced and so lesser amount of outer ions (Cd²⁺) can diffuse through the pores. However, the concentration of uniformly distributed oxalate ion is quite high. So, the ring is formed when the populous oxalate ions react with the incoming cadmium ions. The region from which the oxalate ions diffuse upwards for the completion of reaction is not large and consequently the rings tend to form more closely separated in the harder gel, that is at higher pH.

Dependence of Velocity Coefficient on Concentrations of the Outer Electrolytes

The velocity coefficient K is also observed to be affected by varying concentration of the outer electrolyte. This dependence can be clearly inferred from Table 4 and Fig. 7. It is

observed that with increasing concentration of the outer electrolyte the velocity coefficient (K) increases linearly. It is quite natural that the increased concentration of outer electrolyte enhances the activity of reacting Cd^{2+} ions. At higher concentration the diffusing Cd^{2+} ions will be more, so the precipitation begins at the interface itself and the ring formation occurs below the interface. The growth is facilitated as the ions of inner electrolyte diffuse upward, which result in the large space (absence of inner electrolyte ions) below the ring. Hence Cd^{2+} ions diffusing more rapidly reduce the time of ring formation, thus entailing the observed increase in the velocity coefficient.

Dependence of Velocity Coefficient on the GEL pH

The velocity coefficient is found to be decrease quite linearly with increase in gel pH as shown in Fig.8. This variation is evident from Table 5. As the pH increases, hardness of the gel increases. The increase in hardness reduces the diffusion rate of the outer electrolyte into the gel column. The slow diffusion rate will result in the slow ring formation and hence K decreases. The pictorial representation of the effect as visible of the variation of concentration of the outer electrolyte and gel pH is shown in Fig. 9 (a) and (b) respectively. From Fig. 9 (a) one can say that as the concentration of the outer electrolyte at constant gel pH (4.6) increases, the spacing between the rings increases and the bulk of diffusion column also increases. This favours the increase in spacing constant with the concentration. The diffusion depth increases largely on increasing concentration of outer electrolyte from 0.5 M to 1.0M but remains constant on further increase. The thickness of the ring also increases with concentration. The number of rings does not change with the concentration but at higher concentration of outer electrolyte the dissolution rate is higher so the number of rings observed is less in Fig 9 (a). The visible pH effect (Fig 10(b)) shows that the number of rings increases with gel pH whereas the spacing between the rings decreases, as also indicated by the small values of spacing constant at higher pH. The diffusion column remains more or less the same for different pH values. It may be interesting here to comment on Isemura's¹⁶⁾ inconclusive observation that in some cases the number and separation of bands increase while in other cases decrease, with increasing gel pH. This non-uniform behavior of S is possible, should one consider various systems in which the diffusivity is not decided by the gel pH alone. If the incoming ions are lighter, they can diffuse more effectively through the pores of reduced diameter and in such cases the concentrations of inner and outer ions may be the deciding factors for the behavior of time and space constants.

Another interesting observation is that the cadmium chloride incorporated gel fed with oxalic acid as the supernant solution produces no rings but results only dense precipitation. This again contradicts Isemura's¹⁶⁾ result according to which the interchanging of reactants (inner and outer electrolytes) will not affect the appearance of periodic precipitation. The non-diffusion of the heavier cadmium ions in the upward direction with sufficient velocity which is required for the ring formation is not fulfilled, the continuous diffusion of oxalate ions from the top results in continuous precipitation.

CONCLUSIONS

1. Periodic crystallization occurs in the entire acidic range of pH (4.2 to 5.0) of silica gel set with oxalic acid and fed with cadmium chloride as supernant solution.
2. The time law and the space law are obeyed satisfactorily in our case.

3. As the pH value increases, the velocity coefficient as well as the space constant decreases, whereas the velocity coefficient and space constant increase with the increase of the concentration of feed solution (1M CdCl₂).
4. The deviations from the general observation of Isemura¹⁶⁾ have been explained by considering the individual case of cadmium oxalate Liesegang phenomenon in which the rings are constituted of macrocrystals growing fast with time.



Fig1. Typical Liesegangring pattern obtained of cadmium oxalate



Fig 2. Dense precipitation and dendritic growth pattern obtained of cadmium oxalate in basic range

Velocity coefficient K and Diffusion coefficient 'D_{oA}' at different concentration of CdCl₂
 Specific density of gel 1.04g.cm⁻³ Strength of oxalic acid 0.5M

Sr.No.	Cd Cl ₂ (M)	pH 4.2		pH 4.4		pH 4.6		pH 4.8		pH 5.0	
		K x 10 ⁻³ cm/s ec ^{-1/2}	D _{oA} x 10 ⁻⁵ cm ² /s ec	K x 10 ⁻³ cm/s ec ^{-1/2}	D _{oA} x 10 ⁻⁵ cm ² /s ec	K x 10 ⁻³ cm/s ec ^{-1/2}	D _{oA} x 10 ⁻⁵ cm ² /s ec	K x 10 ⁻³ cm/s ec ^{-1/2}	D _{oA} x 10 ⁻⁵ cm ² /s ec	K x 10 ⁻³ cm/s ec ^{-1/2}	D _{oA} x 10 ⁻⁵ cm ² /s ec
1	0.5	5.99	0.966	5.837	0.917	5.54	0.826	5.369	0.776	5.15	0.714
2	1.0	6.624	0.676	6.44	0.639	6.26	0.604	6.03	0.561	5.81	0.521
3	1.5	7.382	0.672	7.10	0.622	6.90	0.587	6.684	0.551	6.455	0.514
4	2.0	8.14	0.716	7.77	0.652	7.54	0.614	7.435	0.597	7.15	0.552

Table1 (b). Front constant 'k' at different concentration of CdCl₂

Sr. No.	CdCl ₂ (M)	Front constant 'k'				
		pH 4.2	pH 4.4	pH 4.6	pH 4.8	pH 5.0
1	0.5	3.71	3.72	3.72	3.72	3.72
2	1.0	6.53	6.49	6.49	6.48	6.48
3	1.5	8.11	8.14	8.11	8.11	8.11
4	2.0	9.25	9.26	9.26	9.26	9.26

Table. 2 (a) Space constant at different strengths of CdCl₂

Sr. No.	CdCl ₂ (M)	Space constant 'S'				
		pH 4.2	pH 4.4	pH 4.6	pH 4.8	pH 5.0
	0.5	1.0755	1.0664	1.0623	1.0607	1.058
2	1.0	1.0819	1.0723	1.0691	1.0671	1.0639
3	1.5	1.09	1.078	1.0743	1.0728	1.0696
4	2.0	1.0998	1.0854	1.0812	1.0797	1.0755

Table. 4 Velocity coefficient at different concentration of CdCl₂

Specific density of gel : 1.04g.cm⁻³

Strength of oxalic acid 0.5M

Sr. No.	CdCl ₂ (M)	Velocity Coefficient 'K' (x 10 ⁻³ cm.sec ^{-1/2})				
		pH 4.2	pH 4.4	pH 4.6	pH 4.8	pH 5.0
1	0.5	5.99	5.837	5.54	5.369	5.15
2	1.0	6.624	6.44	6.26	6.03	5.81
3	1.5	7.382	7.10	6.90	6.684	6.455
4	2.0	8.14	7.77	7.54	7.435	7.15

Table.5 Velocity coefficient at different gel pH

Specific density of gel 1.04g.cm⁻³

Strength of oxalic acid 0.5M

Sr. No.	gel pH	Velocity Coefficient 'K' (x 10 ⁻³ cm.sec ^{-1/2})			
		CdCl ₂ 0.5M	CdCl ₂ 1.0M	CdCl ₂ 1.5M	CdCl ₂ 2.0M
1	4.2	5.99	6.624	7.382	8.14
2	4.4	5.837	6.44	7.10	7.77
3	4.6	5.54	6.26	6.90	7.54
4	4.8	5.369	6.03	6.684	7.435
5	5.0	5.15	5.81	6.455	7.15

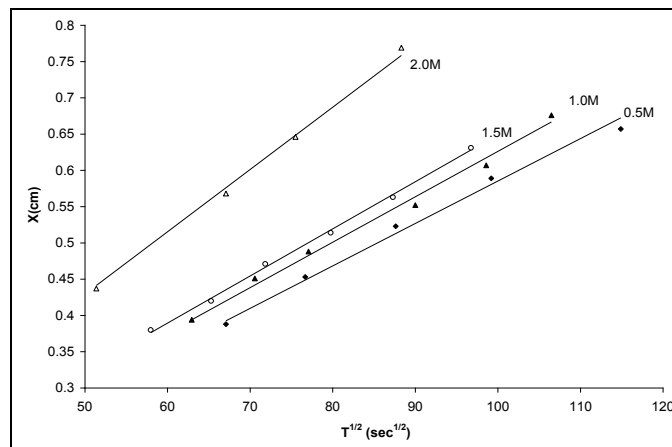


Fig 3. Graphical Relation between Position and Time of Formation of Rings

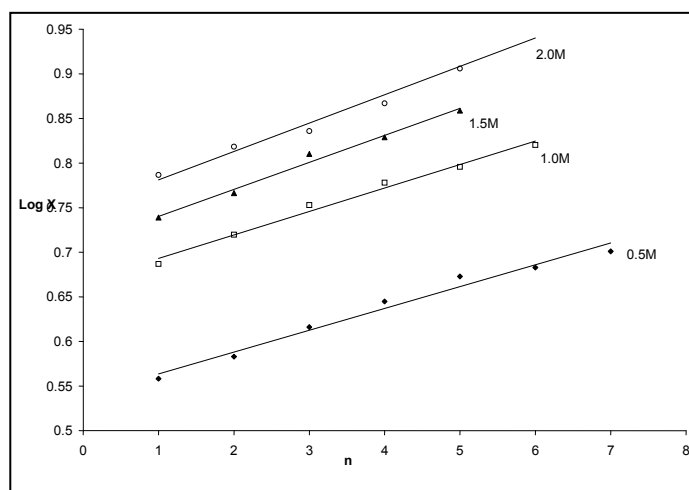


Fig 4. Graphical plot of the spacing of rings at different outer electrolyte concentrations

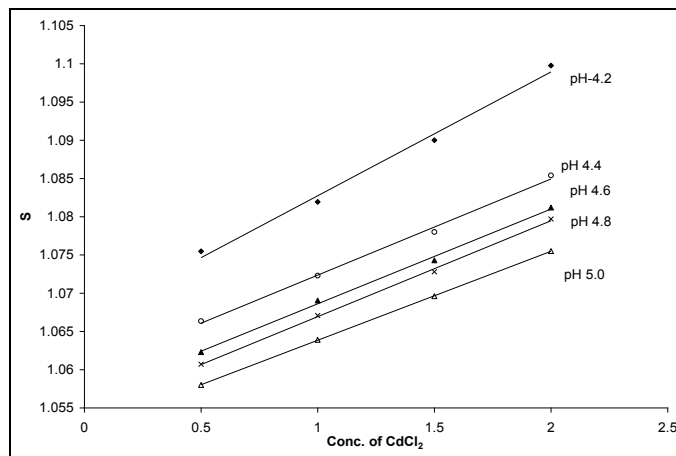


Fig. 5(a). Variation of the spacing coefficient with concentration of CdCl₂

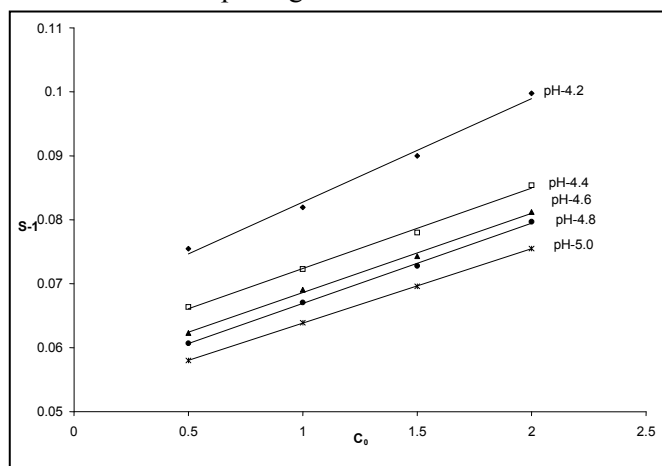


Fig. 5(b). Plot of (S-1) versus CdCl₂ concentration

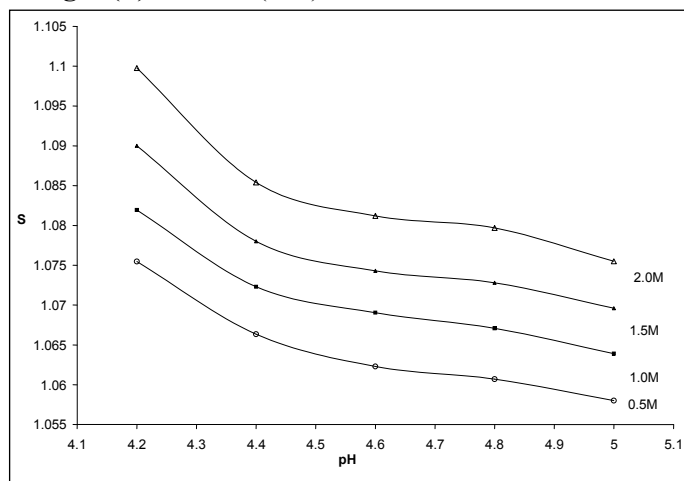


Fig. 6. Variation of the spacing coefficient with gel pH

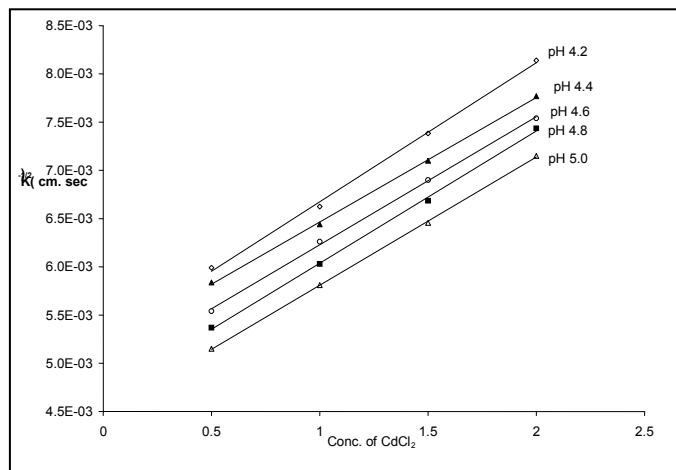


Fig7. Variation of the velocity coefficient with concentration of CdCl₂

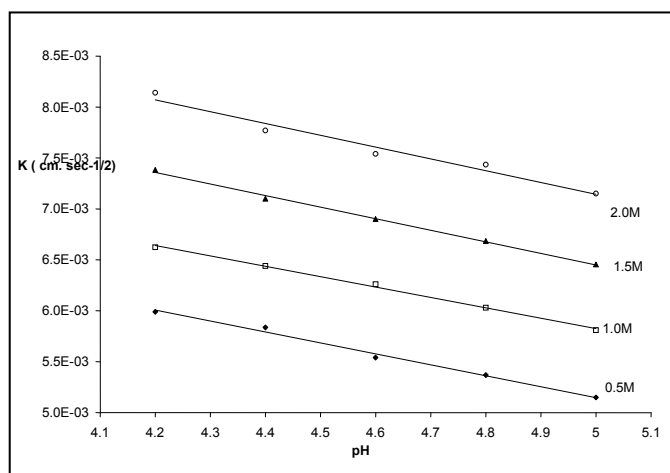


Fig. 8. Variation of the velocity coefficient with gel pH

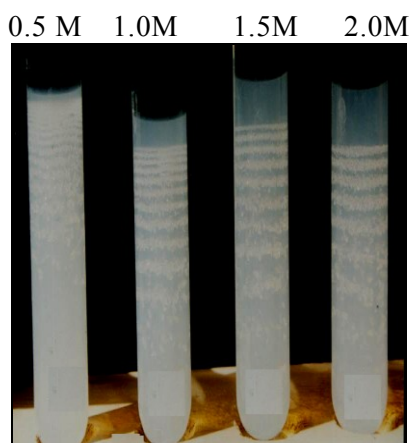


Fig. 9(a). Pictorial representation of the effect of variation of outer electrolyte

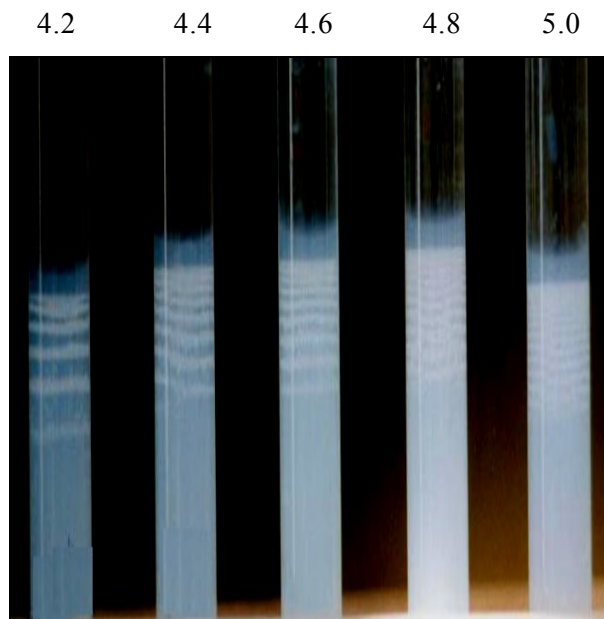


Fig. 9(b). Pictorial representation of the effect of variation of gel pH

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