

A new spacing law for Liesegang rings

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Abstract. The spacing laws of Jablczynski and Mathur are applied to the Liesegang rings of cobalt(II) oxinate, silver iodide and lead chromate in agar gel. Although Jablczynski's spacing law satisfactorily explains the direct Liesegang rings, it totally fails to describe the revert Liesegang rings. Similarly though Mathur's spacing law is applicable to both revert and direct types of periodic precipitation, an appreciable deviation is observed in systems with greater interspacing. A new spacing law, applicable to both revert and direct Liesegang rings, is proposed on the basis of the preferential adsorption theory of Liesegang rings. It is experimentally verified with silver iodide and lead chromate systems.

Keywords. Spacing law; cobalt(II) oxinate; silver iodide; lead chromate; revert and direct Liesegang rings; preferential adsorption theory.

1. Introduction

When a reactant diffuses through a gel containing the other reactant that will form a sparingly soluble precipitate, under suitable experimental conditions the precipitation does not spread continuously or quasicontinuously, but separate precipitation zones evolve in the form of concentric rings. This is known as Liesegang phenomenon named after its discoverer. Many sparingly soluble compounds exhibit this phenomenon. Stern (1967) has given a bibliography of the Liesegang rings exhibited by different sparingly soluble substances.

Two types of Liesegang rings have been reported in literature (Stern 1967). They are direct and revert types. In the direct type, the spacing between successive rings increases with increase in the order of the ring from the gel boundary. Gnanam *et al* (1980), Kanniah *et al* (1981a) and Ambrose *et al* (1982) have reported the direct Liesegang rings of calcite, cobalt(II) oxinate and magnesium hydroxide respectively. In the revert type, the spacing between successive rings decreases as the order of the ring increases from the gel boundary. Mathur and Ghosh (1958), Flicker and Ross (1974) and Kanniah *et al* (1981b, 1983) have reported the revert Liesegang rings of silver chromate, lead iodide and silver iodide respectively.

In this paper the existing spacing laws of Jablczynski (1923) and Mathur (1961) are applied to the Liesegang rings of cobalt(II) oxinate, silver iodide and lead chromate in agar gel. A new spacing law applicable to both revert and direct Liesegang rings is proposed on the basis of the preferential adsorption theory. It is experimentally verified with silver iodide and lead chromate systems.

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2. Experiment

2.1 Direct Liesegang rings of cobalt(II) oxinate

AnalaR oxine (1.3068 g) is dissolved in 2N acetic acid solution. To this solution is added 25% ammonia solution drop by drop until a faint but permanent turbidity is obtained. A few drops of acetic acid are added to this solution which is just sufficient to dissolve the turbidity and produce a clear solution with pH 4.25. This oxine solution is mixed with agar-agar gel solution which is made up to 300 ml with hot distilled water. This gives 0.03 M oxine in 1% agar. Similarly 1% agar-agar solutions containing oxine of concentrations ranging from 0.01 to 0.06 M are prepared. These clear solutions (50 ml) are poured into corning glass tubes of 20 mm diameter and allowed to set. After 3 hr, 10 ml of cobalt(II) nitrate solutions of 1.031, 0.859, 0.687, 0.515 and 0.344 M concentrations are carefully poured into the tubes over the set gel. Within a week, sharp brown coloured disc-like precipitate rings demarcated by clear void spaces are obtained.

2.2 Revert and direct Liesegang rings of silver iodide

Agar gel of 1% by weight is prepared by boiling agar with distilled water until all undissolved particles are removed. Potassium iodide of concentration ranging from 0.001 to 0.0065 M is mixed along with the gel. Silver nitrate solution (5 ml) of concentration ranging from 0.25 to 2 M is taken over the set gel. Since silver iodide is photosensitive, the tubes are covered with black paper. The experiments are carried out at room temperature. Revert Liesegang rings of silver iodide followed by direct type have been observed in the same tube.

2.3 Revert and direct Liesegang rings of lead chromate

Hot 1% agar gel solution (75 ml) containing lead nitrate is poured into a corning glass tube of 20 mm diameter. The concentration of lead nitrate in the gel is kept in the range of 0.001 to 0.01 M. After 3 hr of gel setting, 10 ml of potassium chromate solution of concentration ranging from 0.25 to 2.0 M is taken over the gel. Sharp yellow-coloured rings are formed with pale yellow colloidal lead chromate in the spacing between the rings. The spacing between successive rings progressively decreases, reaches a minimum value and then gradually increases with increasing order of the ring from the gel boundary (figure 1).

The experiments are carried out at room temperature, 30°C. The positions of the rings are measured accurately with a cathetometer. The flocculation value was computed with IBM 1130 computer.

3. Discussion

3.1 Jablczynski's spacing law

Jablczynski (1923) proposed the first spacing law governing the position of the ring (x)

$$x_n = x_0 p^n, \quad (1)$$

where p is known as the spacing coefficient, x_0 is a constant and n is the order of the ring

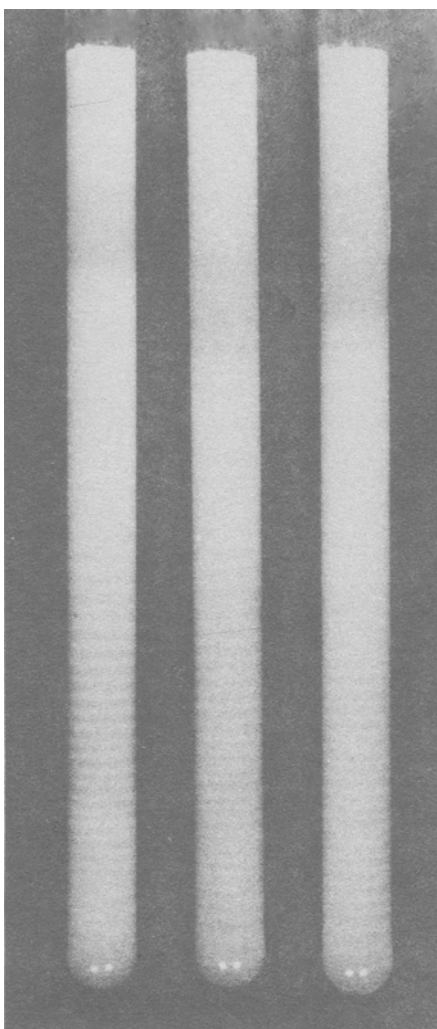


Figure 1. Revert and direct Liesegang rings of lead chromate in 1% agar gel. Concentrations of (i) potassium chromate: 2, 1.5 and 1 M (ii) lead nitrate: 0.005 M.

from the gel boundary. A plot of $\log x_n$ against n should be a straight line. This is true in many systems which exhibit the direct Liesegang phenomenon. Figure 2 represents the experimental verification of Jablczynski's spacing law with the direct Liesegang rings of cobalt(II) oxinate in agar.

Figure 3 represents the plot of $\log x$ against n for silver iodide and lead chromate systems which exhibit the revert type followed by the direct type.

It is very clear from figure 3 that the positions of rings are not governed by Jablczynski's spacing law. The rings are formed at closer and closer distances than predicted by the Jablczynski's spacing law. Although this spacing law satisfactorily explains the direct Liesegang rings, it totally fails to explain the revert type.

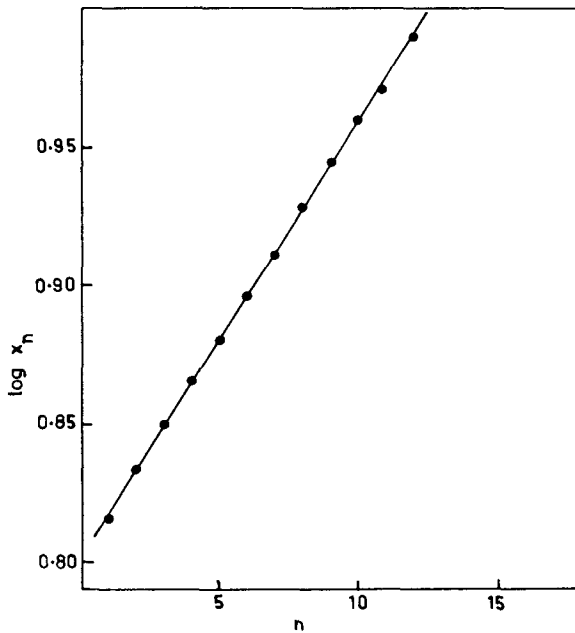


Figure 2. Experimental verification of Jablczynski's spacing law with direct Liesegang rings of cobalt(II) oxinate in agar gel.

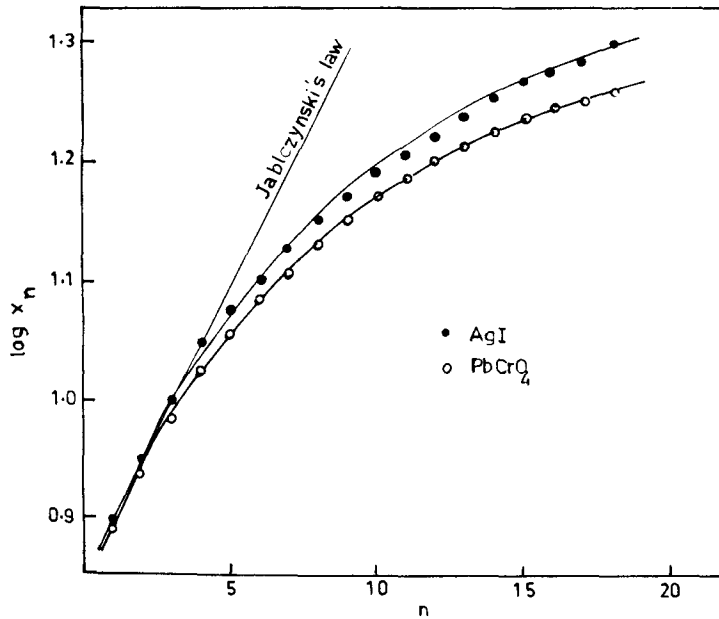


Figure 3. Deviation from Jablczynski's spacing law. Silver iodide system C_{AgNO_3} : 2 M; C_{KI} : 0.005 M. Lead chromate system $C_{K_2CrO_4}$: 1.5 M; $C_{Pb(NO_3)_2}$: 0.003 M.

3.2 Mathur's spacing law

Mathur (1961) modified Jablczynski's spacing law taking the Riemann solution to Fick's diffusion equation as given below:

$$x_n - x_{n-1} = a(S/C_0C'_0) \exp(\alpha x_n), \quad (2)$$

where x_n and x_{n-1} represent the positions of the n th and $(n-1)$ th rings respectively from the gel boundary, S the solubility product, C_0 and C'_0 the initial concentrations of the outer and inner reactants. a and α are the characteristic constants. When α is positive, direct type rings are formed, whereas α is negative for the revert type. Mathur's spacing law can be rewritten as

$$\log(x_n - x_{n-1}) = A + \alpha x_n, \quad (3)$$

where A is a constant. The plot of $\log(x_n - x_{n-1})$ against x_n would give a straight line with positive slope for direct type and negative slope for revert type.

This spacing law has been used to determine the transition point of the revert to direct as represented in figure 4. The point of intersection represents the transition point. However a close analysis of the graph reveals an appreciable deviation from the spacing law especially for the rings with greater interspacing. This is because in the derivation of Mathur's spacing law the rings are assumed to be very close, *i.e.* $x_n - x_{n-1}$ is very small so that

$$\exp[\alpha(x_n - x_{n-1})] \simeq 1. \quad (4)$$

Hence an appreciable deviation from the spacing law is observed whenever the interspacing becomes considerable. In other words, this spacing law is most suitable for

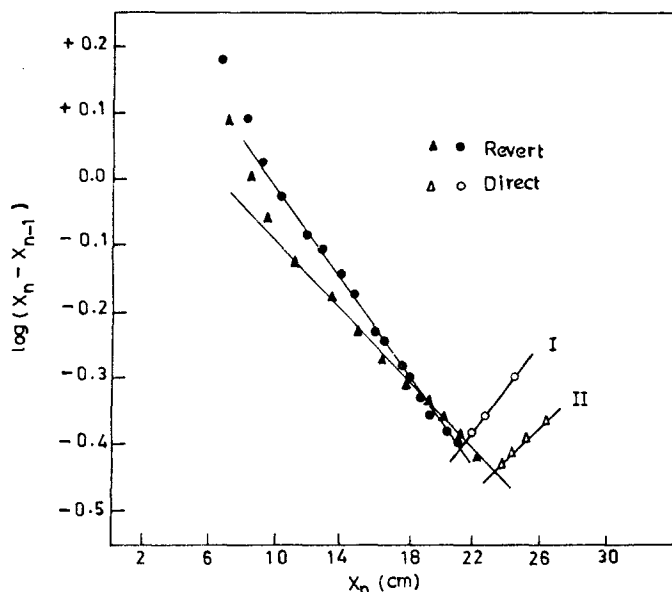


Figure 4. Deviation from Mathur's spacing law I. Silver iodide system; C_{AgNO_3} : 1.5 M; C_{KI} : 0.005 M. II. Lead chromate system, $C_{K_2CrO_4}$: 1 M; $C_{Pb(NO_3)_2}$: 0.005 M.

systems with a small number of closely-packed rings. Silver iodide and lead chromate systems contain more than 25 rings and with considerable interspacing. Hence there is an appreciable deviation from Mathur's spacing law (figure 4).

3.3 New spacing law for the revert and direct Liesegang rings

3.3a *Preferential adsorption theory of silver iodide system*: We have recently published (Kanniah *et al* 1983) the preferential adsorption theory of silver iodide system on the basis of the Derjaguin Landau Verwey Overbeek (DLVO) theory of the colloidal stability (Verwey and Overbeek 1928).

The concentration of silver nitrate taken over the set gel is many times greater than that of inner electrolyte, potassium iodide. When silver nitrate diffuses into the gel impregnated with potassium iodide, it first forms silver iodide particles. The preferential adsorption of excess silver ions on the surface of AgI results in the formation of positively charged silver iodide sol. Thus the silver ions peptise the silver iodide particles. The amount of the silver ions adsorbed on AgI and hence the peptising capacity are proportional to the initial concentration of the diffusing electrolyte. The surface potential of the particle (ψ_0) depends on the concentration of silver ion according to the equation

$$\psi_0 = b \log C_{Ag^+} = -b p Ag, \quad (5)$$

where b is a constant. As the concentration of silver ion progressively decreases from the gel boundary, the adsorption is maximum at the beginning and progressively decreases downwards. The surface potential (ψ_0) and hence the stability of the sol decrease from the gel boundary. The flocculation is effected by the counter ions which reduce the total interaction potential between the sol particles to a minimum value.

According to the DLVO theory of colloidal stability (Kruyt 1952), the characteristic concentration of the outer electrolyte (Γ) to trigger the flocculation turns out to be

$$\Gamma = 8 \times 10^{-33} \psi_0^4 / A^2 Z^2 \text{ mol/l}, \quad (6)$$

where ψ_0 is expressed in mV. As there is a concentration gradient from the gel boundary, the surface potential ψ_0 and hence the flocculation value (Γ) progressively decrease from the gel boundary leading to the formation of bands at closer and closer distances *i.e.*, revert Liesegang rings. As the surface potential progressively decreases, a point is reached where it is equal to zero. This point is called the zero point of charge and in the present case it is the transition point of the revert Liesegang rings to direct rings.

Below the transition point the charge of AgI is reversed from positive to negative due to the release of silver ion from the AgI crystal lattice. In the crystal lattice of AgI the more polarizable iodide ion is more strongly held than the silver ion. When the concentrations of the two ions are equal, the silver ion escapes more readily and the particle is negatively charged (Mysels 1959). As the sol is formed farther and farther away from the transition point, the silver ion escapes more and more resulting in the increase of the negative surface potential. Now the positive ions namely silver and potassium act as the counter ions which trigger the flocculation. As the negative surface potential increases, the flocculation value (Γ) progressively increases with increasing order of the ring. Hence the rings are formed farther and farther away leading to the formation of direct Liesegang rings.

Shinohara (1970) has revised the coagulation theory of Dhar and Chatterji (1924)

and derived the quantitative relation for the flocculation value (Γ) as

$$\Gamma = C_{10} \left[1 - \frac{G(f_1)}{G(f)} \right], \quad (7)$$

where

$$f_1 = f/p \text{ and } p = x_{n+1}/x_n \quad (8)$$

and

$$G(f) = \frac{1}{(2\pi)^{1/2}} \int_0^f \exp\left(-\frac{1}{2}\eta^2\right) d\eta. \quad (9)$$

If the spacing coefficient p is a constant for any two consecutive rings, then Γ is a constant. However in the silver iodide system as the spacing between successive rings progressively decreases up to the transition point and then increases gradually, Γ decreases up to the transition point and then progressively increases with increasing

Table 1. Variation of the flocculation value (Γ) with the position of the ring (x_n) in the silver iodide system (C_{AgNO_3} :0.75 M; C_{KI} :0.005 M).

Order of the ring n	Position of the ring x_n (cm)	Spacing coefficient $p = x_{n+1}/x_n$	Inter-spacing $x_n - x_{n-1}$ (cm)	Flocculation value Γ (mmol/l)
1	7.903	—	—	—
2	8.955	1.133	1.052	10.01
3	9.977	1.111	1.012	7.73
4	10.979	1.104	1.002	7.23
5	11.794	1.074	0.815	4.75
6	12.579	1.067	0.785	4.21
7	13.354	1.062	0.775	3.84
8	14.001	1.048	0.647	2.84
9	14.678	1.048	0.677	2.84
10	15.365	1.047	0.687	2.79
11	15.946	1.038	0.581	2.20
12	16.519	1.036	0.573	2.06
13	17.093	1.035	0.574	1.99
14	17.616	1.031	0.523	1.73
15	18.122	1.029	0.406	1.62
16	18.602	1.027	0.480	1.51
17	19.122	1.028	0.520	1.56
18	19.573	1.024	0.451	1.32
19	20.037	1.024	0.464	1.32
20	20.506	1.023	0.469	1.25
21	20.896	1.019	0.390	1.02
22	21.400	1.024	0.504	1.32
23	21.817	1.020	0.417	1.09
24	22.320	1.023	0.503	1.25
25	22.755	1.020	0.435	1.09
26	23.166	1.018	0.411	0.96
27	23.624	1.020	0.458	1.09
28	24.135	1.022	0.511	1.21
29	25.268	1.047	1.133	2.79

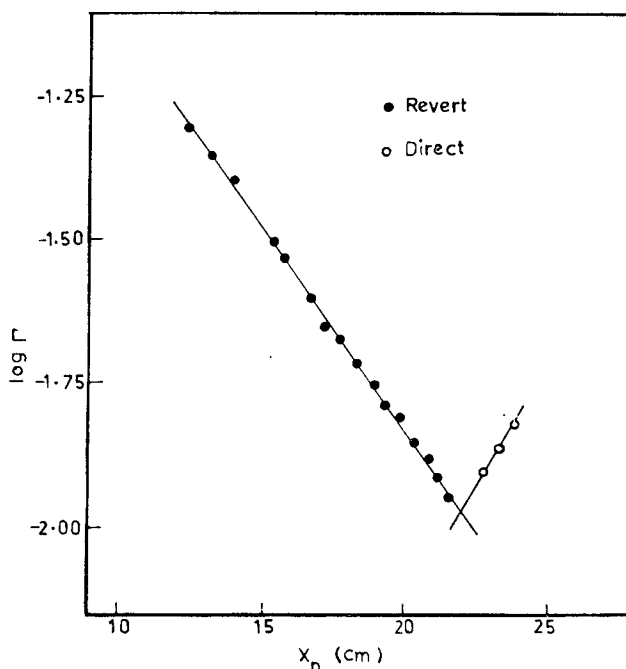


Figure 5. Experimental verification of the new spacing law with revert and direct Liesegang rings of silver iodide C_{AgNO_3} : 1.5 M C_{KI} : 0.005 M.

order of the ring from the gel boundary. Table 1 gives the variation of the flocculation value (Γ) with the order of the ring (n).

The plot of the $\log \Gamma$ against the position of the ring (x_n) gives a straight line as represented in figure 5. This can be mathematically expressed as

$$\log \Gamma_n = a - b x_n, \quad (10)$$

where a and b are constants. Considering two successive rings

$$\log \Gamma_{n+1} = a - b x_{n+1} \quad (11)$$

or

$$\log \frac{\Gamma_n}{\Gamma_{n+1}} = b(x_{n+1} - x_n), \quad (12)$$

where x_{n+1} and x_n are the corresponding distances of the $(n+1)$ th and n th rings from the gel boundary and Γ_{n+1} and Γ_n are the respective concentrations of the outer electrolyte to trigger the flocculation of the sol leading to the ring formation. This spacing law (equation (12)) is applicable to both revert and direct Liesegang rings.

This spacing law is valid under different experimental conditions for obtaining revert and direct Liesegang rings of silver iodide. The best fit of the positions of the rings (figure 5) with the straight line represents the superiority of this spacing law over the existing spacing laws of Jablczynski and Mathur.

3.3.b Lead chromate system: When a concentrated potassium chromate solution is

allowed to diffuse into the gel impregnated with lead nitrate of very low concentration, a negatively charged lead chromate sol is formed due to the preferential adsorption of excess chromate ion on lead chromate particles. Lee and Meek (1968) have established that the adsorption of chromate ion on lead chromate follows a logarithmic relation with the initial concentration of potassium chromate solution taken over the gel. Due to the adsorption of chromate ion, an electric double layer is constituted with chromate ion at the stern layer and the positively charged counter ions—potassium—predominantly at the diffuse layer. The diffuse layer also contains the negative ions due to the interpenetration of the ionic distribution.

The primary stability of the sol results from the surface charge determined by the adsorption of chromate ion. The surface potential (ψ_0) which is a measure of surface charge is related to the concentration of chromate ion as per the Lee and Meek's (1968) relation,

$$\psi_0 = a \log C_{\text{CrO}_4^{2-}} \quad (13)$$

where a is a constant. According to the DLVO theory (Kruyt 1952) the surface potential (ψ_0) is related to the flocculation value (Γ) as

$$\Gamma = 8 \times 10^{-33} \psi_0^4 / A^2 Z^2 \text{ mol/l.} \quad (6)$$

Due to the imposed concentration gradient of the diffusing electrolyte from the gel boundary the concentration of the chromate ion progressively decreases. This results in the lowering of surface potential and hence the flocculation value leading to the formation of rings at closer and closer distances up to the transition point. The zero point of charge is the point of transition from the revert to direct Liesegang rings. Due to the reversal of charge of the sol (Morimoto 1964) after the transition point, a positively-charged sol of lead chromate is formed. With increasing distance from the transition point the magnitude of the positive surface potential increases leading to an increase of flocculation value (Γ). Hence rings are formed further and further apart from each other resulting in the direct type of rings.

By suitably modifying the revised coagulation theory of Shinohara (1970), the flocculation value (Γ) at each ring has been computed (table 2). The proposed spacing law is verified with lead chromate system. The best agreement with the experimental results is well illustrated by figure 6.

4. Conclusions

Jablczynski's spacing law is valid with the direct Liesegang rings only. Mathur's spacing law explains satisfactorily the Liesegang phenomenon of a system with a smaller number of closely packed rings. The proposed spacing law satisfactorily explains both direct and revert systems.

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Table 2. The dependence of flocculation value (Γ) on the position of the ring (x_n) in the lead chromate system ($C_{K_2CrO_4}$: 1 M; $C_{Pb(NO_3)_2}$: 0.003 M).

Order of the ring n	Distance of the ring (x_n) (cm)	Spacing coefficient p	Flocculation value Γ (mmol/l)
1	6.794	—	—
2	8.045	1.184	12.127
3	9.017	1.121	7.096
4	9.716	1.077	4.103
5	11.121	1.074	3.916
6	11.745	1.056	2.833
7	12.408	1.056	2.833
8	12.953	1.044	2.167
9	13.526	1.044	2.167
10	14.052	1.039	1.905
11	14.574	1.037	1.799
12	15.050	1.033	1.589
13	15.544	1.033	1.589
14	16.004	1.030	1.426
15	16.429	1.027	1.286
16	16.870	1.027	1.286
17	17.274	1.024	1.128
18	17.682	1.024	1.128
19	18.075	1.022	1.032
20	18.421	1.019	0.880
21	18.825	1.022	1.032
22	19.215	1.021	0.974
23	19.491	1.014	0.639
24	19.852	1.019	0.880
25	20.180	1.017	0.786
26	20.499	1.016	0.731
27	20.824	1.016	0.731
28	21.140	1.015	0.694
29	21.470	1.016	0.731
30	21.819	1.016	0.731
31	22.133	1.014	0.639
32	22.477	1.016	0.731
33	22.807	1.015	0.694
34	23.129	1.014	0.639
35	23.457	1.014	0.639
36	23.803	1.015	0.694
37	24.157	1.015	0.694
38	24.630	1.020	0.936
39	25.073	1.018	0.823
40	25.620	1.022	1.032

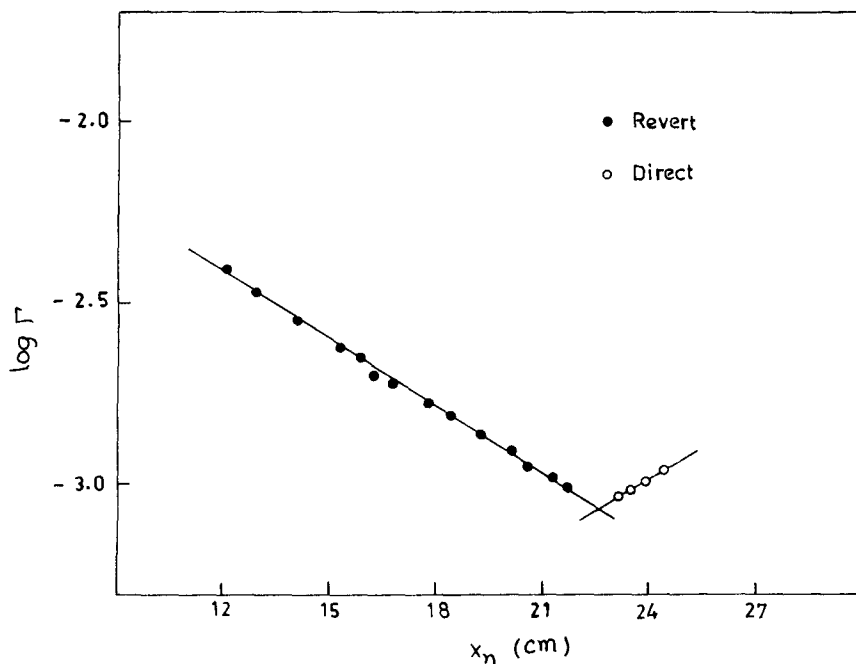


Figure 6. Experimental verification of the new spacing law with revert and direct Liesegang rings of lead chromate $C_{K_2CrO_4}$: 1 M; $C_{Pb(NO_3)_2}$: 0.005 M.

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