*Structural Analysis of Liesegang Ring Systems**

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Since the discovery of the phenomenon of Liesegang ring several types of ring systems have been produced which on the structural basis may be broadly classified into the following categories:

a) Direct and revert systems
b) Macro and micro ring systems
c) Void spaced and continuous banded systems.

In the present paper these classifications have been analyzed in the light of the quantitative theory advanced by the author[1] in an earlier communication to this journal for the phenomenon of Liesegang rings.

Direct and Revert Systems

In the previous communication, the author obtained the following equations for Liesegang ring phenomenon,

$$(x_n - x_{n-1}) = a\left(\frac{S}{C_0 C'_0}\right) e^{\alpha x_n} \qquad (1)$$

or

$$(x_n - x_{n-1}) = K \qquad (2)$$

where x_n and x_{n-1} represent the distances of nth and $(n-1)$th rings respectively from the initial level of diffusion, S the solubility product, C_0 and C_0' the initial concentrations of the two ions and a, α and K the characteristic constants.

It can be seen that the two different types of ring systems are possible as α in Eq. 1 is negative or positive. When α is positive the distances between the successive rings $(x_n - x_{n-1})$ would increase with the increase of x_n as is commonly observed for this phenomenon. When α is negative the rings separation would decrease in the direction of diffusion of flocculating solution. Thus two different types of ring systems, which may be called a "Direct" and Revert" systems respectively could be produced.

Mathur and Ghosh[2] noted that if a diffusing electrolyte renders high peptizing influence or dissolves out the precipitate formed as a result of the interaction of the two ions, the decrease in the concentration of the peptizing ion along the diffusion path would lead to the "Revert" system of rings. The authors have noted that the ferricyanides of copper, iron, nickel and silver are peptized by the excess of the same metal ions, and this effect is more marked in the case of copper, iron, nickel and uranium ferricyanides and at the same time the revert systems have also been observed to be more prominent in these precipitate systems. Pactor[3] obtained a revert type of rings system by diffusing a solution of ammonia through a silver chromate solution peptized by acitic acid in gelatin gel. Hook[4] has obtained revert type of Liesegang ring systems of zinc, nickel, cobalt, ferrocyanides, nickel, zinc and iron cyanides, barium and mercury vandates and cerrous oxalate in gelatin medium and of chromium hydroxide and uranyl carbonate in agar-agar gel.

Periodic precipitations of "Direct" nature are of common occurrence. Silver chromate system in gelatin gel is a well known example of this type of banded structure.

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[1] P. B. Mathur, This Bulletin, **34**, 437 (1961); Ph. D. Thesis, Allahabad University, p. 25—51, (1956); *J. Colloid Sci.*, June (1960).

[2] P. B. Mathur and S. Ghosh, *Kolloid-Z*, **159**, 2, 143 (1958).

[3] A. Packter, *Nature*, **175**, 556 (1955).

[4] A. van Hook, *J. Phys. Chem.*, **41**, 593 (1937).

Macro and Micro Ring Systems

Gel or other peptizing agents influence the precipitation of an sparingly soluble salt by keeping the coarser matter in colloidal state. The nature of the distributed matter in a system of periodic precipitation under the influence of environmental conditions can be ascertain from Fig. 1 which is a graphical representation of the ionic product relation obtained in the previous communication[5].

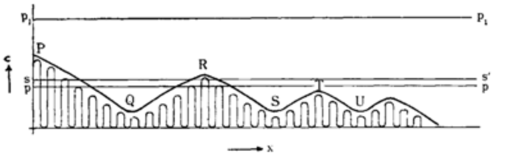

Fig. 1

$$C_nC_n{}' = [C_0C_0{}'\mathrm{e}^{-(\alpha'\pi/2\beta')}]\,\mathrm{e}^{\alpha'(x_n-x_{n-1})}$$
$$\times \sin\{\beta'(x_n-x_{n-1})\}$$
$$\times \cos(\beta' x_n)\mathrm{e}^{-\alpha x_n} \qquad (3)$$

or

$$C_nC_n{}' = a\,\mathrm{e}^{[\alpha'(x_n-x_{n-1})]}\mathrm{e}^{-(\alpha x_n)}$$
$$\times \sin[\beta'(x_n-x_{n-1})]\cos(\beta x_n) \qquad (4)$$

where $C_nC'_n$ is the ionic product and α, α', $\beta'\beta$ and a are characteristic constants. In Fig. 1, SS' represents the solubility product level and PP' the peptizing level. The insoluble substance formed by interaction of diffusing ions would exist in precipitate or in peptized form according as PP' is very close to or high above the SS' level.

When the peptizing level PP' is little above SS' and cuts the ionic product curve at several places, the sparingly soluble matter will precipitate out in the regions where the ionic product curve rises above PP'. Thus, at P, R, T regions the precipitate bands would appear. At intermediate spaces Q, S, U etc., where the ionic curve falls below PP' the residual matter will exist in colloidal state. The distribution of this colloidal matter along the diffusion column would also be of periodic nature following the curve 1. Thus, translucent micro-sealed ring systems of tracer colloidal material would be produced in between the precipitate bands. Such a type of structure has been observed by several workers notedly Hedges and Henley[6], Dounin and Shamyakin[7] and Mathur and Ghosh with silver chromate in gelatin medium.

The possibility of another type of such fine system is also apparent from Eq. 4. If in Eq. 4 the damping coefficients α and α' are almost negligible the factor

$$\exp[\alpha'(x_n-x_{n-1})-\alpha x_n]$$

tends to unity and Eq. 4 reduces to the form

$$C_nC_n{}' = a\sin[\beta'(x_n-x_{n-1})]\cos(\beta x_n)$$

which is an equation of the Simple Harmonic Curve (Fig. 2). In such systems whatsoever be the position of PP' closely packed fine rings without any large size void spaces in between them, would be discerned. The fine ring systems will be of precipitated material when PP' would cut the ionic produt curve, and of colloidal matter when PP' would be situated above it. Mathur and Ghosh have been able to obtain the micro-sized Liesegang ring systems of cobalt and silver ferricyanide under suitable experimental conditions.

Void Spaced and Continuous Banded Systems

Let us now consider the case where damping factor $\exp(\alpha\, x_n)$, in Eq. 4 is large enough and at the same time the peptizing influence of the medium or of the ions present therein is moderately high on the insoluble substances. Such a system will graphically be represented by the curve P, Q, R, S and $P_1P_1{}'$ shown in Fig. 1. If, due to high peptizibility of the insoluble salt the position of PP' is just above the ionic product curve or if PP' cuts the curve at some of its maxima points, the insoluble substance will exist both in colloidal as well as in precipitate form showing a continuous deposition of matter throughout the diffusion column. Due to the fact that the concentrations of ions in the regions of maxima and minima points very markedly, the colloidal particles in the neighbourhood of maxima points P, R, T will be much coarser due to the high concentration of the peptizing matter in this region in comparison to that in the minima regions. Such a system will therefore form bands of different size particles within a

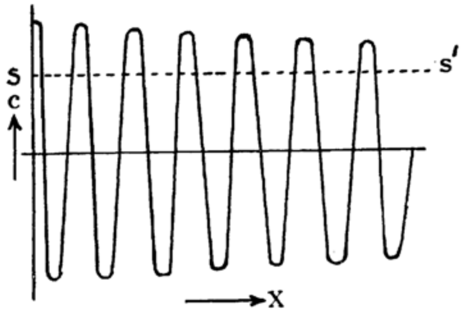

Fig. 2

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[5] P. B. Mathur, *Loc. cit.*

[6] E. S. Hedges and R. V. Henley, *J. Chem. Soc.*, **1928**, 2715.

[7] M. S. Dounin and F. M. Shemyakin, *Kolloid-Z*, **48**, 167 (1928).

continuous deposition, which will appear as alternate bands of different colors.

In cases where peptizing level is very high so much so that high concentration of a stable colloid may be produced, a very fine ring structure of colloidal matter, may appear but if it is too packed it may be left undetected.

Dhar and Chatterji⁽⁸⁾ obtained a continuous banded system for mercuric iodide in agar gel, where a thick red color precipitate bands are followed by yellow ones and vice versa. Hatschek⁽⁹⁾ noted a similar structure for cadmium sulphide in gelatin gel; Rastogi and Chatterji⁽¹⁰⁾ reported for certain insoluble rare earth salts; Mathur and Ghosh for silver ferrocyanide and uranium ferricyanide.

Void spaced systems have already been discussed in the earlier communication. From Fig. 1, it can be seen that when peptizing level PP′ is close to the ionic product curve P, Q, R, S, the precipitate regions will be followed by void spaces and not by thick colloid bands, and so a void spaced ring system will be obtained.

It may, therefore, be concluded that the factors which control the Shape of Liesegang ring systems in gel media are (a) the damping coefficients α and α' of Eq. 3, and (b) the peptizability of the precipitate in particular environment, or say, the stability of the colloid formed under the conditions of the system. However, it may clearly be understood that colloidal formation like other factors simply influence the shape of rings in gel media, but it itself is not the cause of rhythemic phenomenon. The nature of diffusion is mainly responsible for the phenomenon, as explained in the earlier communication.

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8) N. R. Dhar and A. C. Chatterji, *J. Phys. Chem.*, **28**, 41 (1924); *Kolloid-Z.*, 37, 2 (1925).

9) E. Hatschek, *Kolloid-Z*, 37, 297 (1925).

10) M. C. Rastogi and A. C. Chatterji, *J. Indian Chem. Soc.*, **28**, 283 (1951).