CCCLXXIII.—*The Formation of Periodic Structures by Salting-out and by Coagulation.*

By ERNEST SYDNEY HEDGES.

THE question whether the insoluble substance which is finally precipitated in the form of periodic structures such as Liesegang rings exists primarily as a highly supersaturated solution or as a colloidal solution which is protected by the gelatinous reaction medium has already received some attention. The experiments of Sen and Dhar (*Kolloid-Z.*, 1924, **34**, 270) and of Chatterji and Dhar (*Trans. Faraday Soc.*, 1926, **23**, 233; *J. Indian Chem. Soc.*, 1928, **5**, 175) suggest that, when a dilute solution of potassium chromate in gelatin at the concentrations ordinarily used in making Liesegang rings is treated with an equivalent of silver nitrate, the silver chromate, which is not precipitated under these conditions, remains in colloidal solution and shows little diffusion or electrical conductivity. On the other hand, the diffusion and electro-conductivity experiments of Williams and Mackenzie (J., 1920, **117**, 844), of Bolam and Mackenzie (*Trans. Faraday Soc.*, 1926, **22**, 151, 162), and of Bolam (*ibid.*, 1928, **24**, 463) favour the view that the silver chromate exists as a highly supersaturated molecular solution.

Hedges and Henley (J., 1928, 2714) separated the formation of this type of periodic structure into two stages. In the first stage, dilute solutions of the two reagents in sols of gelatin or agar were mixed, and the mixture was allowed to cool and form a gel without production of any precipitate, and in the second stage a concentrated solution of one of the reagents was allowed to diffuse into the gel, whereupon the insoluble substance was precipitated in the form of a periodic structure. It may be concluded from these experiments that the formation of the periodic structure is not the result of a periodic chemical reaction, but is a secondary phenomenon taking place after the completion of the reaction. On the assumption that the final precipitate was present in colloidal form at the end of the first stage, it followed that the rings were formed as a periodic coagulation process in the second stage.

It is perhaps unwise to attempt to distinguish sharply between the condition of a little-understood, highly supersaturated, " molecular " solution and a highly disperse, colloidal solution, but if the solutions obtained at the end of the first stage can be regarded as molecular, the second stage becomes a salting-out process by a common ion rather than one of coagulation. Hedges and Henley (*loc. cit.*, p. 2719) also showed that 1% agar gel would hold as much as five times the amount of lead iodide corresponding to the ordinary solubility in water at that temperature; it was assumed that the excess was present as a colloidal sol protected by the agar, but even on that assumption it must still be supposed that at least 20% of the lead iodide must be molecularly dissolved. It appears, therefore, that the bands of precipitated lead iodide produced when 20% potassium iodide solution is allowed to diffuse into such a mixture may be formed by a periodic salting-out of lead iodide by potassium iodide rather than by a coagulation process.

Experiments have been carried out to determine whether such periodic structures can be formed by a pure salting-out process in the absence of colloids, and thus to differentiate the phenomenon from coagulation as understood by colloid chemists. For this purpose, hydrochloric acid was allowed to diffuse into sodium chloride solutions, for example, and the experiments were conducted in capillary tubes; this method not only obviated the necessity of having a gel present, but also had the advantage of eliminating the complications due to reactions between the gelatinous medium itself and any or all of the reactants or products.

The procedure adopted was to allow the salt solution to rise in a capillary tube of about 0·5 mm. diameter, seal off the top end of the tube, leaving the lower end open, and place it in a horizontal position in a corked test-tube containing the acid, which could thus diffuse into the capillary. This method was found to be superior to the practice of placing the capillary tube upright in the diffusing solution, for in such a position the precipitate often becomes dislodged from the wall, falls down the tube, and interferes with the diffusion process.

An example of the results is afforded by the upper tube in Fig. 1, where the capillary tube contained 30% sodium chloride solution and the outer diffusing liquid was concentrated hydrochloric acid (*d* 1·16). After some days, eight bands of sodium chloride had appeared in the tube. The distances between successive bands, starting at the open end (right in Fig. 1) of the tube, were 4·0, 6·0, 8·5, 11·5, 10·5, and 18·0 mm. (The last band became displaced before the photograph was taken.) It will be seen that the spacing increases throughout the diffusion as in the ordinary Liesegang phenomenon; similarly, the thickness of the successive bands increases from 1·0 to 1·5 mm. Experiments with 20% sodium chloride in the capillary tube were equally successful. Similar periodic structures were obtained in the salting-out of concentrated potassium chloride solutions by hydrochloric acid (lower tube in Fig. 1) and of barium nitrate by nitric acid.

By eliminating both chemical reaction and colloid-chemical processes, these experiments are perhaps the simplest examples of the formation of periodic structures by diffusion yet investigated, and

Fig. 1.

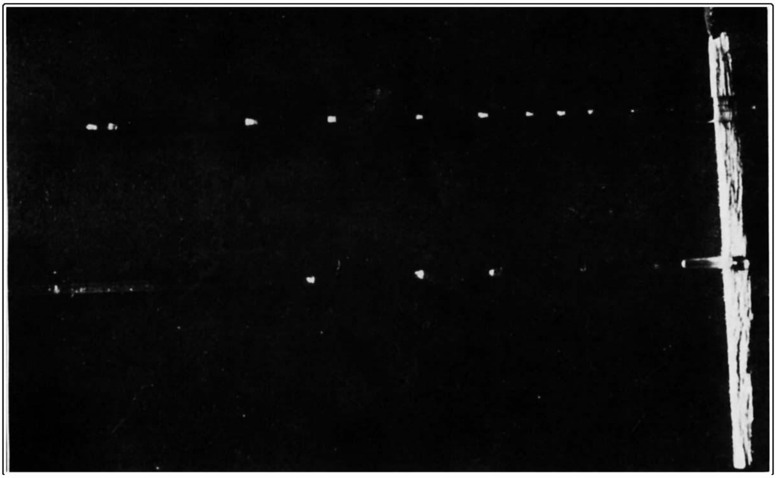

Fig. 2.

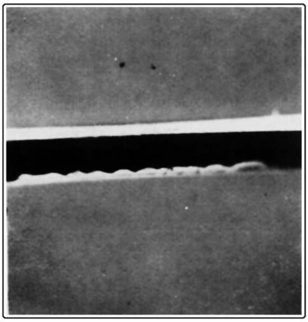

Fig. 3.

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they appear to be at variance with some of the best-known theories of the formation of Liesegang rings. Bradford's "adsorption theory" (*Biochem. J.*, 1916, **10**, 169; 1917, **11**, 14) supposes that the spaces between the rings are caused by the adsorption of the electrolyte contained in the gel by the adjacent layer of precipitate: such adsorption will more probably occur if the precipitate is in a highly disperse state and bands can in some cases be obtained or not, at will, by varying the conditions affecting the dispersity of the precipitate. In the salting-out experiments described above, the "bands" of precipitate consisted sometimes of large single crystals, but generally of aggregates of a few relatively large crystals. The spaces between were perfectly devoid of solid. Adsorption would be negligible on crystals of such extremely small specific surface. The "diffusion wave" theory of Wo. Ostwald (*Kolloid-Z.*, 1925, **36**, 380) postulates the occurrence of a definite chemical action and ascribes the most important rôle to the diffusion of the soluble reaction product. In the experiments described above, however, this third diffusible product has been eliminated: there are only two diffusion waves to be considered—those of hydrochloric acid and of sodium chloride.

Some further experiments have been done on the coagulation of colloidal arsenious sulphide by ferric chloride solutions. Hedges and Henley (*loc. cit.*, p. 2722) observed a periodic coagulation of arsenious sulphide sol contained in an agar gel by allowing solutions of ferric chloride to diffuse into the mixture. In the present experiments, a 0·1% sol of arsenious sulphide was contained in a series of capillary tubes, open at one end, which were then immersed in solutions of ferric chloride varying in concentration from 1 to 30%. In these capillary experiments, definite bands of precipitate were not formed, but the coagulum consisted of an undulatory filament of a "crimped" character. The distance between successive peaks of these "waves" was generally 2—5 mm. At the author's suggestion, these experiments have been repeated at the laboratories of the British Research Association for the Woollen and Worsted Industries, Leeds, by Miss M. H. Norris, under the direction of Dr. S. G. Barker, Director of Research, who has taken the photographs shown in Figs. 2 and 3. The structure in Fig. 2 was obtained by putting a 0·25% (approx.) sol of arsenious sulphide in the capillary tube, open at one end, and immersing it for 2 days in a 10% solution of ferric chloride: Fig. 3 shows a portion under higher magnification. This is a new kind of periodic structure and may be of interest in connexion with the waviness of many natural colloidal fibres such as wool. It appears, therefore, that periodic structures can be produced by simple coagulation as well as by simple salting-out.

The considerations outlined above tend to annihilate a sharp distinction between the coagulation of a sol and precipitation by exceeding the supersolubility limit, and bring Wilhelm Ostwald's "supersaturation theory" ("Lehrbuch der allgemeinen Chemie," Leipzig, 2nd edn., 1898, ii, 778) into line with the coagulation theory of periodic structures. It is not proposed to add to the existing number of theories of the formation of periodic structures, but it may be pointed out that the essential condition for periodicity is the existence of some *critical condition* determining a change which proceeds to completeness once the critical value is reached. In an investigation of the cause of periodic phenomena in electrolysis and in the chemical passivity of iron, it has been shown (Hedges, this vol., p. 1028) that these phenomena are determined by the rate at which a certain critical concentration of ions can be reached by diffusion. In the formation of periodic structures by precipitation it seems possible that a critical concentration is again involved : at least, the coagulation of sols by electrolytes is associated with a definite threshold concentration. A theory of the formation of periodic structures based on the idea of a critical concentration value for coagulation of the primarily formed sol has been advanced by Freundlich ("Colloid and Capillary Chemistry," 1926, p. 735) and appears to be capable of extension to include structures formed by salting-out.

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