X. ON THE THEORY OF GELS. II. THE CRYSTALLISATION OF GELATIN.

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IN a previous paper [1918] it has been shown that the reversible gelation of the natural emulsoids is a crystallisation process resulting from the viscosity of these substances and from their very small diffusion constants which greatly retard the crystallisation of the cooling sols, allowing the accumulation of a large excess concentration. Thus the two factors K and P in von Weimarn's formula are both so large that, with a small value of L , a very great number of crystallisation centres are produced, and a gel is formed. Detailed examination of the theory showed that it was sufficient to explain the numerous properties of gels. It was also pointed out that complex organic substances and those which are highly aggregated in solution tend to crystallise in the form of spherites, built up of a great many crystalline needles arranged radially, the interstices being filled with liquid giving the appearance of a globular crystal. The inference was drawn that organic gels are usually composed of submicroscopic spherites bathed in the mother-liquor from which they have crystallised, though in certain cases the ultimate crystalline particles may be of other forms.

This conception of gelation is in complete agreement with recorded experimental results: the variation in intensity of the Tyndall cone observed by Arisz [1915]; the development of submicrons seen by Menz [1909] in gelating 2 % gelatin, which increased from 4 or 5, showing Brownian movement, in a square division of the field with a side of 9μ , to 80 or 100, at rest, in the same space; the actual observation by Hardy [1912] of microscopic spherites, *i.e.* 10μ , in reversible carbon tetrachloride gels of 5-dimethylaminoanilo-3 : 4-diphenylcyclopentene-1 : 2-dione; and the globulitic ultramicroscopic structure of natural organic hydrogels from which the water had been expressed, recorded by Bachmann [1911]. Moreover it was shown that gelatin can readily be precipitated by alcohol in the form of spherites.

The utility of von Weimarn's theory is not confined to the explanation of the colloid state. It indicates, further, the conditions necessary to obtain a given substance in any desired form. If his formula explains the usual occurrence of gelatin in the colloid condition, it should be possible, by suitable modification of the factors, to reduce the number of crystallisation centres sufficiently to obtain microscopic crystals of gelatin from water. The form in which such crystals would be expected to occur is that of spherites.

Since Bütschli [1896] found that the liquid expressed from 5 % gelatin gels contains from 0.16 to 0.46 % of gelatin, the solubility of this substance in water must be about this value. To obtain larger crystals of gelatin it should be necessary merely to reduce the concentration of the crystallising sols to about this degree. Hydrosols of Nelson's "Crystal" leaf gelatin were made of 0.5 and 0.3 %. These were quickly heated to 100° and filtered into small crystallising dishes which had been previously cleaned with chromic acid mixture. The dishes were covered with lids and the liquid allowed to evaporate spontaneously at room temperature. The sols were only very slightly opalescent at first, but, particularly in the case of the 0.5 % sols, the opalescence soon developed to an extraordinary degree, reaching a dense milky, and almost opaque, appearance by the third day. After a few days the cloudiness disappeared and a faint light buff-coloured precipitate was seen on the base of the vessels. The amount of this precipitate slowly increased.

Fig. 1.
Gelatin spherites. $\times 800$.

After about 30 days the supernatant liquid was poured off and the preparations examined under the microscope. In addition to numerous spherites there were, however, many bacteria present. The experiments were, therefore, repeated in the presence of 0.1 % mercuric chloride¹ with similar results, except that bacteria were entirely absent and the spherites perhaps more numerous.

The buff-coloured precipitate was examined most conveniently on the base of the dish with a $\frac{1}{15}$ " oil-immersion objective and 8 $\times$ eyepiece giving a magnification of about 800. That from the 0.3 % sols usually gave the best results. The diagram shows the appearance. Numerous single spherites were seen, mostly of apparently about 2.0 to 2.2 μ , or actually from 0.25 μ to 0.28 μ in diameter. In addition there were many small and some large aggregates of spherites. A number of typical ones are shown in Fig. 1,

¹ The molecular theory of solution [Bradford, 1919] gives reasons for supposing that dilute HgCl_2 would have little effect on the crystallisation of gelatin from water.

usually not more than two or three would be visible at once. The smaller spherites appear to prefer aggregation into filaments of which the individual elements were fairly distinct, but perhaps not quite as marked as in the diagram. The aggregates of larger spherites were usually in the form of colonies. Frequently the filaments appeared to originate from a large spherite, as shown, very much in the same way, on a smaller scale, as filaments often appear to have grown from spherites of silver dichromate and other inorganic substances. Except for the filaments and the more numerous detached spherites, the whole appearance is very similar to that of gelatin precipitated from a dilute sol by alcohol, or to the globulitic appearance observed ultra-microscopically by Bachmann, and to the spherites of mastic and gamboge obtained by Perrin.

Having regard to the appearance at first of the remarkable opalescence and its diminution as the precipitate appears, it cannot be doubted that gelatin crystallises from water exactly as indicated by von Weimarn's theory. The only possible complication in the cooling of the hot sols is that gelatin may melt in contact with water at a comparatively low temperature, so that the first separation may be into two liquid phases, one rich and the other poor in gelatin. Subsequent crystallisation from the more concentrated phase would result in still smaller submicrons.

In conclusion the writer wishes to express his indebtedness to Prof. J. B. Farmer for the kind loan of a high power microscope.

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