XVII. ADSORPTIVE STRATIFICATION IN GELS.

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In a previous paper [Bradford, 1916] the author proposed the theory that the Liesegang phenomenon might be due to gradual adsorption of the solute in the gel by the growing precipitate, so that, the adjacent layer of gel presently becoming exhausted of solute, the reacting substance would be able to diffuse further into the gel before commencing to form a fresh stratum of precipitate. Hatschek [1914] had proved that Ostwald's hypothesis of metastable solutions was not of general application. Moreover experiments with gels containing additional quantities of the soluble products of the double decomposition, which had been assumed by some to play an essential part in the formation of the strata, showed no appreciable effect on their character or separation. The theory affords an explanation of the fact observed by Pringsheim that diffusion takes place from the hypertonic into the hypotonic region, whether liquid or gel, and that, as recorded by the author, in the absence of a precipitate, mutual interdiffusion results. By working with a coloured solute, such as potassium chromate, in the gel, the gradual exhaustion of the zone near the precipitate could be observed. This is shown in Fig. 1 (Plate I) which represents a tube prepared with N/20 K_2CrO_4 in 1 % agar on which a N/5 solution of $Pb(NO_3)_2$ was poured. Stratification became more evident lower down the tube, but the yellow colour was then less marked. Experiments in 1 % agar in which columns of fuller's earth were embedded above dye solutions showed similar adsorption, though not so intense, since the surface was not being constantly renewed by precipitation.

The agar gel is easily prepared by boiling 10 g. of agar sticks in a litre of water and straining through muslin while hot into a wide-mouthed bottle. The resulting gel should be perfectly clear, otherwise stratification may be hindered, or altogether prevented. When required for use a quantity of the

jelly is warmed in a beaker on the water-bath and strained into stoppered test-tubes graduated to contain 15 and 25 cc. The tubes are previously prepared by adding the requisite quantity of standard solutions of the reagents intended, so that, when filled to the 15 cc. mark with agar, the gel will be of the desired concentration. When the gel is set, standard solutions are poured above up to the 25 cc. mark. The concentrations which frequently give the best results are about $N/20$ for the gel and N to $N/5$ for the solution above.

Experiments have been made with a variety of insoluble substances. Potassium iodide treated with lead nitrate, and manganese sulphate with liver of sulphur, are noticeable as rapidly producing clearly defined strata. The structure of the manganese sulphide in Fig. 2 (Plate I) closely resembles that of certain limestone formations from Fulwell Hill district. Precipitates which refuse to stratify when prepared in straight tubes, generally yield the desired result when the reacting solutions are poured into the two limbs of a U-tube half filled with agar gel. Copper carbonate and ferrocyanide, cobalt ferri-cyanide and barium sulphate are examples. As the concentration of the gel falls slowly in U-tube experiments, owing to the reserve of the more dilute reagent in solution above the gel, the discs of precipitate are formed at nearly equal intervals after the first two or three. A necessary condition for the production of clearly defined strata appears to be that the reacting solutions should not be too strong. From his experiments on the adsorption of soluble substances by filter paper Evans [1906] showed that the proportion of solute removed increases with dilution, but that, in the cases examined, no adsorption could be observed in strong solution. After diffusing through a column of gel in a U-tube, the concentrations of the meeting solutions are reduced to the necessary dilution, while sufficient quantities of the reagents are available to produce well defined discs. So far as has been observed, under these conditions stratification is well developed.

The distances between the layers should depend mainly upon C , the concentration of the gel, and the ratio U/C , U being the concentration at the boundary surface between the solid and gel phases at the temperature of the experiment. The distances should therefore be characteristic of the solute in the gel. They should also be affected by the permeability of the precipitate to the reagent diffusing through, and, to some extent, by the rate of diffusion of the reagent in the gel. If the adsorption of one solute is affected by the presence of a considerable quantity of another, as seems to be the case, stratification would also be influenced by increasing the concentration of the

Fig. 1

Fig. 2

Fig. 3a

Fig. 3b

reagent above the gel. In the case of a pair of reagents with different ratios U/C , the distances apart of the strata should turn upon which of the reagents is dissolved in the gel. This is illustrated by the tubes represented in Figs. 3 *a* and 3 *b* (Plate I). The former contained N/20 KI in 1 % agar with N/2 $\text{Pb}(\text{NO}_3)_2$ solution above, while in the latter tube the gel was made up with N/20 $\text{Pb}(\text{NO}_3)_2$ and treated with N/2 solution of KI.

Fig. 5

Fig. 6

Experiments with tubes, Fig. 4 (Plate II), containing

- (i) N/30 KI agar + N $\text{Pb}(\text{NO}_3)_2$, (ii) N/30 KI agar + N/2 $\text{Pb}(\text{NO}_3)_2$,
 (iii) N/60 KI agar + N $\text{Pb}(\text{NO}_3)_2$ and (iv) N/60 KI agar + N/2 $\text{Pb}(\text{NO}_3)_2$

show how, in this case, the distances apart of the layers are dependent rather upon the concentration of the solute in the gel than upon that of the reagent above. The curves, Figs. 5 and 6, were drawn freely through

points obtained by plotting the distances apart of the strata as ordinates against the distances down the tube as abscissae. The lower curves, which correspond to nos. (i) and (ii), are too nearly coincident to be drawn on the same diagram. There is a little more distinction between the upper curves. As the strata take some days to form, the irregularities of the points may be due to variations of temperature. In many cases, however, the formation of the laminae is more regular.

Since Lagergren [1899] had observed a negative adsorption in the solutions of certain salts, *e.g.* sodium chloride, it seemed desirable to ascertain whether stratification could be obtained in gels impregnated with such a substance. Accordingly gels were prepared containing sodium chloride of various concentrations, and upon these were poured solutions of silver nitrate. The character of precipitate produced was quite different from that resulting with other solutes, being merely a diffuse cloudiness without any definite margin indicating the limit of the diffusion, which also took place much more quickly than had hitherto been observed. In no instance was any stratification noticed. However tubes prepared with silver nitrate of similar concentrations in the gel, and sodium chloride above, also showed no layers. This precipitate however was bounded by a definite margin, as in other cases, until the gel had become nearly exhausted of solute, when a diffuse precipitate rapidly extended to the bottoms of the tubes.

The differences in the character of the AgCl precipitate, according to which reagent is contained in the gel, recall similar divergencies well-known in volumetric analysis when decinormal solutions of silver nitrate and sodium chloride are mixed. It may be that the two varieties of milky and curdy precipitates are due to their formation in solutions having, in the one case negative, and in the other, positive adsorption values, which would affect the concentrations of the solutions in the neighbourhood of the precipitates. This would seem to be supported by the fact that many metallic chlorides give a curdy precipitate when silver nitrate is added to them in dilute solution.

Since gels containing sodium chloride could not be made to produce stratification in straight tubes, experiments were made in U-tubes containing pure 1 % agar, the limbs of which were filled up with solutions of sodium chloride and silver nitrate respectively. Contrary to expectation, stratification was produced whichever reagent was hypertonic, although the same differences in the character of the precipitates were noticed. When hypertonic sodium chloride diffused into silver nitrate a dense curdy column of silver chloride was produced, separated, at intervals of about a centimetre, by clear cut

i

ii

Fig. 4

iii

iv

interspaces about a millimetre thick of transparent gel. Under the reverse condition only a slight diffuse cloudiness was formed on the first meeting of the solutions. This extended along the tube for about 12 or 15 mm., gradually filling the area of the tube and becoming a little denser. As further diffusion took place the first very light precipitate gradually disappeared, as if it had been swept up towards the denser portion by the diffusing reagent. This happened in every case, and, as other instances of the motion of visible particles in the gel have been observed, the effect may be due to this cause. After a time thin discs of denser precipitate appeared to be forming in the diffuse column. This was attributed to the backward diffusion of the sodium chloride after the strength of the silver solution had been diminished both by precipitation and adsorption. Obviously this explanation was not of general application. Consequently U-tubes of agar gel were treated with N/10 AgNO_3 and N/100 NaCl. After the production of the first light streaks, a great number of thin discs began to make their appearance at about 4 mm. apart, the distance rapidly decreasing to about 1 mm. On account of the low concentration of sodium chloride employed the discs could not be explained by alternate diffusion of the reagents. It seemed to follow, either that sodium chloride is positively adsorbed by silver chloride, or that the lamination resulted from the action of negative adsorption.

Attempts were then made to determine the nature of the adsorption of sodium chloride from solution by precipitated silver chloride. 100 cc. of decinormal NaCl solution were poured into well-stoppered bottles and to these were added 50 cc. of decinormal silver nitrate, thus producing a milky precipitate of silver chloride in a N/30 solution of sodium chloride. The bottles were allowed to stand 48 hours with occasional shaking, the clear supernatant liquid was then drawn off, 50 cc. at a time, in a pipette provided with a stopcock to prevent agitation of the precipitate. Titrations with decinormal silver nitrate indicated an adsorption of -0.06 millimols per gram of AgCl in thirtieth normal solution, and of -0.04 millimols in 0.0094 normal solution at 14° . Lagergren's figures for charcoal in 0.98 normal concentration were -0.09 millimols per gram at 0° . These experiments indicated that the stratification in sodium chloride gels must be explained by negative adsorption.

Further observations with U-tubes showed the occurrence of three types

¹ 50 cc. supernatant liquid required 16.9, 16.9, 16.85, 4.7, 4.7 and 4.8 cc. N/10 AgNO_3 respectively.

of stratification: (i) separate discs with no remaining diffuse precipitate, as previously described in the case of N/100 NaCl, (ii) a number of denser discs of chloride with extensions of very diffuse precipitate in the direction of diffusion and clear interspaces, and (iii) a column of diffuse precipitate interspersed, at intervals of about 2 mm., with very thin laminae of much denser precipitate. These effects may possibly be explained as follows. Owing to the negative adsorption of sodium chloride, the region of gel near the precipitate becomes gradually weaker in solute, while the next layer increases in strength. The excess of sodium chloride in this zone will tend to diffuse away, but will be hindered by the momentum of the particles flowing down the tube towards the precipitate. If the gel is very dilute, the region next the precipitate may not retain sufficient solute to produce a precipitate and the silver salt will be able to diffuse further until it enters the zone of stronger sodium chloride. This would give rise to a stratification of the first type. A gel which had been treated with a somewhat more concentrated solute might yield a precipitate gradually becoming less dense to zero before the diffusing silver salt reached the stronger layer of sodium chloride. This would correspond to type two. If the sodium chloride were again a little stronger, the clear spaces might not be produced at all, as in the third type.

Experiments in hand, which have now been interrupted, indicate that the remarkable influences of different gels upon the results obtained may be explained by v. Weimarn's theory on the assumption of protective action. For example lead iodide gives stratifications of gelatinous precipitate with difficulty in 5 % gelatin, while coarse precipitates in beautiful laminae occur in 1 % agar, and merely large aggregates in silicic acid gels. These results can be modified by varying the solubility of the precipitate, the concentration of the solute, or in other ways.

The following table (p. 175) records the positions of the strata formed in a number of experiments, measured in millimetres from the top of the gel. In many cases there were previous strata which were too close together for their positions to be read on a scale. The gel was 1 % agar except in the first case and the substance first mentioned was dissolved in the gel.

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No.

No.	Silver dichromate in 10 % gelatin	3.6	7.6	11.75	16.2	21.2	26.25	32.1	38.1	44.25	53.1												
9a																							
13	N/30 CaCl ₂ + conc. Na ₂ CO ₃	26.0	29.0	34.5	43.0	54.0																	
14	N/20 CaCl ₂ + conc. Na ₂ CO ₃	22.0	23.5	26.75	30.0																		
19	N/20 Na ₂ CO ₃ + dil. CaCl ₂	20.5	22.5	25.0	28.0	32.0	35.5																
20	N/20 Na ₂ CO ₃ + dil. CaCl ₂	20.5	22.5	25.5	28.5	32.5	36.0																
21	N/20 Na ₂ CO ₃ } + dil. CaCl ₂	20.5	22.5	24.5	—	33.0	35.5																
22	N/20 Na ₂ CO ₃ } + dil. CaCl ₂	20.5	23.0	—	—	31.5	35.5																
38	dil. AgNO ₃ + conc. K ₂ Cr ₂ O ₇	14.0	16.3	19.5	23.7	29.0	35.5	44.0															
50	N/20 Na ₂ CO ₃ + conc. CaCl ₂	24.5	28.5	32.5																			
51	N/20 Na ₂ CO ₃ } + conc. CaCl ₂	24.0	28.5	33.5	38.0																		
79	N/60 K ₂ Cr ₂ O ₇ + N/5 Pb(NO ₃) ₂	56.1	57.2	58.5	59.8	61.0																	
119	N/50 KI + N Pb(NO ₃) ₂	0.4	1.0	1.9	2.9	4.0	5.2	6.5	8.1	9.9	12.0	14.5	17.1	20.2	23.4	27.0	30.9	35.0	39.4	44.1			
120	N/20 KI + N Pb(NO ₃) ₂	5.0	5.7	6.5	7.4	8.4	9.5	10.7	12.0	13.4	15.1	17.0	19.1	21.4	23.8	26.2	29.5	33.4	37.7	42.3			
129	N/50 KI + N/5 Pb(NO ₃) ₂	0.5	1.1	1.9	3.0	4.2	5.6	7.2	9.1	11.2	13.7	16.6	20.3	24.6	shorter tube								
139	N/50 KI + N Pb(NO ₃) ₂	0.6	1.3	2.3	3.4	4.8	6.2	7.8	9.4	11.2	13.6	15.7	18.3	21.8	25.2	28.8	32.5	36.5					
140	N/50 KI + N/2 Pb(NO ₃) ₂	1.3	2.4	3.7	5.0	6.8	8.8	11.2	13.5	16.3	19.7	23.0	26.7	30.8	35.0								
130	N/20 MnSO ₄ + 5 % K ₂ S ₂	2.7	3.8	4.5	5.7	6.8	7.9	9.1	10.1	11.3	13.0	14.3	15.9	16.8	17.9	18.9	20.0	23.0	27.0	32.4	40.3	51.2	
133	0.25 % K ₂ S ₂ + N MnSO ₄	2.0	—	—	8.0	10.5	15.0	19.0	26.0	40.0													
134	0.09 % K ₂ S ₂ + N MnSO ₄	7.0	11.0	16.0	24.0	33.0	45.0																
154	N/30 KI + N Pb(NO ₃) ₂	0.6	1.1	1.6	2.4	3.2	3.9	5.0	6.2	7.5	9.3	10.8	12.8	15.0	17.1	20.3	23.6	26.8	30.5	34.8	39.7		
155	N/30 KI + N Pb(NO ₃) ₂	0.5	0.9	1.4	2.3	3.1	3.9	5.1	6.3	7.6	9.4	11.6	13.8	16.5	19.5	22.6	26.7	30.5	35.3	40.0			
156	N/60 KI + N Pb(NO ₃) ₂	0.6	1.3	2.3	3.6	5.9	9.2	12.6	16.9	21.9	26.7	35.0											
157	N/60 KI + N Pb(NO ₃) ₂	0.4	1.3	2.8	4.9	7.6	10.5	13.6	17.8	24.2	31.6												
158	N/30 KI + N/2 Pb(NO ₃) ₂	0.6	1.3	2.5	2.9	3.6	4.8	6.4	8.3	10.5	12.7	15.6	18.7	22.4	26.4	31.6	35.9						
159	N/30 KI + N/2 Pb(NO ₃) ₂	0.9	1.6	2.3	3.3	4.2	5.7	7.0															
160	N/60 KI + N/2 Pb(NO ₃) ₂	1.0	2.2	4.3	7.6	11.8	16.7	23.4															
161	N/60 KI + N/2 Pb(NO ₃) ₂	0.9	2.7	4.3	7.2	11.2	15.8	21.3															
184	N/20 KI + N/2 Pb(NO ₃) ₂	3.4	4.0	4.8	5.6	6.3	7.2	8.1	9.0	10.2	11.6	13.1	14.9	16.8	18.8	21.6	23.8	25.2	27.9	30.7	33.8	37.1	41.8
186	N/20 Pb(NO ₃) ₂ + N/2 KI	18.4	18.9	19.5	20.1	20.7	21.3	22.0	22.7	23.4	24.1	24.8	25.5	26.3	27.2	28.1	29.1	30.2	31.3	32.4	33.5	34.7	35.8
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