LXXXIX.—*Colloidal Platinum. Part V. The Coagulation by Electrolytes in Acid Solution.*

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THE coagulation of colloidal platinum in acid solution differs in some essential characteristics from that in basic solution. The latter is dealt with in the next communication.

The natural acidity of platinum sols and their coagulation by various acids have already been discussed (J., 1928, 551). The experiments with hydrochloric and nitric acids as coagulants were repeated, the coagulated (frozen) solution being used as comparison solution. The more exact results led to the same conclusion, namely, that during coagulation none of the added acid is removed by the coagulum. The interpretation of the acid coagulation as being due to a depression of ionisation of a strong acid, probably $H_2Pt(OH)_6$ (see J., 1928, 2018), which occurs in considerable amount on the surface, is in keeping with the theory of colloid structure and surface ionisation, as developed by Pauli (see, *e.g.*, *Kolloid Z.*, 1926, **38**, 22; " Eiweisskörper und Kolloide," J. Springer, Wien, 1926; Pauli and Valkó, *Z. physikal. Chem.*, 1926, **121**, 161).

Ionic Exchange at the Colloid Surface.—It has been shown by Pauli and co-workers (*loc. cit.*) that, for such colloids as ferric hydroxide, aluminium hydroxide, and arsenious sulphide, only a fraction of the stabilising surface ionogen is actually ionised, or, in terms of the modern electrolyte theory as applied to colloids (Bjerrum, *Z. physikal. Chem.*, 1924, **110**, 756; Pauli and Valkó, *loc. cit.*), that the activity of the colloid ion is less than unity. It is also shown (*e.g.*, Pauli and Schmidt, *Z. physikal. Chem.*, 1927, **129**, 199) that on the addition of a foreign electrolyte there is an ionic exchange at the colloid surface, and that this precedes, and leads to, coagulation. Achar and Usher (J., 1927, 1875) have also shown that the addition of a neutral salt to a suspension of stearic acid produces free acid, due to a kationic surface exchange.

Now it is doubtless true that the hexahydroxyplatinic acid at the surface of the colloidal platinum particle is also only partly ionised, and in keeping with the above, the addition of a salt should cause a kationic interchange at the surface, with the liberation of acid. It is important to the general behaviour of platinum sols to show whether such a change does or does not take place.

EXPERIMENTAL.

Owing to the very low concentration of the colloid the choice of methods is limited, but the conductivity method appeared to be most capable of accurately detecting any such change. Details concerning the conductivity cells used, and also the preparation of the pure platinum sols, are set out in previous papers. In the presence of salts, conductivity measurements do not give a direct indication of the hydrogen-ion concentration. Accordingly recourse was had to a comparative method which proved very satisfactory. One litre of the platinum sol was prepared, and boiled for 30 minutes. The preparation was then divided into halves, and one half was frozen, the colloidal platinum being thereby completely removed. On reboiling the coagulated (frozen) sol for 2 minutes, one obtained a conductivity a little greater than that of the original platinum sol. This could be diminished as required by dilution. Two comparison solutions were thus obtained: one contained the colloidal platinum with its usual environment of free hexahydroxy-acid, and the other contained exactly the same environment but no colloid particles. By using these solutions side by side, one can detect the changes due to the colloid particles themselves.

A weighed sample of the platinum sol (about 34 g.) was introduced into the conductivity cell and placed in the thermostat at 25° until its conductivity reached a steady value. The salt solution (*e.g.*, silver nitrate) was then added from a 5 c.c. burette till the coagulation point was passed, and the conductivity–concentration curve was drawn. All the precautions previously outlined were observed. The experiment was repeated with the coagulated (frozen) solution of the same initial conductivity.

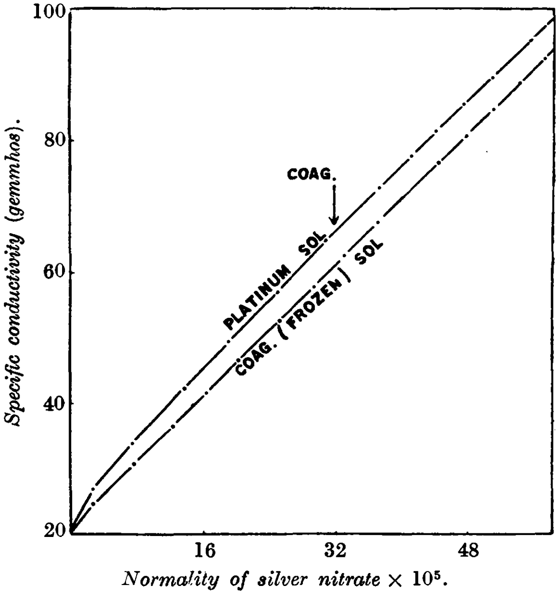
TABLE I.

Volume of solution initially in cell, 35 c.c. Normality of added $AgNO_3$, 0·002*N*.

Platinum sol.				Coagulated (frozen) sol.			
$AgNO_3$ conc. × 10^5.	κ.	$AgNO_3$ conc. × 10^5.	κ.	$AgNO_3$ conc. × 10^5.	κ.	$AgNO_3$ conc. × 10^5.	κ.
—	20·19	41·38	77·73	—	20·23	33·12	62·62
2·70	26·55	44·40	81·47	2·71	24·70	37·26	67·72
7·58	33·98	47·64	85·69	7·59	30·90	41·07	72·33
13·67	42·25	51·01	89·86	12·34	36·78	44·52	76·64
19·10	49·37	55·67	95·43	16·29	41·78	47·87	80·83
25·01	57·01	58·09	98·37	20·06	46·54	51·35	84·98
30·85	64·77	60·05	100·58	25·09	52·55	54·53	88·86
37·28	72·74	—	—	29·32	57·95	57·37	92·30

It will be convenient to discuss one set of curves at once, and the data for the silver nitrate titrations are accordingly set out in Table I, and the corresponding curves in Fig. 1. From these it is seen that the addition of silver nitrate to the platinum sol always results in a larger conductivity than the corresponding addition to the coagulated (frozen) sol. The explanation of this increased conductivity must be in terms of the liberation of an ion of greater mobility, and one must therefore conclude that some of the hydrogen ions at the surface of the colloid and an equivalent amount of silver ions from solution have exchanged places. The maximum divergence in the curves is seen to be of the order of 5 gemmhos, and on the assumption that this is wholly due to the kationic interchange, the concentration of silver ion so removed (or of hydrogen ion set free) is written as 5/(349,500—63,400), *i.e.*, 0·000017N. (The mobilities of the hydrogen ion and the silver ion at 25° are taken as 349·5 and 63·4 respectively.)

FIG. 1.



Salts with Univalent Kations.—With potassium nitrate and sodium chloride, the exact divergence in the curves was difficult to obtain. This was not unexpected. The coagulation concentrations of such salts are of the order 0·004N (compare 0·0003N for silver nitrate), and accordingly their curves have to be carried to such high conductivities that the relatively small differences sought are less accurately picked out. With these salts, however, positive evidence of the interchange was forthcoming.

Salts with Bivalent Kations.—Barium chloride, calcium nitrate, and copper sulphate, all of which have relatively low coagulation concentrations (approx. 0·0002*N*), show the same sort of divergence as that outlined for silver nitrate. The maximum divergence was somewhat smaller, and lay between 2·5 and 4·0 gemmhos.

Salts with Tervalent Kations.—Aluminium sulphate and aluminium chloride gave corresponding results, but ferric chloride was anomalous (see later). The curves for aluminium sulphate are particularly interesting: they showed a maximum divergence (coagulation concentration 0·000024*N*) of 4 gemmhos, and since they presented no anomalies, the foregoing general interpretation holds. Now Burton (*Phil. Mag.*, 1906, **12**, 472) has calculated the charge on colloidal silver particles on the assumption that, on coagulation with aluminium sulphate, the whole of the salt is adsorbed. The calculation is assumed to be applicable to any colloidal metal. The reason for the extremely high values obtained is now evident. The relative positions of the curves for colloidal platinum show that the whole of the aluminium sulphate is not adsorbed, nor, in keeping with the general results, is there any evidence that any of the salt is adsorbed.

The Coagulation Process.—Bjerrum (*loc. cit.*) and Pauli and Valkó (*loc. cit.*) have shown that the modern theory of strong electrolytes is capable of extension to colloid solutions. Every colloid particle is an ion of high valency with a definite activity. The corresponding "gegenion" or colloid contra-ion will also have its own activity. Any increase of the latter will result in a decrease in the activity of the colloid ion. When this activity tends towards zero, *i.e.*, when the charge on the colloid tends to disappear, the colloid becomes unstable and coagulation ensues. As colloidal platinum is an acid sol containing the hydrogen ion as the contra-ion, the explanation of the coagulation by different acids at a fixed p_H follows.

The foregoing experimental evidence shows that on addition of a salt, *e.g.*, silver nitrate, there is always a kationic interchange, and that some of the surface hexahydroxy-acid is converted into the corresponding silver salt. Any further increase in the silver nitrate concentration not only produces more of the surface silver salt, but decreases the activity of the corresponding colloid ion. At a definite silver-ion concentration, the latter activity has been sufficiently decreased to allow coagulation to ensue. This explanation appears to be perfectly general.

The well-known increase in coagulating power of different salts with increase in the valency of the coagulating ion is explained in terms of the increase in the attractive force between the higher-valency ion and the colloid ion. All bivalent kations are accordingly stronger coagulants than univalent, and all tervalent stronger than bivalent.

Ions of the same valency have not exactly the same coagulating power, and here the effect of the atomic volume of the ion and other specific properties come into question. In this connexion one might notice that the silver ion, of low atomic volume, has a high coagulating power, not only towards platinum, but to all negative sols.

Partial Kationic Interchange.—Ferric chloride exhibits some peculiarities which can be directly explained. The curves obtained by adding this salt to the platinum sol and to the coagulated (frozen) sol do not show a deviation comparable with that for aluminium sulphate; in fact, the maximum deviation is only about 1 gemmho. Now the author has measured the hydrolysis of these two salts at the low concentrations employed, and whilst the aluminium sulphate is hydrolysed to the extent of about 35%, ferric chloride shows over 90% hydrolysis. Coagulations with the latter solution are then largely acid coagulations, where the ferric ion (owing to its extremely low concentration) plays perhaps a secondary part. The coagulation concentrations concerned support this view. The less hydrolysed aluminium sulphate coagulates at 0·000024*N*, whereas for the highly hydrolysed ferric chloride the corresponding concentration is 0·0001*N*. The latter value is much closer to the coagulating value for either hydrochloric or sulphuric acid, *viz.*, 0·0002*N*.

It is now clear why the ferric chloride addition curves show such a small deviation. (The pure acid sols show no deviation whatsoever.) These results further directly indicate that the ferric hydroxide of hydrolysis takes no appreciable part in the coagulation.

All the solutions concerned in the foregoing work are acid solutions of low concentration, the acid being the free hexahydroxy-acid. Now the kationic interchange will be subject to (but not necessarily solely controlled by) the law of mass action, and the question then arises whether all such salt coagulations are not mixed coagulations of acid and salt, ferric chloride being a rather extreme case. In all probability this is so, and the coagulum contains some of the original surface acid as well as the newly formed surface salt. Herein lies the explanation of the decrease in the coagulation concentration of any salt as the sol is made more acid. A quantitative study over the possible acid range is incomplete, but the following figures illustrate the effect of increasing the acid content:

	For 0·00005*N*-$H_2Pt(OH)_6$ (free).	For same with addition of 0·000102*N*-HNO_3.
Coag. conc. of NaCl	0·004*N*	0·0018*N*
,, ,, $AgNO_3$ ...	0·0003*N*	0·00015*N*
,, ,, $BaCl_2$ ...	0·0002*N*	0·00012*N*
,, ,, $FeCl_3$ ...	0·0001*N*	0·00007*N*

It is evident that coagulation concentrations have no definite significance unless the p_H of the solution is stated.

In neutral solutions the coagulation concentrations are slightly greater than those in the pure (naturally acid) platinum sol. For these measurements sodium or potassium hydroxide must be used as neutralising agent, for the salts of these bases with the free platinic acid are poor coagulants, and therefore introduce a minimum of complications. One must be careful not to pass the neutralisation point in such solutions, for the free hydroxides have far-reaching influences (see following paper).

Summary.

Experimental evidence is produced which shows that, on the addition of salts to colloidal platinum sols, the kation of the salt replaces the hydrogen ion of the surface hexahydroxy-acid. This kationic interchange precedes, and in fact directly leads to, coagulation. The coagulation process is discussed.

In acid solutions the kationic interchange is only partial and the coagulum contains some of the surface acid. This is shown to explain the increase in the coagulation power of a salt as the p_H of the sol is decreased.

It is also shown that with ferric chloride and aluminium sulphate, at the usual low concentrations, the hydroxides set free by hydrolysis play no important part in the coagulation.

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