LXXI.—*Colloidal Platinum. Part III. Its Natural Acidity and its Coagulation by Acids.*

By STUART W. PENNYCUICK and R. J. BEST.

IN Part II of this series * (Pennycuick, J., 1927, 2600), it was shown that colloidal platinum solutions were definitely acid in nature, behaving more like strong acids than weak acids on titration with bases. It will now be shown (a) that the natural acidity of colloidal platinum solutions can be measured with the quinhydrone electrode, (b) that the coagulation of platinum sols by different acids takes place at approximately the same p_H, and (c) that after coagulation the natural acidity of the solutions still remains.

EXPERIMENTAL.

The p_H of Pure Platinum Sols.—The platinum sols were prepared by the method previously described, *viz.*, by sparking pure platinum poles in conductivity water (0·4 gemmho). The p_H values of these sols could not be determined by the hydrogen electrode, owing to far-reaching changes in the nature of the colloid which are now being investigated. The quinhydrone electrode, however, proved entirely satisfactory. It was always used in conjunction with a normal calomel electrode, which was prepared from mercury distilled in a vacuum, potassium chloride thrice crystallised from conductivity water, and calomel prepared according to the authors' method (*Australian J. Exp. Biol. Med. Sci.*, 1926, **3**, 173). The quinhydrone was prepared according to Biilmann and Lund (*Ann. Chim.*, 1921, **16**, 321), and a polished platinum electrode proved superior to one of gold. The electrode vessel, having a total capacity of about 8 c.c., was connected to the middle vessel containing saturated potassium chloride by a glass tube containing 3% agar saturated with the salt. By having one end of this connecting tube reasonably close to the platinum electrode, and by using a highly sensitive galvanometer, readings could be taken to 0·1 millivolt in spite of the high resistance of the sols. (The p_H of the conductivity water used was obtained with the above chain and was approximately 6.) The whole system

* Part I appeared in the *Australian J. Exp. Biol. Med. Sci.*, 1927, **4**, 99.

was sunk in a thermostat at 30°. The various p_H values were calculated from the formula

$$p_H = -\log[H^+] = [(0·6953 - 0·2835) - E_{obs.}]/0·06011.$$

This formula uses the standard value for the normal calomel electrode, *viz.*, 0·2864 at 18°, with a temperature coefficient of $-0·00024$/degree, and also the Biilmann and Krarup relation (J., 1924, **125**, 1954) for the quinhydrone electrode, $E_t = 0·7175 - 0·00074t$.

Before each determination the quinhydrone electrode vessel was washed with conductivity water, air-dried, and subsequently handled only with filter paper; it was twice rinsed with the solution to be used, filled, corked, and placed in the thermostat. Readings were taken as soon as temperature equilibrium had been reached. Great precautions were necessary in order to obtain reproducible values with unbuffered solutions of such dilute acids.

The p_H values were taken for nine different pure platinum sols. They ranged from 4·60 to 4·28, the corresponding hydrogen-ion concentrations being 25×10^{-6} to 52×10^{-6}. The unboiled sols always showed a relatively high p_H and on standing or on boiling in borosilicate vessels showed a marked decrease in p_H; *e.g.*, a freshly prepared unboiled sol showed p_H 4·60; after boiling for 20 minutes this changed to p_H 4·47; and after a further 30 minutes' boiling to p_H 4·30. The acidity as measured by the quinhydrone electrode was always slightly less than that obtained by conductimetric titration, as had been anticipated by Pennycuick (*loc. cit.*). The evidence, however, definitely indicates that the quinhydrone electrode measures the true p_H of these sols, for (*a*) the values obtained are steady and reproducible; (*b*) no anomalies or irregularities appear; and (*c*) on mixing an acid of p_H, say, 4·284, with a platinum sol of the same p_H, the mixture also shows a p_H of 4·284.

The Coagulation of Colloidal Platinum by Acids.—Although the coagulation of colloids by salt solutions has received much attention, relatively little attention has been paid to the coagulation by acids. Tartar and Gailey (*J. Amer. Chem. Soc.*, 1922, **44**, 2212) and Tartar and Draves (*J. Physical Chem.*, 1926, **30**, 763) have shown that the negatively charged mastic sol is coagulated by different acids at approximately the same p_H, and that the coagulation concentration of salts is without significance unless the p_H of the sol is also specified. They have also shown that mastic sols are inherently acid solutions. It therefore appears that although platinum and mastic sols would seem to be markedly dissimilar in nature, yet they are in fact remarkably alike. Now platinum sols are definitely acid, and if their structure corresponds to that suggested by Pennycuick

(*loc. cit.*), they might be expected to show the same p_H on coagulation by different acids. This was found to be the case.

Acids of eight different types were used (see Table I), oxalic acid having to be discarded owing to its undergoing slight decomposition. All the work was carried out in borosilicate vessels, and conductivity water ($\kappa < 1$ gemmho) was used for dilutions. The method of coagulation was that adopted in Part I of this series (*loc. cit.*). The approximate coagulation concentration was first obtained by preliminary tests, and then the acid solutions were made of such concentrations as to have comparable powers of coagulation, so that at coagulation the platinum sol would always suffer the same dilution. The coagulation was determined after standing for 24 hours. The p_H values of the clear supernatant liquids were measured by the quinhydrone electrode at 30°, after the platinum had settled out. Determinations were always carried out in pairs, and if one pair showed a variation greater than 0·01 unit a second pair was taken. In Table I, the concentrations required for

TABLE I.

Hydrogen-ion concentration of platinum sol = 3×10^{-5}.

Acid.	Coag. conc.	p_H.	[H+] at coag.	[H+] of acid alone.	Difference.
Hydrochloric	0·196	3·69	20×10^{-5}	18×10^{-5}	2×10^{-5}
Sulphuric	0·184	3·69	20 ,,	17 ,,	3 ,,
Nitric	0·192	3·66	22 ,,	18 ,,	4 ,,
Benzoic	0·820	3·63	23 ,,	21 ,,	2 ,,
Tartaric	0·500	3·59	25 ,,	20 ,,	5 ,,
Salicylic	0·295	3·57	26 ,,	24 ,,	2 ,,
Succinic	2·135	3·57	26 ,,	24 ,,	2 ,,
Citric	1·200	3·44	36 ,,	31 ,,	5 ,,

coagulation (col. 2) are given in milliequivs. of titratable hydrogen per litre, calculated on the total volume of platinum and added acid. (The maximum error in the hydrogen-ion concentrations in cols. 4 and 5 is 1×10^{-5}, and therefore that in col. 6 is 2×10^{-5}.)

The coagulation occurs within a narrow p_H range, *viz.*, 3·44—3·69. It can therefore be concluded that the hydrogen-ion concentration is the controlling factor in the coagulation of colloidal platinum by acids. The variation in the p_H at coagulation, although small, is nevertheless real. Part at least of this is due to a decided difference in the rates at which the coagulating particles coalesce and become visible. Although readings were taken only after the solutions had stood for 24 hours, it was observed that with the acids towards the top of the table no further changes took place after about 8 hours, but with the acids towards the bottom of the table the actual flocculation appeared to be a much slower process. It is evident,

however, that the part played by the anion is often negligible and always very small.

The values of the hydrogen-ion concentrations (col. 4), when compared with the normalities of the coagulating acids (col. 2), appear to be too high, for the three mineral acids give hydrogen-ion concentrations which indicate slightly more than 100% ionisation. The platinum sols, however, were originally acid, and it would therefore appear that some (at least) of this acidity still remains even after the platinum is all precipitated. To test this point, solutions of the various acids were prepared of concentrations exactly equal to the coagulatory concentrations shown in col. 2, and their hydrogen-ion concentrations were then determined as before; the results, given in col. 5, show that the supernatant liquor after the platinum has been coagulated is more acid than a pure acid solution of exactly the same concentration of added acid, the excess acidity being given in the last column. The platinum sol used for these coagulations had an initial hydrogen-ion concentration of 3×10^{-5} and $\kappa_{30^\circ} = 18$ gemmhos. From cols. 4 and 5 it appears that the total acidity after coagulation is approximately the initial natural acidity plus the acidity of the added acid, *i.e.*, *during the coagulation process no acid is removed*.

Conductimetric Investigation.—As was shown in Part II (*loc. cit.*), the weak solutions involved respond to conductimetric investigation with a remarkable degree of accuracy, and such methods were therefore expected to give more exact information concerning the non-removal of acid during the coagulation process. Briefly, the method adopted consisted in placing a good conductivity water ($\kappa = 0.6$ gemmho) in the cell, adding increasing quantities of acid, and plotting the specific conductivity–acid concentration curve. The same quantity of platinum sol was then placed in the cell, and the experiment repeated. A comparison of the resulting curves gave the necessary information.

Three cells, of the type previously described, were used (constants 0·0109, 0·0204, and 0·0212). They were washed with conductivity water and air-dried before use. The acids were added from 3 c.c.-burettes, and during the whole process the cells were strictly air-tight. After each addition, the solutions were stirred by a carbon dioxide-free air stream passing through a wash-bottle in the bath. The temperature of the experiment was 30°. Four acids were used, *viz.*, hydrochloric, nitric, tartaric, and citric, as being representative of those given in Table I. The concentration and quantity of the added acid were previously calculated, so that in the case of the platinum sols the whole of the platinum would not only be coagulated but completely deposited, leaving the solution quite

clear.   As would be expected from the foregoing work, hydrochloric and nitric acids caused coagulation at approximately the same specific conductivity, viz., 190 gemmhos for the particular sol used, tartaric acid at a slightly higher conductivity, 200 gemmhos, and citric at a still higher conductivity, 280 gemmhos.   Hydrochloric and nitric acids showed strictly comparable curves under all conditions, and accordingly results for the former only are detailed.   The behaviour of the two organic acids showed no outstanding differences, and only the results for tartaric acid are quoted.   The results are set out in Tables.II and III, and the corresponding curves in Figs. 1

TABLE II.

Normality of added HCl, 0·004N.   Volume of solution initially in cell, 37 c.c.   Pt sol boiled for 50 minutes, $\kappa = 22\cdot3$.

| (A). Water of $\kappa = 0\cdot61$.		(B). Pt sol of $\kappa = 22\cdot3$.		(C). HNO$_3$ of $\kappa = 21\cdot5$.		(D). Tartaric acid of $\kappa = 22\cdot3$.	
(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).
—	0·61	—	22·3	—	21·5	—	22·3
28	12·86	27·8	33·9	26·9	33·28	33	34·08
60	26·45	60	47·67	58·6	47·28	76	50·98
91	40·28	91	61·44	89·9	61·30	119	68·15
121	53·47	122	74·64	121	74·74	158	84·85
157	69·97	156	89·74	155	90·46	198	101·5
201	89·1	203	109·6	199	110·1	237	117·9
230	102·4	232	122·0	229	123·1	273	133·8
270	120·8	276	141·8	277	144·4	312	149·8
325	144·3	323	162·5	324	164·9	348	165·7
391	174·2	388	190·5	369	185·0	383	180·4
434	193·6	433	210·4	413	204·8	418	196·5
468	207·4	468	226·1	456	223·9	452	211·0
531	236·5	557	264·5	538	260·1	517	239·2

TABLE III.

Normality of tartaric acid added, 0·01N.   Volume of solution initially in cell, 37 c.c.   Pt sol boiled for 50 minutes, $\kappa = 23\cdot1$.

(A). Water of $\kappa = 0\cdot54$.		(B). Pt sol of $\kappa = 23\cdot1$.		(C). HNO$_3$ of $\kappa = 22\cdot9$.		(D). Citric acid of $\kappa = 23\cdot6$.	
(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).
—	0·54	—	23·1	—	22·9	—	23·64
67	19·7	67	40·5	83	43·51	67·1	38·19
152	38·0	146	57·5	196	66·0	149	54·16
230	53·5	225	72·4	298	84·96	225	67·63
304	67·17	299	85·4	404	102·1	297	79·91
390	82·40	382	99·3	502	117·1	384	93·63
498	99·3	491	116·2	600	131·1	494	109·7
569	110·1	571	126·9	695	144·1	567	119·9
671	125·2	678	141·2	796	156·6	673	134·2
789	140·2	789	156·2	896	168·6	791	150·2
884	152·2	882	167·7	991	180·5	882	160·8
847	160·4	971	178·6	1080	191·2	947	168·6
1054	173·7	1076	190·9	1169	201·1	1059	181·5
1136	183·7	1161	200·7	1260	210·8	1165	192·3
1290	201·1			1340	219·8	1254	203·2

and 2.   In each table column (*a*) gives 10^6 times the concentration of added hydrochloric acid (Table II) or tartaric acid (Table III) based on the total volume of the resulting solution, and column (*b*) gives the specific conductivity (κ) in gemmhos.

In Figs. 1 and 2, curves A represent the specific conductivities of the pure acid at various concentrations, whilst curves B represent the specific conductivities of the platinum sol at corresponding

FIG. 1.

Normality of HCl $\times 10^4$.
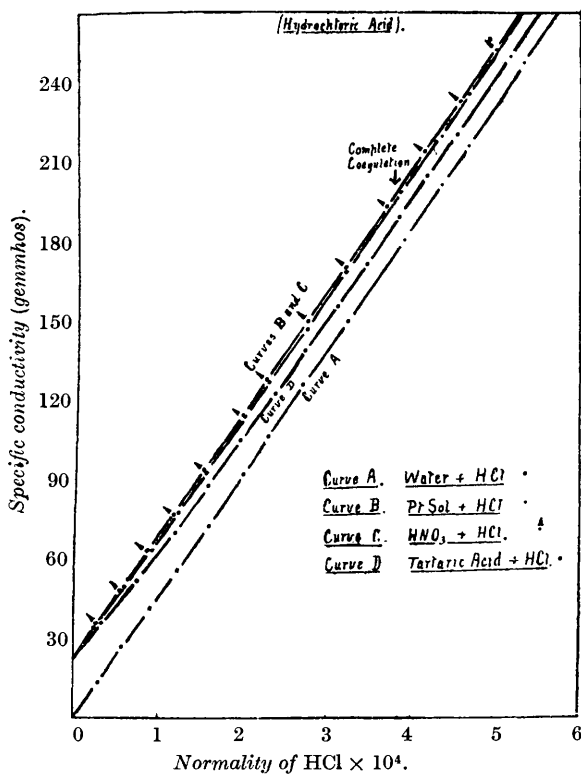
(added) acid concentrations.   The latter curves go well past the coagulation points.   It is at once evident that after coagulation the total conductivity of the solution is the approximate sum of the initial and added acid conductivities, thus confirming the conclusion from the foregoing determinations of p_H, that *during the coagulation process no acid is removed.*   It might be objected, however, that the slight convergence of the curves indicates an actual removal of the acid.   This is not so, for it will be noticed that the convergence of the curves still persists *even after all the platinum has been precipitated.*

(This was also the case with the curves which have been omitted.) It must therefore be concluded that during coagulation none of the initial nor of the added acid is removed. The convergence of the A and B curves is due to either or both of the following : (a) the mutual repression of ionisation of the platinum acid and the added acid, (b) the diluting effect of the added acid on the volume of the platinum sol taken and therefore on the platinum acid present. The latter effect is inherent in the method used and can be calculated

FIG. 2.

Normality of tartaric acid × 10⁴.
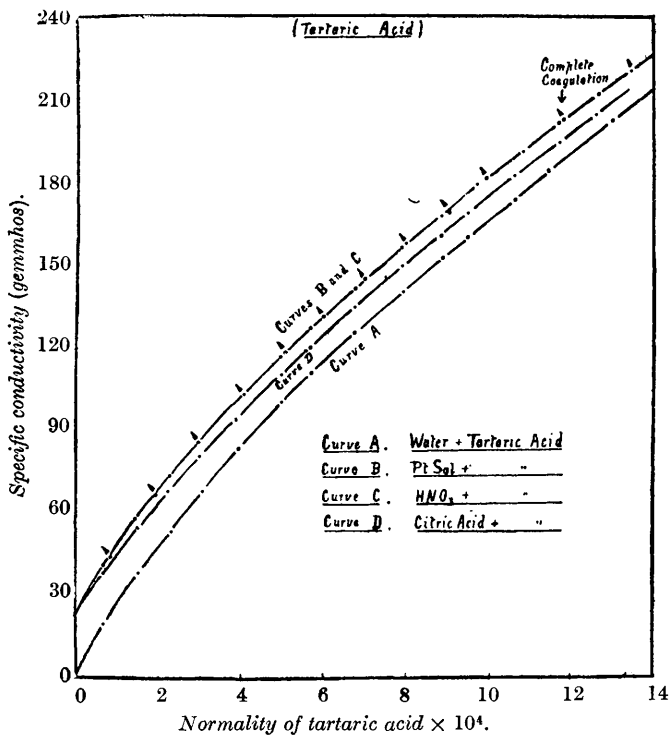
from the dilution figures. Since 37 c.c., the original volume of the platinum sol, always received a total addition of 5 c.c. of acid, the conductivity due to the platinum acid should be decreased in the ratio 42 : 37. This decrease coincides so closely with the experimental convergence of the curves, particularly when they are plotted on a larger scale, that the first explanation can be ruled out, and it is concluded that the added acid does not materially repress the ionisation of the natural platinum acid, which therefore behaves as a strong acid. This conclusion was completely confirmed by

replacing the platinum sol with a strong acid of the same conductivity and repeating the experiment.

To this end some conductivity water was placed in the cell, and nitric acid added in very small amounts until the solution showed a specific conductivity approximately that of the platinum sol used. Conditions were so arranged that the total volume was now 37 c.c. The solution then received increments of hydrochloric acid under exactly the same conditions as the platinum sol. The results are set out in column C of Table II and curve C in Fig. 1. Curves B and C are extremely close together, but in view of the fact that the experimental error is so small as to be represented by the size of the dots in the figure, it would appear that the platinum-sol curve, B, actually falls very slightly below the strong-acid curve, C.

If, on the other hand, a dilute solution of tartaric acid ($\kappa = 22\cdot3$ gemmhos) is treated in exactly the same way, the resulting curve (D, Fig. 1; see col. D, Table II) falls well below the corresponding B and C curves. This is what would be expected and is due to the depression of the ionisation of the weak tartaric acid by the strong hydrochloric acid.

On repeating these experiments, starting with dilute solutions of nitric and of citric acid, and adding tartaric acid, corresponding results were obtained (see columns C and D, Table III; curves C and D, Fig. 2). In this case, however, there is no measurable difference between the platinum-sol curve (B) and the strong-acid curve (C). Strictly comparable results were obtained when citric acid was the added acid.

From these results two conclusions stand out : first, that during coagulation no acid is removed, and secondly, that the natural acid originally present in the platinum sol is a strong acid comparable in strength with nitric acid.

An attempt was made to follow the p_H–acid concentration changes for the above solutions. As with the previous p_H measurements the technique proved difficult and the experimental error was high. One set of results only is quoted (Table IV); it shows the hydrogen-ion concentrations of a range of hydrochloric acid solutions and those of platinum solutions of the same (added) hydrochloric acid concentration.

TABLE IV.

Pt sol of $[H^+] = 4 \times 10^{-5}$.

[H+] of acid alone, $\times 10^5$ 13	24	34	44
[H+] of Pt sol, $\times 10^5$ 16	26	37	47
Difference $\times 10^5$ 3	2	3	3

These, and in fact all the results obtained by this method, show

definitely that after coagulation the solution has a higher acidity than that due to the added acid, but so far the $E.M.F.$ results afford only qualitative support to the above conductimetric work. This evidence is of value, however, for it shows by the most direct method that in platinum sols we are undoubtedly dealing with acid solutions.

Discussion.

In Part II (loc. cit.) it was suggested that the colloidal platinum particles consisted of aggregates containing both atoms of platinum and complex anions of probable constitution PtO_4. The anions formed a protecting ionised surface to the colloidal particles. It was further suggested that the positive kations, the hydrogen ions, were free, and as such could be titrated with bases. The present work, while supporting the general nature of this structure, reveals some essential differences. Although the platinum particles are of the structure outlined, the results now indicate that their hydrogen-ion partners are not free but form a double layer at the surface. The free strong acid in solution would appear to be a platinic acid, and although no valid alternative interpretation of these results is available, yet it is surprising that such an acid should be capable of existence in the free state, and still more so that it should behave as a strong acid. The presence of this acid accounts for the stability of the sols and for their ease of preparation in the purest con-ductivity water. Further, the acidity and the conductivity of platinum sols is due entirely to this free acid, and it remains in solution after all the platinum has been coagulated.

The increase in acidity (and conductivity) on boiling or on ageing is tentatively accounted for as follows : The colloidal platinum par-ticles consist of atoms of platinum plus PtO_4 anions. At high temperatures some of these, probably the larger, suffer disin-tegration. This disintegration sets free a certain number of PtO_4 anions which with their hydrogen-ion partners form platinic acid. Part of the disintegrated particle thereby becomes unstable and forms a slight precipitate such as is always produced on boiling. Ultra-microscopic investigations are now being carried out which will probably throw further light on the coagulation process.

The similarity in nature between solutions of colloidal platinum and of mastic is now emphasised. Tartar and Draves's mastic sols (loc. cit.) were definitely acid (p_H 4·08—3·47), and by ultra-filtration and dialysis the acidity was traced to organic acids in true solution. Moreover, after coagulation the solutions retained their original acidity. Rabinowitsch and Burstein (Biochem. Z., 1927, **182**, 110) titrated mastic sols with alkali and obtained conductivity

curves with sharp minima, and Hotta (*ibid.*, **183**, 72) confirmed the acid nature of the sols by electrometric measurements. They also found that both the conductivity and the hydrogen-ion concentration increased on keeping.

Summary.

The previous work revealing the acid nature of colloidal platinum sols is confirmed by direct measurement of the p_H with the quinhydrone electrode. Such measurements show that platinum sols become more acid on keeping or on boiling.

It is shown that the coagulation of colloidal platinum by acids occurs at an almost constant p_H.

Definite evidence is produced that during the coagulation by acids no acid is removed by the platinum particles.

It is shown that the natural acidity of platinum sols is due to a free acid, probably platinic acid, which at these low concentrations behaves as a strong acid.

Note added, January 14th, 1928.—Further work indicates that the acid is hexahydroxyplatinic acid, $H_2Pt(OH)_6$.   S. W. P.

UNIVERSITY OF ADELAIDE,
    SOUTH AUSTRALIA.