CCLXXVII.—*Colloidal Platinum. Part IV. The Existence of Hexahydroxyplatinic Acid in Colloidal Platinum Solutions.*

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IN Part III (this vol., p. 551) it was shown that solutions of colloidal platinum, when prepared by the Bredig method and with extreme precautions, contain a free strong acid which remains in solution after the platinum has been coagulated. Those results are now confirmed, and evidence is produced that the strong acid is hexahydroxyplatinic acid.

Preparation and Procedure.—The colloidal platinum was made in water of specific conductivity (κ) less than 0·4 gemmho, and with the precautions previously outlined. Only relatively fresh sols were used, *i.e.*, those not more than a week old. After preparation, the sol was boiled for 20 minutes (unless otherwise stated) and then kept in the ice-box to minimise further changes. After 2 days the larger suspended particles appeared to have settled out, for the results outlined in this paper were not appreciably altered when the sols were centrifuged.

The titrations were carried out as described in Part II (J., 1927, 2600). The bases used were exactly 0·001*N*, and were kept in waxed bottles. A simple manipulation allowed of the transfer of the base to the titrating pipette and thence to the cell, without any contamination by atmospheric carbon dioxide.

Isolation of the Free Acid.—The evidence (Part III, *loc. cit.*) clearly indicated that the free acid was a strong acid, comparable in strength with hydrochloric acid. The titration curves (Part II) were, however, not strictly comparable with curves of strong acids, and the author concluded from such titrations that platinum sols were " really unique, and that they cannot strictly be compared either with strong or with weak acids." This apparent contradiction makes it fairly evident that the platinum particles themselves play a disturbing part during neutralisation of the platinic acid by the base.

Now, if the platinum sol is frozen into a solid block (from the outside to the centre), and then re-melted, the whole of the metal is completely precipitated. The solution remaining is not only as clear as water, but after standing or centrifuging, it shows no ultramicroscopic evidence of any remaining suspension. The conductivity of the clear solution is generally about 25% less than that of the original sol. This decrease is probably due to the smaller solubility of the free acid at the lower temperature. The original (and in fact a much higher) conductivity can be obtained by re-boiling the sample containing the coagulated platinum. The higher conductivities so obtained indicate that some of the platinic acid forms part of the colloidal particle. The coagulation by freezing is strictly irreversible.

Sols from which the platinum has been removed by freezing are designated throughout this paper as " coagulated (frozen) sols."

Titration of the Acid in the Coagulated (Frozen) Sol.—The acid being thus isolated, attempts were made to identify it; but owing to the small quantity present (about 8 mg./l. in an ordinary sample), trustworthy quantitative methods were extremely difficult to apply. Titration of the coagulated (frozen) sol with various bases, however, would definitely test the previous evidence in favour of the acid being a strong acid. This would not only give some indication of the nature of the acid present, but a comparison of the titration curves with those obtained by the titration of the original platinum sol would afford some information as to the action between the added base and the colloidal particles.

Different samples of the coagulated (frozen) sol, of κ = 10—24 gemmhos, were accordingly titrated at 30° with calcium, barium, sodium, and potassium hydroxides. Since the first two bases gave

TABLE I.

[N = normality of added base, $\frac{1}{2}Ca(OH)_2$.]

Coagulated (frozen) sol–$Ca(OH)_2$.		Hexahydroxyplatinic acid–$Ca(OH)_2$.		H_2SO_4–$Ca(OH)_2$.	
$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.
—	15·55	—	15·68	—	15·73
15·0	11·48	9·7	12·77	13·1	11·88
23·6	9·20	17·8	10·34	24·2	8·69
32·0	7·40	24·8	8·40	30·2	7·08
38·8	7·27	29·4	7·26	34·7	6·43
45·6	8·29	36·0	6·83	43·2	7·57
53·8	9·90	40·4	7·46	50·9	9·16
61·5	11·71	48·0	9·06	60·0	11·48
71·3	14·06	55·5	10·85	67·4	13·46
78·6	15·89	62·8	12·74	71·6	14·53
87·2	18·05	71·2	14·87		

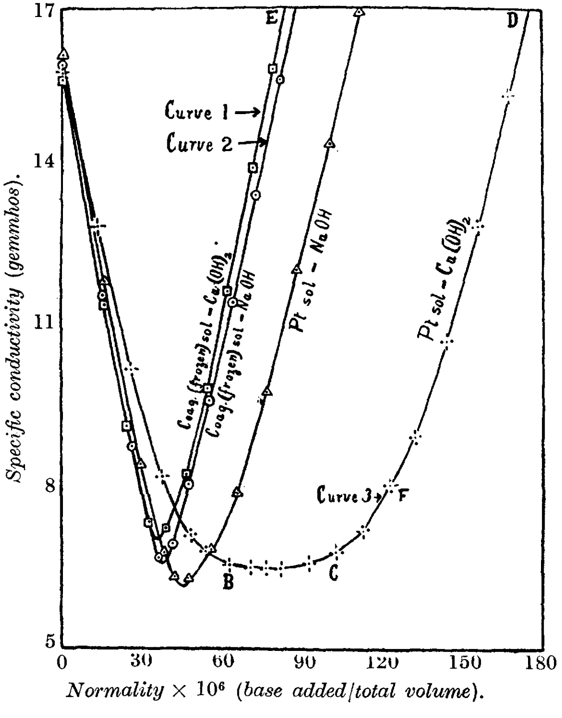
TABLE II.

(N = normality of added base.)

Coagulated (frozen) sol–NaOH.		Pt sol–NaOH.		Pt sol–$Ca(OH)_2$.	
$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.
—	15·96	—	16·15	—	15·82
15·1	11·64	16·0	11·91	12·7	12·94
25·5	8·79	29·5	8·47	25·2	10·28
35·7	6·70	38·1	6·81	37·1	8·22
40·5	7·00	41·2	6·37	47·5	7·14
47·4	8·10	46·8	6·34	53·0	6·83
55·6	9·66	55·3	6·87	62·1	6·57
63·6	11·51	65·2	7·93	70·6	6·53
72·8	13·54	76·5	9·82	76·1	6·53
81·6	15·68	88·5	12·12	81·6	6·54
		100·2	14·50	92·2	6·62
		111·8	16·98	102·7	6·83
				113·0	7·22
				122·9	8·07
				132·4	8·99
				143·9	10·77
				155·8	12·93
				167·5	15·39

similar results, only those for calcium hydroxide are shown; and for a like reason the results of the last two bases are illustrated by sodium hydroxide (see Tables I and II, and Fig. 1, Curves 1 and 2). The two curves are similar in shape and have almost the same minima, the sharpness of which is characteristic of titration curves of strong acids; moreover, weak acids give different types of curves with these two bases (see J., 1927, 2609). The sodium hydroxide curve shows the lower minimum, as would be expected from the mobilities of the sodium and calcium ions, *viz.*, 58·3 and 69·96, respectively (see H. S. Taylor, "A Treatise on Physical Chemistry," 1924, p. 540). In each case the end-points agree satisfactorily with those calculated from the initial conductivities and ionic mobilities.

FIG. 1.



From this evidence one can conclude quite definitely that the free electrolyte present in platinum sols is a strong acid, and in view of the method of preparation it must be a platinic acid. Now only one such acid is known, *viz.*, hexahydroxyplatinic acid, $H_2Pt(OH)_6$, prepared and investigated by Wöhler (*Z. anorg. Chem.*, 1904, **40**, 423) and by Bellucci (*ibid.*, 1905, **44**, 168). These authors show that it is a strong dibasic acid, more stable than the corresponding chloroplatinic acid, and that its salts undergo no hydrolysis at 25°. It therefore seemed probable that this was the acid formed during the preparation of platinum sols, but since it is described as being insoluble, an investigation of its solubility limits and its titration curve was necessary in order to strengthen this conclusion.

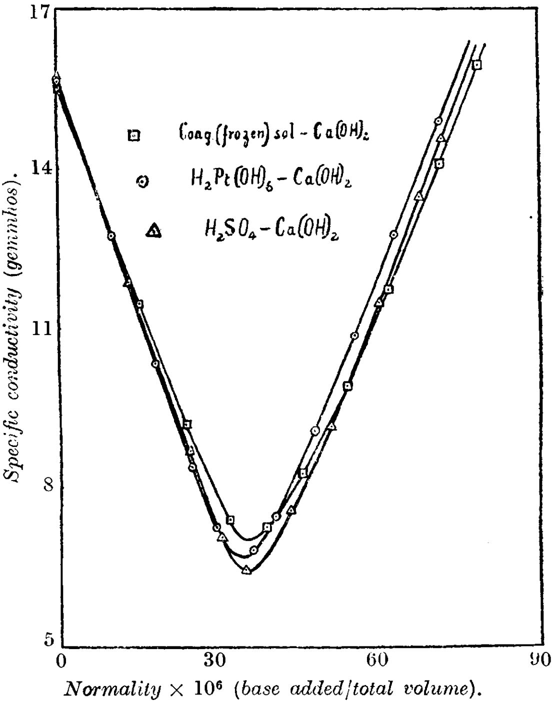
Preparation and Titration of Hexahydroxyplatinic Acid.—The acid was prepared by boiling chloroplatinic acid with excess of 10% sodium hydroxide solution, diluting the product, and neutralising it with acetic acid in the cold (see Bellucci, *loc. cit.*). The resulting white or yellowish-white precipitate was washed very thoroughly with conductivity water, being warmed with successive additions of 500 c.c. of the water for the final washings. The purified material, when heated to 60° with excess of conductivity water, gave an acid solution having $\kappa_{30^\circ} = 7{\cdot}5$ gemmhos, which increased to 36 gemmhos after 40 minutes' boiling in a borosilicate flask. Platinum sols when boiled for the same time in the same way showed a specific conductivity of about 25 gemmhos. (Various samples of conductivity water were subjected to the same treatment as controls, and always showed $\kappa < 0{\cdot}9$ gemmho.) It is thus evident that the solubility of the hexahydroxy-acid (on boiling) is quite sufficient to account for the conductivity of the platinum sols (also on boiling).

A complication now arises, however. Wöhler (*loc. cit.*) has shown that the white hexahydroxy-acid, which may be formulated as $PtO_2,4H_2O$, loses 1 mol. of water on boiling and gives an ochre-gold trihydrate, which is also probably a strong acid corresponding to $H_2PtO(OH)_4$. On prolonged boiling or on heating in the dry state, it is further dehydrated to the brown $PtO_2,2H_2O$ and then to the monohydrate, but the final molecule of water is very difficult to remove. These changes take place in the insoluble portion of the acid, but it is not known whether they also occur with the dissolved acid; it is certain, however, that the conductivity of the supernatant liquor is increased during these changes in the precipitate.

Owing to the above changes, the solubility product of the hexahydroxy-acid could not be determined. Also, the reason why the sample of hexahydroxy-acid was not boiled during the washing is now apparent.

If the ochre-gold product, or even the brown product, or a mixture of the two, be boiled with conductivity water, some passes very slowly into solution. Different samples of these solutions at widely varying stages of boiling were titrated with sodium and calcium hydroxides, and in every case the shape and position of the curves showed the solution to be that of a strong acid. Only one set of results is given, *viz.*, that of the once-boiled hexahydroxy-acid * (boiled 25 minutes) when titrated with calcium hydroxide (see Table I and Fig. 2). This curve compares very closely with the corresponding curve for the coagulated (frozen) sol shown in the same figure. It is quite probable that a small and undetected amount of colloidal platinum remains in the coagulated (frozen) sol despite the freezing process. This platinum would cause a slight displacement in the titration curve which would account for the small divergence in the two curves.

FIG. 2.



In order to estimate the experimental error involved in the titration of these acid solutions of such low concentration, a very dilute sulphuric acid solution, stored and handled in exactly the same way as one of the previous solutions, was titrated with calcium hydroxide. The results are in Table I and Fig. 2. The normality

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* Although this solution was considered to be the most comparable with the platinum sols (boiled 20 minutes), the boiled solutions of the lower hydrates (*e.g.*, $PtO_2,2H_2O$) showed titration curves whose turning points corresponded very closely indeed to that of the hexahydroxy-acid.

calculated from the initial specific conductivity is 0·000034, and that read from the curve is 0·000035. The conductivity at the turning point is calculated from the mobilities as 5·4 gemmhos, whereas the observed conductivity is 6·4 gemmhos: this difference may be attributed to the unavoidable contamination during boiling and handling.

Titration of the Platinum Sol.—Results for the titration of platinum sols have already been published (J., 1927, 2600), but they were repeated on material prepared in such a way that the curves should be strictly comparable with those obtained from the coagulated (frozen) sols. A sample (800 c.c.) of the pure sol was prepared in the usual manner and divided into halves; one half was frozen, and the subsequent solution formed the coagulated (frozen) sol, whilst the other half was titrated directly with sodium and calcium hydroxides (see Table II and Fig. 1). Comparison of these curves with those for the free electrolyte itself (Curves 1 and 2) shows the part played by the platinum particles when the sol is titrated.

Discussion.

The foregoing experiments afford strong evidence that the free acid present in platinum sols is the strong hexahydroxyplatinic acid, probably in conjunction with some of its lower hydrates. Further, the conclusion that some of the platinic acid forms part of the colloidal particle is strengthened by the following direct evidence. If the sol be siphoned over from the dregs soon after preparation, and then centrifuged, the conductivity on boiling increases markedly —from approximately 6 to 25 gemmhos, or even higher. As has been shown, the whole of this conductivity can be ascribed to the strong acids present, and these must have separated from the colloid particle during boiling. It might be suggested that the acid is really formed during boiling by the oxidation of the finely divided particles, but this is not so, for on continued boiling (without loss of volume) a maximum conductivity of approximately 39 gemmhos is reached after about 8 hours—further boiling gives no further increase but ultimately causes coagulation. Also, if the preparation and the boiling take place in an atmosphere of nitrogen, exactly the same results are obtained. We must conclude, then, that the boiling actually liberates the acid from the colloid particle. Further, if a sol with a specific conductivity of 17 gemmhos is centrifuged, coagulated by freezing, and then boiled for 2 hours, the conductivity increases to about 28 gemmhos, thus leading to the same conclusion. Incidentally, it may be mentioned that if the dregs from the original preparation be washed in the cold, and then boiled with conductivity water, the very small conductivities obtained, about

5 gemmhos, indicate that very little acid is carried down by the dregs.

From the total evidence produced, the author interprets the formation of the colloid particles in the following way. During the sparking process and the atomisation of the platinum, some oxidation occurs, probably at one of the poles, with the formation of molecules of hexahydroxyplatinic acid. The anions of the strong acid condense with platinum atoms to build up aggregates of $Pt–H_2Pt(OH)_6$. Each particle thus acts as a multivalent acid micelle of perhaps very high valency. The acid molecules, or at least those at the surface of the particles, tend to ionise. The ionisation of such a multivalent micelle is still open to investigation, but we can well imagine that such ionisation would be relatively slight owing to the big residual charge that would result. As, however, the bound acid is a strong acid, the tendency to ionise will be particularly great, and the result may be interpreted as a dynamic equilibrium at the surface which gives rise to the so-called double layer.

We are now in a position to discuss the titration curves shown in Fig. 1. The wide divergence between the Pt sol–$Ca(OH)_2$ curve and the corresponding coagulated (frozen) sol–$Ca(OH)_2$ curve is very striking, and indicates that the colloidal platinum particles remove considerable quantities of calcium hydroxide. In the absence of evidence to the contrary, the most satisfactory explanation of the removal of the base appears to be the simplest chemical explanation, *viz.*, that on the gradual addition of calcium hydroxide to the platinum sol, the greater part of the base is neutralised by the free platinic acid, but a small amount is neutralised by the acid at the surface of the colloid particle. This proceeds until the whole of the free acid is neutralised, up to, say, the point B on Curve 3. Any further base is then completely neutralised at the surface of the particles to form the calcium salt of the hexahydroxyplatinic acid which is bound at the surface. The early coagulation of the platinum after the point C indicates that the tendency of the micelle to ionise is not very great, *i.e.*, that the double layer at the surface is disappearing.

At the points E and D, we have the same quantity of calcium hexahydroxyplatinate present—assuming that none has diffused away from the colloid surface in the case of the point D. Further, since the conductivities at these two points are the same, and calcium hydroxide is the only other electrolyte present, it follows that the difference in concentration at E and D represents the amount of base removed by the colloid particles. This difference is $0{\cdot}000091N$, and the surface acid neutralised by this excess of base would also be represented by $0{\cdot}000091N$, which in the free state would give rise to a conductivity of 39 gemmhos. When the sol was boiled till it gave a maximum conductivity, the total increase found, due to the liberation of the bound acid, was only 23 gemmhos. The difference of 16 gemmhos may be due to the boiling process not liberating the whole of the acid, or perhaps to the solubility limit of the hexahydroxy-acid, the highest conductivity found for the boiled hexahydroxy-acid being of the order 36 gemmhos.

The Pt sol–NaOH curve (Fig. 1) is essentially different. The relative sharpness of the turning point and the high coagulation concentration indicate that the double layer is more difficult to destroy, and that therefore the sodium salt at the surface of the micelle ionises more freely. Speaking generally, we may say that the greater coagulating power of bivalent bases is due to the formation on the micelle of surface salts, which when so held show a smaller tendency to ionise. This is in keeping with the well-known fact that bivalent bases are less ionised than univalent bases at comparable concentrations.

Two further circumstances may be emphasised. (1) The platinum sol was generally prepared in a stream of carbon dioxide-free air, but this atmospheric oxygen was not responsible for the oxidation of the platinum to the hexahydroxy-acid during sparking, for a preparation carried out in a stream of nitrogen gave strictly comparable conductivities, and on boiling and titration (in a stream of nitrogen) the same set of curves was obtained. (2) If the freezing mixture used during the preparation be dispensed with, and the sol be allowed to become warm, there is always more platinum wastage and a much weaker sol results. This cannot be ascribed to coagulation by heat, for platinum sols can be boiled quite safely for several hours. Now it has been shown that hexahydroxyplatinic acid must be prepared in the cold, and it would therefore appear that the initial preservation of the acid (by the use of a freezing mixture) is essential to the preparation of a strong stable sol.

Summary.

The existence of a strong (free) acid in colloidal platinum sols has been verified by coagulating the platinum by freezing and then titrating the remaining clear solution.

It is believed that there is present either the strong hexahydroxyplatinic acid or a mixture of this acid with some of its dehydrated forms.

Evidence is produced that the hexahydroxy-acid enters into the structure of the colloid particle, and it is suggested that ionisation of the surface acid accounts for the stability of the colloid.

Coagulation of platinum sols by bases is discussed in terms of the neutralisation of this surface acid.

The author is very much indebted to Mr. A. E. Scott, B.Sc., for the preparation of the sample of hexahydroxy-acid used in this work.

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[*Received, April* 30*th*, 1928.]