XC.—*Colloidal Platinum. Part VI. The Behaviour of Platinum Sols in Basic Solution.*

By STUART W. PENNYCUICK.

(1) *The Action of Bases at the Colloid Surface.*

BEFORE the coagulation in basic solutions can be discussed, it is necessary to establish the part played by bases alone.

Any well-prepared sample of colloidal platinum is continually undergoing constitutional changes. This is shown by the steady increase in conductivity of the sol, as measured over several days (see J., 1928, 551). These changes demand that, where strict comparisons are to be made, either the same solution or strictly comparable solutions must be used. This condition is observed throughout the following work.

The Neutralisation of the Surface Hexahydroxy-acid.—If the platinum sol is titrated with barium and with sodium hydroxide, curves D and B respectively are obtained (see Fig. 1A; also J., 1928, 2111), although when the coagulated (frozen) sol is titrated with the same two bases, the corresponding curves are almost coincident and may be represented by curve C (which is actually that relating to barium hydroxide). This fundamental difference between the action of the two bases needs explanation.

The difference in concentration at the points B and C (*viz.*, 1·6 × 10^{-5} equiv.) represents the amount of sodium hydroxide removed by the colloid particles. In keeping with the results already recorded, this removal is interpreted as due to the neutralisation of the surface acid, probably $H_2Pt(OH)_6$, with the formation of the corresponding surface salt. One may conclude then, that the total surface acid, ionised and un-ionised, corresponds to 1·6 × 10^{-5} equiv.

In the same way, the difference in concentration at the points D and C represents the amount of barium hydroxide removed by the colloid particles. This is read from the curves as 6·7 × 10^{-5} equiv. Of this, only 1·6 × 10^{-5} equiv. is needed to neutralise the surface acid, and the remainder must therefore be taken up by the surface in some other manner. Further evidence in this direction is provided by the back titration of the removed barium hydroxide.

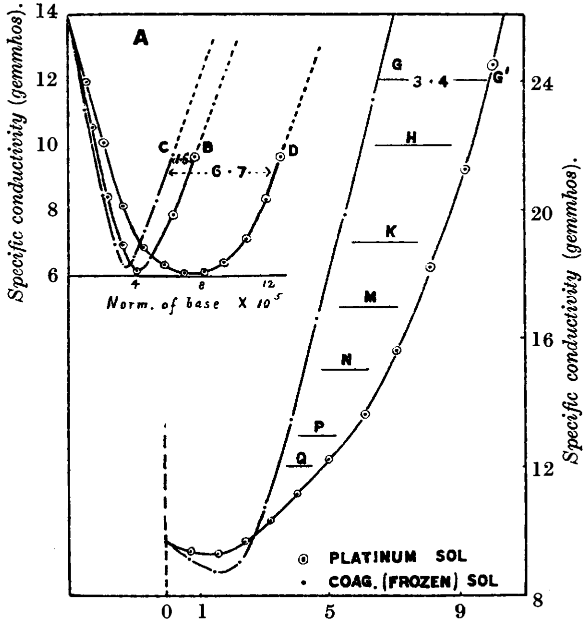
TABLE I.

Titration and Back-titration.

Platinum sol.				Coagulated (frozen) sol.			
Titration.		Back-titration.		Titration.		Back-titration.	
Normality $Ba(OH)_2$ × 10^5.	κ.	Normality HNO_3 × 10^5.	κ.	Normality $Ba(OH)_2$ × 10^5.	κ.	Normality HNO_3 × 10^5.	κ.
—	13·92	—	9·66	—	13·88	—	9·66
1·02	11·98	0·78	9·36	1·05	11·10	0·67	9·11
2·09	10·07	1·58	9·29	2·15	8·42	1·45	8·76
3·28	8·14	2·40	9·70	2·78	6·91	2·22	9·05
4·47	6·82	3·18	10·37	3·34	6·16	2·98	10·70
5·81	6·15	3·97	11·14	3·97	6·60	3·81	13·43
6·92	6·02	4·99	12·27	4·72	7·38	4·65	16·62
8·26	6·06	6·07	13·68	5·44	8·34	5·48	19·86
9·54	6·39	7·12	15·61	6·15	9·35	6·36	23·41
10·88	7·09	8·13	18·17	6·40	9·66	7·13	26·60
12·10	8·37	9·16	21·35	—	—	7·84	29·41
13·08	9·66	10·05	24·58				

Back-titration of the Barium Hydroxide.—A colloidal platinum sol and the comparable coagulated (frozen) sol were titrated with barium hydroxide in the usual manner. In each case the titration was stopped when the solutions contained the same amount of free base, *i.e.*, when they showed the same conductivities (C and D in Fig. 1A). Each solution was then immediately back-titrated with nitric acid. The results are set out in Table I and in the second part of Fig. 1. The divergence of the curves shows at once that a large amount of the removed base is brought back into solution by the acid. Now the fraction of barium hydroxide which can be so reclaimed at any given acid concentration can be calculated from the curves. Consider the points G and G′. Both solutions contained the same initial amount of free hexahydroxy-acid, and they both received the same excess of *free* barium hydroxide (since initially they corresponded to points C and D respectively), and as we are going to deal with the difference in conductivities at G and G′, the conductivities due to these substances, or rather to their salts, can be neglected. Of the $3{\cdot}4 \times 10^{-5}$ equiv. of extra acid added at G′, some remains as free acid and some has been replaced by barium nitrate. Let x represent the normality of the latter. Then $(0{\cdot}000034 - x)$ will represent the normality of the extra acid left as such. (The value of x may be greater than 0·000034, but it must be

FIG. 1.



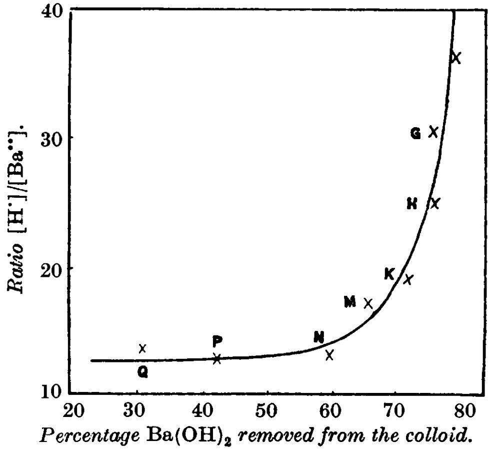
B = Pt *sol*–NaOH *titration*. D = Pt *sol*–$Ba(OH)_2$ *titration*.
C = *Coagulated (frozen) sol*–$Ba(OH)_2$ (*or* NaOH) *titration*.

less than 0·000099, which is the total acid concentration at G′.) The resulting conductivity due to these two factors is the difference in conductivity at G and G′, namely, zero. We therefore write that the conductivity of (0·000034 − x) equiv. of nitric acid plus that of x equivs. of barium nitrate equals zero. Using the relation: normality = x (in gemmhos)/ionic mobility × 1000 (Pennycuick, J., 1927, 2605), and using the mobility figures for 25°, $H^{\cdot} = 349{\cdot}5$, $\frac{1}{2}Ba^{\cdot\cdot} = 65{\cdot}5$, and $NO'_3 = 71{\cdot}3$, we obtain

$$(0{\cdot}000034 - x) \times 421{,}000 + 137{,}000\,x = 0, \text{ whence } x = 0{\cdot}000050.$$

The normality of barium ion removed from the surface is therefore $5{\cdot}0 \times 10^{-5}$, and since the total amount taken up by the platinum

FIG. 2.



had the value $6{\cdot}7 \times 10^{-5}N$, it follows that 25% of the barium is still held at the surface.

The full significance of these results is seen by calculating the above ratio over the whole range of the acid curves and plotting percentage of barium ion brought back into solution against the ratio $[H^{\cdot}]/[Ba^{\cdot\cdot}]$. Results for the points G, H, K, M, N, P, and Q are thus shown in Fig. 2. From these it is seen that some 60% of the barium ion is brought back into solution at a low and practically constant hydrogen-ion concentration, approximately $1{\cdot}1 \times 10^{-5}N$; of the remainder, another 15% is brought back fairly readily by increasing the $[H^{\cdot}]/[Ba^{\cdot\cdot}]$ ratio, but the final 25% of the surface barium ion is replaceable (if at all) only as the acid concentration becomes relatively high. Keeping in mind the figures already quoted, it can be concluded that from 20 to 25% of the base has formed the barium salt of the hexahydroxy-acid, and that the remainder is held at the surface in some less effective manner. In other words, a maximum of 20—25% of the surface of colloidal platinum particles consists of hexahydroxyplatinic acid.

The Nature of the Rest of the Surface.—It might be suggested that the rest of the surface is pure platinum and that the base is adsorbed thereby. This, however, does not appear to be correct, as is shown by the following experiment. Some platinum gauze and foil of a total surface area of 550 sq. cm. were thoroughly cleansed and placed at the bottom of an enlarged conductivity cell. This received 100 c.c. of conductivity water and then a steady addition of barium hydroxide. The specific conductivity was plotted against the barium hydroxide concentration, and the curve compared with that obtained in similar circumstances but without the platinum. A very slight deviation in the curves was obtained which corresponded to the removal by the pure platinum surface of approximately $0{\cdot}2 \times 10^{-5}$ equiv. of barium hydroxide. The platinum sols used in this work contained 0·130 g. of platinum per litre, and, taking the average radius of the colloid particle as 30×10^{-7} cm., one can calculate from the figures already quoted, that 550 sq. cm. of colloidal platinum surface in 100 c.c. of solution would remove $4{\cdot}6 \times 10^{-5}$ equiv. of barium hydroxide. Allowing for the inaccuracies involved in the calculation of the colloid surface, one must conclude that the removal of the extra base by the colloid cannot be ascribed to an adsorption at a pure platinum surface.

Now it is well known that platinum forms a whole series of oxides and oxy-acids (see Wöhler, *Z. anorg. Chem.*, 1904, **40**, 423; Bellucci, *ibid.*, 1905, **44**, 168), and there can be no doubt that during the preparation of colloidal platinum by the Bredig method a variety of oxidation products will be formed. The author has shown that, of these, some having strong acid properties [*e.g.*, $H_2Pt(OH)_6$] are bound at the surface and function as the colloid ionogenic stabilising agent. It is now suggested that the rest of the surface is composed of lower and less active oxides, which are too weak to form acids with water, but are able to form salts with bases. In connexion with this explanation, it should be noticed that Fuchs and Pauli (*Koll.-Chem. Beih.*, 1925, **21**, 412), working on colloidal gold, and Pauli and Valkó (*Kolloid-Z.*, 1926, **38**, 289), on colloidal silicic acid, conclude that the surfaces of these colloids contain inactive (non-ionogenic) molecules, which can be activated or rendered ionogenic by, *e.g.*, the addition of potassium bicarbonate. In fact, the latter workers have suggested that this property will be found to be common to all negative colloids.

On the assumption that part of the surface of colloidal platinum is covered by a weakly acidic oxide, and part by a strong acid, the results obtained from the " back-titration " experiments follow naturally. In the rest of this paper it will be shown that such a constitution explains the many important reactions of colloidal platinum in basic solution.

The Action of Bases at the Colloid Surface.—The difference between the effects of sodium and barium hydroxides (Fig. 1A) may first be examined. On the gradual addition of sodium hydroxide, the free acid and the surface acid are first neutralised, and then the sodium hydroxide tends to combine with the surface oxide to form the corresponding salt. With colloidal gold and colloidal silicic acid (see references above) it has been shown that comparable reactions take place, which are indicated by the increase in the charge on the colloid particle. On the addition of further sodium hydroxide, a state will be reached in which the high charge on the colloid will suppress the reaction that tends to increase its charge, and some of the surface oxide will remain inactivated or uncombined. When the conditions are altered so as to decrease the charge on the particle, *e.g.*, by the addition of a sodium salt, more of the surface oxide will become activated. This can proceed until the whole of the oxide has reacted, and normal coagulation will then ensue. Experimental results will be quoted which amply support this view.

With barium hydroxide, the same reaction proceeds, but it is fundamentally affected by the strong electric force between the colloid ion and the bivalent barium ion (see Part V, preceding paper). In fact the activity of the colloid ion containing the barium salt is so small (as revealed by the low coagulation concentration of the barium ion) that the surface charge is never high, and the whole of the surface combination can take place at low barium hydroxide concentration. This explains the flat minimum in the titration curve (Fig. 1A), and moreover, it is in agreement with the observations on colloidal gold (Fuchs and Pauli, *loc. cit.*), where it is found that on the addition of barium hydroxide there is practically no initial increase in the charge on the gold particle.

The author is convinced that no good purpose will be served by interpreting the above results in terms of a difference in adsorption at the oxide surface. Although it is not improbable that here we have a connecting link between a physico-chemical surface reaction and an adsorption, explanations in terms of the latter, as applied to colloid surface reactions, have been so abused that the author feels that in such cases this term must be used with extreme caution.

(2) *The Coagulation by Electrolytes in Basic Solution.*

Univalent Bases and their Protective Action.—The protective action of univalent bases on negative colloids is quite general, and in the preparation of colloidal gold and silver a weak solution of a univalent base is essential. This effect was for many years generally ascribed to an adsorption of the hydroxyl ion, but Pauli (" Eiweisskörper und Kolloide," J. Springer, Wien, 1926) has conclusively shown that it is due to the production of alkali complex salts which form the surface ionogens of the colloid.

If a solution of colloidal platinum is made alkaline with a univalent base, the alkali exerts a well-defined protective action on the colloid, and the coagulation concentration of different salts is increased remarkably. For example, when a platinum sol is made $0{\cdot}0067N$ with respect to sodium hydroxide, the coagulation concentration of salts with univalent kations is increased about 800%—in the case of sodium chloride from 0·004 to $0{\cdot}032N$. With a similar alkalinity ferric chloride shows a 90-fold increase in coagulation concentration, *viz.*, from 0·0001 to $0{\cdot}0090N$. As pointed out in the preceding paper, it is again evident that coagulation concentrations have no definite significance unless the $p_{\rm H}$ of the sol is defined.

In terms of the foregoing, the author interprets this general phenomenon as follows. In the absence of the base, the salt coagulation (see Part V) is due to the repression of the ionisation at the colloid surface of the salt of the strong platinic acid. The latter covers approximately one-fifth of the surface, and it would appear that the remaining four-fifths containing the oxide coating are unaffected during such coagulations. (Qualitative evidence in this direction is afforded by adding barium hydroxide to a barium chloride coagulum, whereupon it is found that a large amount of the base is completely removed by the precipitate.) If a univalent base be now added to the uncoagulated sol, part of the oxide is converted into the active surface ionogenic salt. Any attempt to repress the colloid charge by the addition of further foreign salt is accompanied by a further activation of the surface oxide and the restoration of the charge. This can proceed until the whole of the surface oxide has reacted, and further salt addition will then cause coagulation in the normal manner.

It is now evident why sodium hydroxide itself coagulates at a much higher concentration than sodium chloride, the respective concentrations being 0·052 and $0{\cdot}004N$.

As already explained, bivalent bases, owing to the electrostatic forces concerned, combine with the whole of the surface oxide at very low basic concentrations. The residual charging effect is therefore extremely small, and could only be detected in very favourable circumstances. It seems to be demonstrable in the case of acid clay suspensions (Oakley, J., 1927, 3054), but with colloidal platinum sols the author was unable to show the protective action of barium hydroxide in any single case. It further becomes evident that the protective action of univalent bases on bivalents alts such as barium chloride and calcium nitrate must also be a minimum, for the bivalent hydroxide is immediately formed in the solution and reacts accordingly.

With salts of tervalent kations, the protective action of univalent bases is very pronounced. This is in keeping with results already recorded in Part V, where it was shown that the weak tervalent hydroxides play no important part (at the low concentrations concerned) in the coagulation process.

Hydrolysed Salts.—The general effect of hydrolysis on the coagulating power of a salt can now be explained. Where salts of univalent kations are hydrolysed to form basic solutions, the free base will have a protective action, and the coagulation concentration of such salts will be greater than that for unhydrolysed salts. For example, with a neutral sodium salt, the coagulation concentration of the sodium ion may be written as 0·004N ; with sodium acetate, however, it is 0·012N, and with sodium cyanide 0·018N.

If a salt is hydrolysed to form an acid solution, the coagulating power may be greater or less than usual, according to whether the coagulating power of the hydrogen ion is greater or less than that of the kation of the salt. With ammonium chloride, for example, the hydrogen ion resulting from hydrolysis has a higher coagulating power than a univalent kation (approximately in the ratio 0·004 : 0·0002) ; accordingly ammonium chloride should be a better coagulant than neutral univalent salts. Actually, it has about twice the coagulating power of the neutral sodium salts. (With ammonium salts a second reaction may play some part, and this is receiving attention.) The coagulating power of tervalent kations, on the other hand, is much greater than that of the hydrogen ion, approximately in the ratio 0·0002 : 0·000024. Accordingly, with the highly hydrolysed ferric chloride, the production of free hydrochloric acid, and the removal of ferric ion as insoluble or colloidal ferric hydroxide, will result in this salt having a lower coagulating power than less hydrolysed tervalent salts. Ferric chloride is about a quarter as effective as the less hydrolysed aluminium sulphate in coagulating a platinum sol.

(3) *The Repeptisation of the Platinum Coagulum.*

It is well known that, in general, the coagulum produced by electrolytes is flocculent and by no means compact. This is the case with colloidal platinum, no matter what coagulating salt is used. With many colloids, the coagulum is of such a loose and open structure that it can be repeptised with a suitable solution, or merely by washing. It has invariably been the case to speak of colloidal platinum as an irreversible colloid which, once coagulated, can never be repeptised (see Freundlich, " Colloid and Capillary Chemistry," English edn., 1926, p. 470). The author has been unable to find any case in the literature of the repeptisation of a platinum coagulum.

Now when a platinum sol in its natural (slightly acid) state is coagulated by a salt, it has been shown that the surface oxide is apparently unaffected by the process. Further, the fact that a barium chloride coagulum can still take up a large quantity of barium hydroxide indicates that the flocculent coagulum is sufficiently porous to allow the base to reach and react with the surface oxide. It therefore appeared that, if the foregoing explanation was valid, almost any platinum coagulum should be repeptisable by a univalent base. Experiment showed that this was the case.

Sols coagulated by salts with univalent kations, such as rubidium nitrate, sodium sulphate, and potassium chloride, were all readily repeptised by a small amount of sodium or potassium hydroxide. For example, a sol was completely coagulated by $0{\cdot}007N$-sodium chloride, and then completely repeptised when made $0{\cdot}0001N$ with respect to sodium hydroxide; moreover, the following experiment was performed. A sol was just coagulated with potassium chloride, the coagulum settling in one hour; it was then repeptised with a little sodium hydroxide, recoagulated with further potassium chloride, repeptised again, and so on. The action could be carried on until conditions demanded that the whole of the surface compound be formed, whereupon sodium hydroxide could exert no further repeptising action. In each case the repeptised solution was stable over a period of several months, and, further, the particles were still negatively charged.

As expected, the coagulum formed by a salt with a bivalent kation could not be thus repeptised. The reason for this is evident from a previous discussion.

The coagulum formed by a salt with a tervalent kation is readily repeptised. The explanation for this has also received attention. One important feature is that the repeptised sol (like every other such sol examined) still carries a negative charge. In excess of aluminium salt, it is well known that the colloid suffers a reversal of charge. With the low aluminium salt concentrations used, no unusual or abnormal features were revealed, and it is evident that at low concentrations these salts accord with the general theory.

It is significant that the whole of the above results on repeptisation were suggested by, and therefore are in accord with, the theory as outlined.

In virtue of the foregoing, one would further expect that an acid coagulum (brought about by coagulating colloidal platinum with an acid) would be readily and easily repeptisable by a univalent base. Different acids were used, and the phenomenon appears to be so general that no figures need be given. As in the previous cases, the repeptised particles are stable over some months and are negatively charged. (It is obvious that the repeptisation will not occur where the concentration of free base exceeds $0{\cdot}052N$, the coagulation concentration of the base.)

A silver nitrate coagulum when treated with a small quantity of sodium hydroxide showed partial repeptisation. The solution assumed the brown colour of a dilute platinum sol, but a large amount of the coagulum became converted into large coherent masses. The formation of the insoluble silver hydroxide was obviously playing some interfering part. A silver nitrate coagulum, however, is completely repeptised at a concentration of $0{\cdot}002N$-potassium cyanide. Here the cyanide tends to remove the silver as a complex ion, whilst at the same time the potassium hydroxide of hydrolysis peptises the coagulum.

Since the coagulation process is interpreted throughout this work as a repression of the ionisation of the colloid ion, it might be concluded that every coagulum should be repeptisable simply by washing. This, however, assumes that the coagulated particles have a minimum of cohesion amongst themselves. Actually it was found that, when a freshly precipitated sol was washed and then shaken with conductivity water, the particles appeared to get smaller (took longer to settle) and in some cases were completely repeptised. A coagulum which had stood for several days was invariably more difficult to peptise. The results may be briefly summarised. The coagulum produced by a univalent base was the most easily peptised. This could be brought about by one washing, *i.e.*, by allowing the coagulum to settle, removing the supernatant liquor, replacing it by an equal volume of conductivity water, and shaking. One washing was also sufficient to repeptise a coagulum formed by a salt with a univalent kation, such as sodium sulphate. Such repeptised sols were not completely stable, for on standing for two months, they showed a slight clearing at the top. Cataphoresis experiments showed that they were still negatively charged. With salts of bivalent kations, the coagulum was never completely repeptised, but whereas the original coagulum was precipitated in 1 hour, the washed coagulum took two or three days to settle. A similar behaviour was noticed in the case of salts with tervalent kations.

In coagulating power, the silver ion is comparable with bivalent kations rather than univalent, and accordingly, a silver salt coagulum cannot be repeptised by washing. An acid coagulum shows a behaviour intermediate between that of a univalent and that of a bivalent salt. On being washed it appears to go into solution, shows a definite clearing on top at the end of a week, and is practically all precipitated at the end of a month.

The precipitated particles formed by coagulating a platinum sol by freezing do not resemble an ordinary salt coagulum in appearance. They are extremely fine and compact, and by no means flocculent. They show no evidence of peptisation on washing, or even on warming with sodium hydroxide.

Finally, it should be mentioned that many of the conclusions in this and the preceding paper were reached quite independently of Pauli's more recent work. Where comparisons can be made, it has been shown that the results are in striking agreement with that author's general theory of colloids.

Summary.

From results obtained by the addition of bases to colloidal platinum solutions, it is concluded that approximately 25% of the colloid surface consists of hexahydroxyplatinic acid.

Evidence is produced for the belief that the rest of the surface contains weakly acidic oxides of platinum.

In terms of this hypothesis, the different actions of univalent and bivalent bases at the colloid surface are explained, as is also the remarkably effective protective action of univalent bases against salt coagulation.

Contrary to general belief, platinum sols are reversible. The conditions of repeptisation are outlined and the results explained in terms of the theory.

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