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Electrochemistry of Platinum Sols

Part II. On the conductivity of platinum sols

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In the first paper of this series[1], N. Bach and N. Balashova have shown that besides the well-known oxygen-platinum sols, whose negative charge depends on the formation of surface oxides on the particles, it is possible to prepare hydrogen-platinum sols, with a negative charge on the metal surface itself and hydrogen ions in the outer part of the double layer. Sols of both kinds are quite stable and behave like typical acidoid sols. Later these authors succeeded in preparing a third type of platinum sols[2], with a positive charge of the metallic surface, and anions in the outer part of the double layer.

The existence of three different types of platinum sols, predicted by A. Frumkin[3] in connection with his studies on platinized platinum electrodes, was thus proved. These sols correspond to the three different consecutive states which are characteristic of the surface of the electrode, when it passes from cathodic to anodic[4] polarization.

In a recent paper on hydroxo-platinum sols, W. Pauli[5] expresses doubts as to the existence of stable hydrogen-platinum

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[1] N. Bach u. N. Balashowa, Acta Physicochimica URSS, **3**, 79 (1935).

[2] N. Bach a. N. Balashova, Nature, **137**, 716 (1936).

[3] A. Frumkin, Trans. Farad. Soc., **31**, 69 (1935).

[4] A. Šlygin u. A. Frumkin, Acta Physicochimica URSS, **3**, 791 (1935); A. Šlygin, A. Frumkin u. W. Medwedowsky, Acta Physicochimica URSS **4**, 911 (1936); A. Frumkin and A. Šlygin, Acta Physicochimica **5**, 819 (1936).

[5] W. Pauli u. A. Baczewski, Monatshefte für Chemie, **69**, 204 (1936).

sols, and suggests that the observed negative charge is due, in this case also, to surface oxides on the particles, which have not been completely reduced by hydrogen. These remarks refer to the preliminary results, communicated by Prof. A. Frumkin during the discussion on colloidal electrolytes at the Faraday Society in 1934[3], and not to the more detailed paper which has since been published[1]. It seems therefore worth while to remind here shortly the data which we consider as affording decisive evidence that acidoid hydrogen-platinum sols really exist.

Sols prepared by pulverisation of platinum by means of an a. c. arc in a hydrogen atmosphere have a negative cataphoretic charge and do not adsorb acids. When oxygen, diluted with nitrogen, is bubbled through such a sol, adsorption sets in after a certain amount of gas has passed, reaches more or less rapidly a maximum and then decreases; the curves compare very closely with similar curves obtained with electrodes of platinized platinum. If the platinum sols are alternately saturated with oxygen and hydrogen, adsorption and desorption follow each other exactly in the same way as on electrodes. In the latter case, the absence of adsorption of acid when the electrode is saturated with hydrogen is due to the fact that the platinum surface sending hydrogen ions in the solution takes a negative charge and is unable to attract anions. The outer part of the double-layer consists of hydrogen-ions. We have no reasons to suppose that, in sols, the lack of acid adsorption in a hydrogen atmosphere has any cause, other than on electrodes.

Thus it is most simple and natural to suppose that hydrogen-platinum sols have the following constitution: the metal particles send in the solution hydrogen ions, which form the outer part of the double layer, and thereby acquire themselves a negative charge. Besides the electrical double layer which is thus formed, the platinum surface is covered by an adsorbed film of atomic hydrogen; this can be seen from the course of the acid adsorption curves during oxidation, and is also in full agreement with the behaviour of platinum electrodes.

The existence of positive platinum sols, obtained by very slow oxidation of negative hydrogen-platinum sols, definitely proves that hydrogen sols are distinctly different from negative oxygen-platinum sols, since the latter can be odtained by further oxidation of the positive sols. The analogy between the particles of a platinum sol and platinum electrodes is thus complete, and we may consider each particle as a small gas electrode, whose charge and adsorptive properties are determined by the gas atmosphere.

We have already stated that our hydrogen-platinum sols are quite stable. When sealed in tubes in an atmosphere of hydrogen, sols containing about 200 mg platinum per litre could be kept for weeks without coagulating[6]. These sols could also be concentrated without coagulating to a volume several times smaller than the original one, by boiling in a constant stream of hydrogen. Pauli did not succeed in obtaining stable sols by saturating his hydroxo-sols with hydrogen, either purified and concentrated by electro-decantation, or not purified[7]. In every case his sols coagulated within a short time. It is quite possible that during the reduction of a hydroxo-sol in presence of a considerable amount of electrolytes (the specific conductivity of Pauli's unpurified sols was about $8—12 \cdot 10^{-6}\ \Omega^{-1}$, that of ours being only $2—3 \cdot 10^{-6}\ \Omega^{-1}$), conditions are less favourable for stability at the zero charge point than when sols are directly prepared in an atmosphere of hydrogen. As to the purified sols, it is difficult to compare them with our hydrogen-Pt sols, since we never reached a concentration of 1,5—1,9 g/lit.; at 0,4 g/lit. our sols are quite stable in an atmosphere of hydrogen. The conductivity of hydroxo-platinum sols markedly increases with time[8]. The conductivity of hydrogen-Pt-sols remains, on the contrary, constant during several days if they are kept in an atmosphere of hydrogen. This shows that the latter have a more definite and stable structure than the hydroxo-sols.

In the present study we undertook to determine the changes of conductivity which occur in platinum sols when they coagulate without addition of electrolytes as a result of their being frozen. Knowledge of the nature of the conductivity of sols affords a deeper insight into their constitution. The hydrogen-platinum sols are particularly interesting in that respect, because we have a fairly definite conception of their structure. If this conception is exact, it can be expected that in very pure hydrogen sols the conductivity is mainly

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[6] Unpublished data of N. Balashova.

[7] l. c. p. 229.

[8] S. W. Pennycuik, J. Chem. Soc., London, **1927**, 2600.

due to the platinum particles and the hydrogen ions of their ionic atmosphere, and not to foreign electrolytes present in the solution.

The change of conductivity after freezing and re-melting was studied on hydroxo-Pt sols by S. W. Pennycuick[9] and by W. Pauli[5], and on chloroxo-Pt sols by the latter[10]. In most cases they noted a decrease of conductivity after freezing and remelting, reaching about 20—30%. These results are, however, not strictly reproducible. They depend on rather complicated processes of desorption of electrolytes from the particles of the hydroxo- and chloroxo-Pt-sols during coagulation, frequently followed by further reactions. In such cases it is certainly exact, as was emphasized by Pauli[5], that the liquid obtained after melting the frozen sol is not identical with the intermicellar liquid. However, in the case of H_2-Pt-sols, which are formed without any foreign electrolytes, we may consider the coagulation as going on without any adsorption or desorption, so that the liquid obtained after coagulating the sol by freezing is really identical with the intermicellar liquid.

We did not attempt to separate the intermicellar liquid from the particles by means of ultra-filtration, because we thought it better to refrain from using any methods in which the sol comes in contact with organic membranes, whose presence may alter the conditions of stability and the properties of the double layer.

Experimental part

The sols were prepared by the method described in part I[1] by sparking platinum wire electrodes connected with 110 V a. c. mains through a rheostat, the current being 10—15 amp. Apparatus I, in which the sol was prepared, was connected as shown in Fig. 1, by the ground joint 3 to the freezing apparatus II. The latter contains electrodes for the conductivity measurement and a tube for bubbling hydrogen, which is also used to transfer the sol from I into II under the pressure of the hydrogen. Owing to the ground joint 3, apparatus II can be turned about the horizontal axis formed by the tubes 1 and 2. This allows the liquid to be poured over from part *a* in which the conductivity is measured to part *b* in

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[9] S. W. Pennycuick, J. Chem. Soc. London, **1928**, 2108.

[10] W. Pauli u. Th. Schild, Koll. Z., **72**, 165 (1935).

which the sol is frozen out and remelted, and then back to part *a* without contact with air. All the parts of the apparatus were made of Jena glass. A system of three-way stopcocks allows of filling all the parts with a definite gas beforehand, and of accomplishing all the operations in its atmosphere.

In order to freeze the sol, a thick-walled beaker containing a mixture of crushed ice and sodium chloride at — 9°C, was gradually raised under tube *b* containing the sol. When the sol begins to freeze, a thin layer of white transparent ice forms on the walls of the tube, and thickens gradually, removing towards the middle of the tube the sol which becomes more and more concentrated. When the whole liquid is frozen, a thin platinum stick appears along the axis of the tube, surrounded by gas bubbles; after the ice is melted, the platinum settles to the bottom of the tube in loose aggregates, and the clear liquid is poured back into tube *a* in order to measure the conductivity. As a rule, H_2-Pt-sols do not coagulate completely after freezing and melting for the first time, so that the

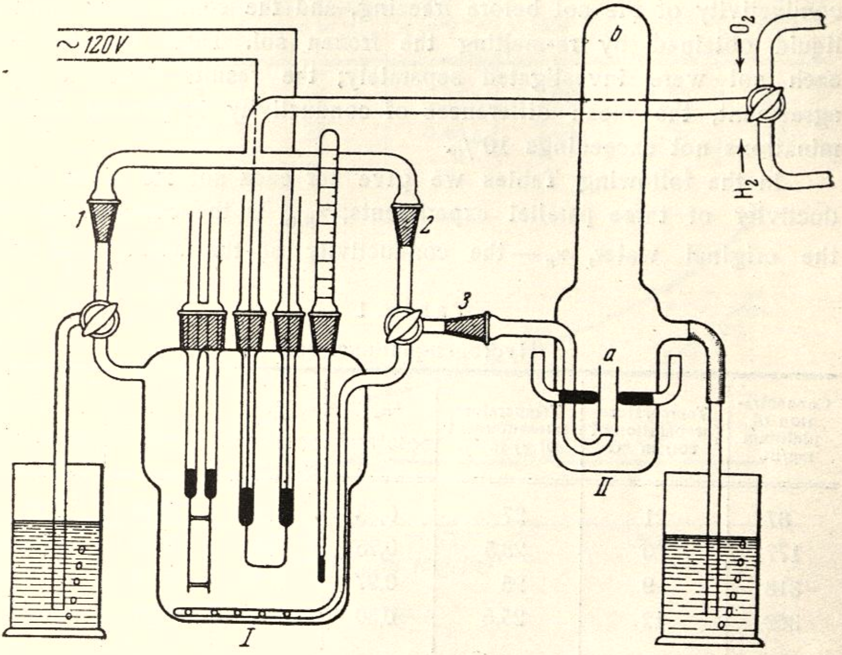

Fig. 1.

operation must be repeated two or three times. The O_2-Pt-sol coagulates completely after the first freezing and melting, which, corroborates **Pauli's** observations.

This study was carried out on H_2-, O_2- and Air-Pt- sols of different platinum concentrations and prepared at different temperatures. In each case we determined the conductivity of the bi-distillate, saturated with gas, in which the sol was prepared, the conductivity of the sol before freezing, and the conductivity of the liquid obtained by re-melting the frozen sol. Three samples of each sol were investigated separately; the results were in fair agreement, the mean differences of conductivity in parallel determinations not exceedings 10%.

In the following Tables we give for each sol the mean conductivity of three parallel experiments; $\varkappa_{H_2O}$ is the conductivity of the original water, $\varkappa_s$ — the conductivity of the sol, $\varkappa_l$ — of the

Table 1

Hydrogen-platinum sols

Concentration of platinum mg/lit.	Temperature (preparation of sol) in °C	Temperature (measurement of $\varkappa$) in °C	$\varkappa_{H_2O}$ $\times 10^6 \Omega^{-1}$	$\varkappa_s$ $\times 10^6 \Omega^{-1}$	$\varkappa_l$ $\times 10^6 \Omega^{-1}$	$\varkappa_c$ $\times 10^6 \Omega^{-1}$
87	21	27	0,33	1,3	0,66	0,63
177	20	23,5	0,25	2,04	1,02	1,02
318	9	25	0,27	2,95	0,73	2,22
362	12	25,5	0,30	4,30	1,08	3,22

Table 2

Oxygen-platinum sols

Concentration of platinum mg/lit.	Temperature (preparation of sol) in °C	Temperature (measurement of $\varkappa$) in °C	$\varkappa_{H_2O}$ $\times 10^6 \Omega^{-1}$	$\varkappa_s$ $\times 10^6 \Omega^{-1}$	$\varkappa_l$ $\times 10^6 \Omega^{-1}$	$\varkappa_c$ $\times 10^6 \Omega^{-1}$
164	0—2	1	0,15	0,41	0,28	0,17
190	0—1	1	0,17	0,68	0,44	0,24
290	0—1	1	0,15	2,38	1,90	0,48
137	25	26	0,24	1,86	1,58	0,28
348	25	26	0,32	4,29	4,01	0,28

liquid obtained after re-melting the frozen sol, and $\varkappa_c = \varkappa_s - \varkappa_l$.

The corresponding curves are given in Fig. 2 for H_2-Pt-sols and in Fig. 3 for O_2-Pt-sols.

Table 3

Air-Pt-sols

Concentration of platinum mg/lit.	Temperature (preparation of sol) in °C	Temperature (measurement of $\varkappa$) in °C	$\varkappa_{H_2O}$ $\times 10^6 \Omega^{-1}$	$\varkappa_s$ $\times 10^6 \Omega^{-1}$	$\varkappa_l$ $\times 10^6 \Omega^{-1}$	$\varkappa_c$ $\times 10^6 \Omega^{-1}$
204	15—17	25	0,44	1,72	1,15	0,57
350	14—16	25	0,43	2,06	1,26	0,80

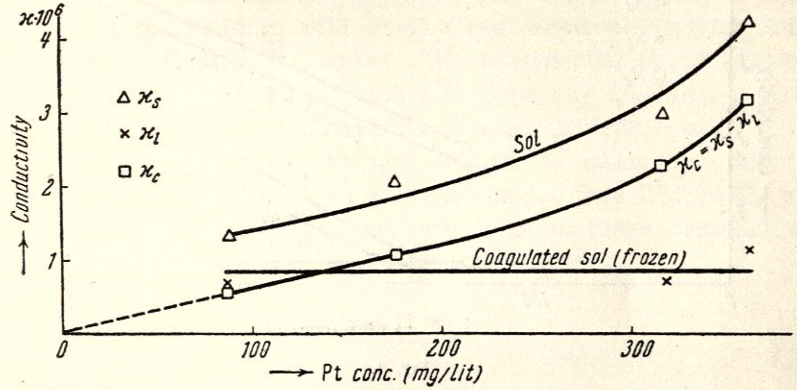

Fig. 2.

Discussion

It can be seen from Table 1 and Fig. 2 that the conductivity of H_2-Pt-sols increases regularly with the concentration of the sol, whereas the conductivity of the liquid obtained after coagulating the sol is nearly constant. It has been already mentioned above that the latter liquid can be considered in the case of H_2-Pt-sols as identical with the intermicellar liquid; $\varkappa_c$ is therefore that part of the conductivity of the sol which is due to the mobility of the colloid particles themselves and to the H^+-ions of the diffuse double layer, and may be called the colloid's own conductivity. The data above show that this part of the conductivity of a H_2-Pt-sol increases continuously with the concentration of the sol and reaches at 362 mg/lit., a value equal to 75% of the total conductivity.

Extrapolating the $\varkappa_c - C_{Pt}$-curve towards $C_{Pt} = 0$ (dotted line) we see that it goes through the zero-point, i. e. that $\varkappa_c$ disappears when the platinum concentration is zero, which confirms that $\varkappa_c$ is really due to the colloid particles themselves and their ionic atmosphere.

The conductivity of the intermicellar liquid is about $0{,}7 \cdot 10^{-6}\ \Omega^{-1}$ higher than that of the original water; this is probably due to electrolytes passing in solution during the formation of the sol, or to a small amount of colloidal platinum particles remaining in solution if the coagulation is not quite complete. Suitable experimental conditions will probably make it possible to exclude this residual effect.

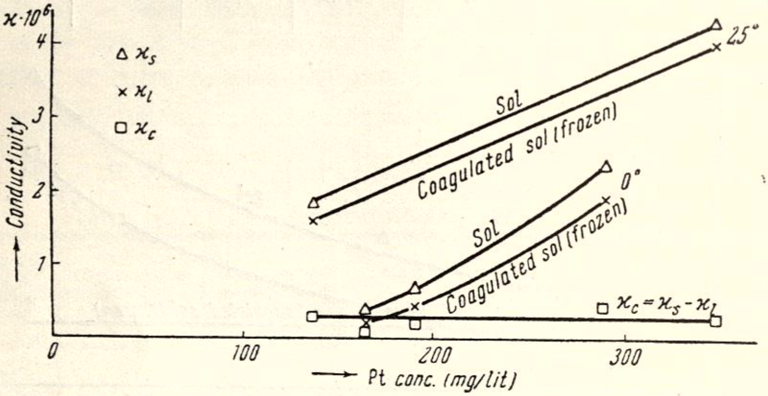

Fig. 3.

Table 2 and Fig. 3 show that things are quite different with oxygen-Pt-sols. The sol conductivity increases with the concentration of Pt but at the same time the conductivity of the coagulated sol also increases; the supernatant liquid of the remelted frozen sol is no longer identical to the intermicellar liquid. Its conductivity is much higher than that of the original water: e. g. for the 348 mg/lit. sol it was twelve times higher; this shows that the liquid contains a considerable amount of dissolved electrolytes, which increases with the concentration of the sol. Whether these electrolytes are really soluble platinum oxides, as Pennycuick and Pauli think, or whether they come from impurities present in the platinum, was not determined analytically.

In the case of O_2-Pt-sols, the freezing method does not give us any means to determine the colloid's own conductivity, nor to interpret the constitution of the sol from conductivity measurements, since the atomisation of platinum is accompanied by the formation and adsorption of electrolytes, and coagulation by their desorption.

In Air-Pt-sols the difference between the conductivity of the sol and of the liquid obtained after freezing and remelting (Table 3) is somewhat higher than in O_2-Pt-sols, and increases with the concentration. We must consider in these sols the possibility that the nitrogen of air combines with oxygen and forms electrolytes, besides the soluble platinum oxydes. The intermicellar liquid becomes so complicated that it is impossible to draw any conclusions as to the structure of the colloid from the freezing experiments.

The results we have obtained confirm the assumption that the structure of hydrogen-Pt-sols is much simpler than that of O_2- and Air-Pt-sols, and that they consist mainly of platinum particles and their ionic atmosphere, formed by hydrogen ions.

Summary

1. Platinum sols of various concentrations, prepared by arcing platinum in an atmosphere of hydrogen, oxygen or air at different temperatures, were coagulated by means of freezing and remelting.

2. In the case of H_2-Pt-sols, the liquid obtained by melting the frozen sol is identical with the intermicellar liquid. The difference between its conductivity and that of the sol corresponds to the colloid's own conductivity; this difference increased with the concentration of the sol and reached $75^0/_0$ of the total conductivity when the concentration was 360 mg per litre.

3. Platinum sols prepared in an atmosphere of hydrogen consist of platinum particles and hydrogen ions, forming the diffuse part of the double layer.

4. In the case of O_2-Pt-sols the difference between the conductivity of the coagulated and original sols is constant at all con-

centrations; it cannot be interpreted as the colloid's own conductivity, because of the presence of electrolytes.

5. Air-Pt-sols are similar to O_2-Pt-sols, but their structure is still more complicated.

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