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Electrochemistry of Platinum Sols.

IV. The particle charge of hydrogen-platinum sols

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The existence of stable hydrogen-platinum sols with a negative charge of the surface and hydrogen ions in the outer sheet of the double layer has been proved by Bach and Balaschowa[1]. These sols are typical acidoid sols, but in contradistinction to the systems hitherto investigated, they are almost free from foreign electrolytes. It has been shown by Bach and Rakov[2] that their conductivity is mainly due to the mobility of the particles themselves and to the hydrogen ions of the ionic atmosphere.

The close relationship between the properties of platinum sols and those of platinum electrodes has been discussed in detail in the first papers of this series[1, 2, 3, 4]. It may be concluded that each particle of the sol behaves as a minute gas electrode whose properties are determined by the gas atmosphere.

The object of the present research was a detailed investigation of the double layer structure at the surface of the sol particles. The experimental data were obtained from measurements of adsorption of NaOH and $Ba(OH)_2$ by means of conductometric titration, from ultramicroscopic particle counts and from cataphoretic velocity measurements in the presence of varying amounts of alkali. Comparison of these data with the conductivity of the sols allowed of evalua-

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

[2] N. Bach a. A. Rakov, Acta Physicochimica URSS, **7**, 85 (1937).

[3] N. Balaschowa a. N. Bach, Acta Physicochimica URSS, **7**, 899 (1937).

[4] In the sequel these papers are referred to as Part I, II and III.

ting to what extent the ions forming the outer sheet of the double layer participate in the conductivity of the sol.

Assuming the potential of the zero charge point to be the same at the surface of the sol particles and of the platinized platinum electrode, we could determine the value of the total potential drop at the surface of the particles. From this value and the charge per unit surface the electrokinetic potential was calculated according to Stern[5].

A serious shortcoming of Stern's theory when applied to colloidal particles is the assumption that the thickness of the double layer is small compared to the radius of the particle. A method for calculating the charge of the diffuse part of the double layer for any radius and for different values of the electrokinetic potential has been given by Müller[6]. Comparison of the charge density, calculated by this method for different particle radii[7] and our data for ζ, with the values obtained experimentally, led us to revise the value of the surface obtained from ultramicroscopic counts.

According to the classical theory of electrokinetic phenomena the cataphoretic velocity differs from zero only in the case of non-conducting particles. The experiment shows, however, that in the majority of cases, metallic sols have cataphoretic velocities of the same order of magnitude as non-metallic ones. This contradiction remains unexplained to the present day. Considering the conductivity of both the particles and the medium, Henry[8] evolved new equations for cataphoresis, differing from the classical ones in their numerical coefficients. For metallic sols, however, these equations also give a cataphoretic velocity equal to zero. Neither can the important improvement introduced by Hermans[9] in the cataphoresis equations as a result of considering the relaxation effect in the double layer be applied to conducting particles.

The electrophoresis of metallic sols may be considered in connection with the polarizability of the particles, if we assume that

5 O. Stern, Z. Elektrochem., **30**, 508 (1924).
6 H. Müller, Kolloidchem. Beih., **26**, 274 (1928).
7 We are indebted to M. I. Temkin for the suggestion to apply Müller's method.
8 D. C. Henry, Proc. Roy. Soc., London, **133**, 106 (1931).
9 Hermans, Phil. Mag., (7) **26**, 650 (1938).

when the surface is completely polarized the current ceases to flow through the particle and the latter acts as a non-conductor.

Henry[8] has shown that, in accordance with the above assumption, the electrokinetic effect on a silver wire in $AgNO_3$-solutions is close to zero under conditions of minimal polarization.

Platinum sols doubtless belong to metallic sols with polarizable surfaces, which may explain the high value of their cataphoretic velocity.

Experimental part

Preparation of H_2—Pt sols

The method of preparation was that described in Parts I, II and III; it was used without any significant change.

Platinum was pulverized in pure water in an atmosphere of hydrogen in a 50 cycle alternating-current arc at 115—120 V. and 12—15 A. Water was saturated with hydrogen in the apparatus prior to the arcing, until the conductivity became constant ($\varkappa = 0.15 - -0.40 \times 10^{-6}\,\Omega^{-1}\,\text{cm.}^{-1}$).

All parts of the apparatus in which this investigation was carried out were made of Jena glass. None of the ground joints were lubricated with grease, all of them being only wetted with pure water.

Freezing out and titration of the sols

Sols prepared in apparatus *I* (Fig. 1) were transferred under a pressure of hydrogen, without contact with the outer atmosphere, into the apparatus for freezing and titration (*IV*, Fig. 1) differing from that described in Part II only in the presence of the ground joint (*8*), which allowed of introducing a micro-burette (*III*, Fig. 1) with a narrow capillary end (Fig. 1 *A*).

The freezing out of the sol and determination of the conductivity were carried out as described in Part II. After a constant conductivity had been reached, the end of the micro-burette *III* was inserted into the ground joint (*8*) under continuous passage of hydrogen. The volume of the drops was 0.006—0.008 cm.[3]. During the titration the liquid was stirred by the hydrogen bubbles. The titrated solutions of NaOH or $Ba(OH)_2$ were kept in flask *II* under an atmosphere of hydrogen.

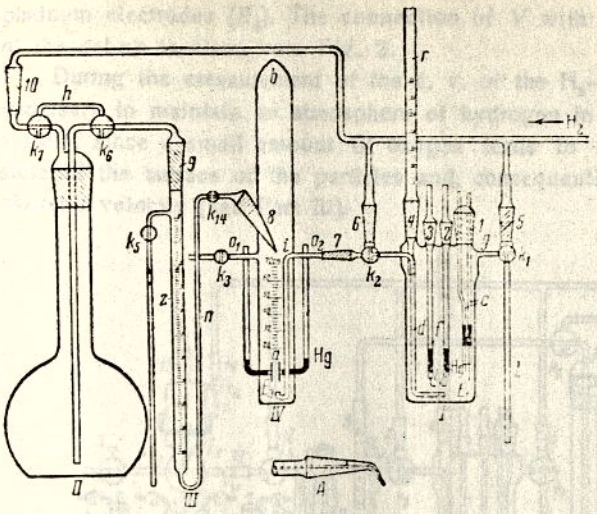

Fig. 1.

Measurements of the cataphoretic velocity of the H_2—Pt sols

The cataphoretic velocity (c. v.) of the sol was determined by the moving boundary method in the apparatus described in Part III and shown in Fig. 2 (*VI*). In our experiments, the specific conductivity of the supernatant liquid was equal to that of the sol, so that the velocity of the descending boundary was equal to that of the ascending one.

During the measurement of the c. v., the electric field was commuted every 15—20 min. The whole measurement lasted from 30 to 80 min.

To measure the c. v. at various points of the curve of conductometric titration of H_2—Pt sols with alkali, separate portions of the sol were transferred into apparatus *V*. After the addition of the amount of alkali corresponding to a given point, the portion of sol was transferred to part *D* of apparatus *VI* where the cataphoretic velocity was determined.

Apparatus *V* (Fig. 2) for the titration of the sols is a cylindrical graduated vessel, 50 $cm.^3$ in volume, with two sealed smooth

platinum electrodes (E_4). The connection of V with the other parts of the set-up is clear from Fig. 2.

During the measurement of the c. v. of the H_2—Pt sol it was necessary to maintain an atmosphere of hydrogen in all parts of the system, since a small amount of oxygen leads to changes in the state of the surface of the particles and, consequently, in the cataphoretic velocity (see Part III).

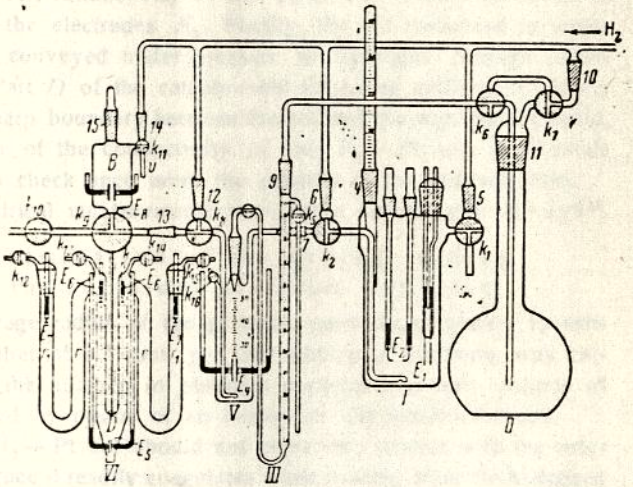

Fig. 2.

The parts V and VI were kept in a water bath at 25° C ± 0.02° C.

The conductivities of the supernatant liquid and sol were equalized by addition of electrolytes. When measuring the c. v. of the pure H_2 — Pt sol the water in the upper part (B) of apparatus VI was acidified with HCl. The very slight amount of HCl contained in the solution in contact with the sol during the measurement of the c. v. does not noticeably affect the structure of the double layer; the addition of KCl, which would have been needed in greater amount owing to its smaller conductivity, would have led to hydrolytic adsorption of KOH at the surface of the particles, to an increase in the acidity of the liquid and changes in the structure of the double layer. On the contrary, when measuring the c. v. of the sol reduced

to minimum conductivity by addition of alkali, the conductivity of pure water was made equal to that of the sol by addition of KCl. In this case, the insignificant amount of KCl cannot measurably alter the structure of the double layer, inasmuch as the H^+-ions are already replaced by Na^+-ions. After equalization of the conductivities, the liquid was transferred through the capillary k from the upper part B to the graduated part D, to the side tubes r and the end tubes r_1. The conductivity of the water was controlled at 25° C by means of the electrodes E_5. Finally, the sol contained in apparatus V was conveyed under pressure of hydrogen through capillary k into Part D of the cataphoresis apparatus sufficiently slowly to ensure a sharp boundary between the sol and the supernatant liquid. Determination of the conductivity of the H_2—Pt sols in D made it possible to check once more the equality of the conductivities.

The electrical measurements were made according to Kruyt[10].

Determination of the average radius of the colloidal platinum particles

The average radius of the platinum particles, necessary to estimate the number of H^+-ions per unit surface of platinum, was calculated from the number of platinum particles per unit volume of sol, determined by means of an immersion slit ultramicroscope.

As the H_2—Pt sol should not come into contact with the outer atmosphere, since it readily coagulates when passing from the hydrogen to the oxygen state, it was protected by electrodialyzed gelatine while still in the atmosphere of hydrogen and then diluted with pure water.

Results

Relation between the conductivity of the H_2—Pt sol and its concentration

Table 1 gives the conductivity of sols of various concentrations.

Coagulation of H_2—Pt sols by the freezing-out method

To achieve complete coagulation, it was necessary to freeze and remelt the sol three of four times. The results of the experiments carried out with sols of various concentrations are given in Table 2.

[10] H. A. Kruyt a. van der Willingen, Koll. Z., 44, 22 (1928).

Table 1

Conductivity of H_2 — Pt sols with increasing concentration of platinum; $t = 25°$ C

Concentration of sol (mgr./litre)	$(\varkappa_{sol} - \varkappa_{H_2O}) \times 10^6$ (Ω^{-1} cm.$^{-1}$)	$(\varkappa_{sol} - \varkappa_{H_2O}) \times 10^6$ per 100 mgr./litre Pt (Ω^{-1}cm.$^{-1}$)
100	0.82	0.82
195	1.60	0.82
215	1.68	0.78
290	2.33	0.81
315	2.51	0.80
400	3.24	0.81
405	3.21	0.79
445	3.55	0.80
460	3.69	0.60
		Average . . . 0.82

Table 2

The change in the conductivity of the H_2 — Pt sol upon coagulation by freezing; $t = 25°$ C

Concentration of sol (mgr./litre)	$(\varkappa_{sol} - \varkappa_{H_2O}) \times 10^6$ (Ω^{-1} cm.$^{-1}$)	$(\varkappa_{liq.*} - \varkappa_{H_2O}) \times 10^6$ (Ω^{-1} cm.$^{-1}$)	Percentage decrease in conductivity
195	1.60	0.46	71
240	1.93	0.48	75
290	2.33	0.48	84
400	3.24	0.80	75
408	3.38	0.80	76
		Average . . .	76%

* $\varkappa_{liq.}$ is, as in Part II, the conductivity of the liquid obtained after melting the frozen sol.

For control, pure water was frozen under the same conditions as the sol. The conductivity of the water before freezing was

0.31×10^{-6} Ω^{-1} cm.$^{-1}$ at 25° C; after freezing and remelting twice, it became 0.37×10^{-6} Ω^{-1} cm.$^{-1}$, so that the change of conductivity does not exceed experimental errors.

In Fig. 3 the results given in Tables 1 and 2 are shown graphically.

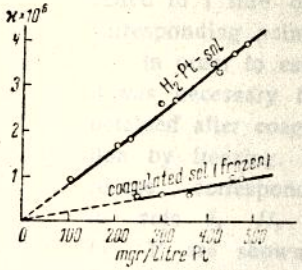

Fig. 3

Titration of the H_2—Pt sol with NaOH solution before and after freezing

About thirty conductometric titrations with a $4 \times 10^{-3} N$ NaOH solution were carried out with sols of various concentrations. Fig. 4 shows typical curves for the titration of sols of increasing platinum concentration:

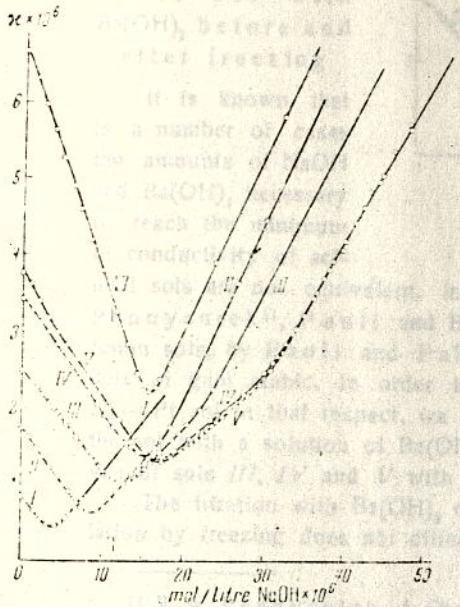

Fig. 4.

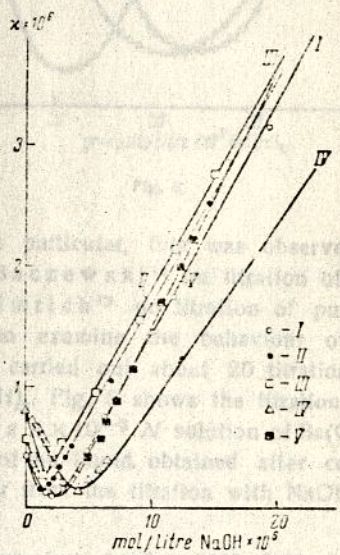

Fig. 5.

I *II* *III* *IV* *V*

100 mgr./l. 200 mgr./l. 240 mgr./l. 405 mgr./l. 445 mgr./l.

The abscissae give the amounts of NaOH in micro-equivalents added to 1 litre of sol; the ordinates — the conductivities at the corresponding points.

In order to estimate the electrolytes remaining in the solution it was necessary to titrate not only the sol but also the liquid obtained after coagulation by freezing. The curves, corresponding to sols *I*, *II*, *III*, *IV*, *V* are shown in Fig. 5.

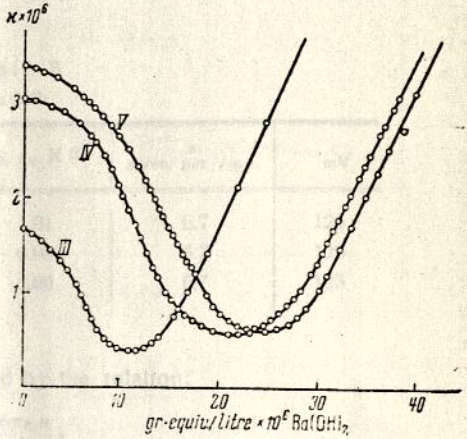

Fig. 6.

Titration of the H_2—Pt sol with $Ba(OH)_2$ before and after freezing

It is known that in a number of cases the amounts of NaOH and $Ba(OH)_2$ necessary to reach the minimum of conductivity of acidoid sols are not equivalent. In particular, this was observed by Pennycuick[11], Pauli and Baczewski[12] on titration of platinum sols, by Pauli and Palmrich[13] on titration of purified sols of gum arabic. In order to examine the behaviour of the H_2—Pt sol in that respect, we carried out about 20 titrations of the sol with a solution of $Ba(OH)_2$. Fig. 6 shows the titration curves of sols *III*, *IV* and *V* with a 4×10^{-3} *N* solution of $Ba(OH)_2$.

The titration with $Ba(OH)_2$ of the liquid obtained after coagulation by freezing does not differ from the titration with NaOH.

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[11] S. W. Pennycuick, J. Chem. Soc., London, **1928**, 2108; J. Am. Chem. Soc., **52**, 4621 (1930).
[12] W. Pauli u. Baczewski, Monatshefte Chem., **69**, 204 (1936).
[13] W. Pauli u. Palmrich, Koll. Z., **79**, 64 (1937).

Determination of the cataphoretic velocity of H_2 — Pt sols at various points of the conductometric titration curve

Our measurements have shown that the electrophoretic velocity does not depend upon the concentration of the sol within 100—460 mgr./litre and is equal to 5 μ/sec. per V/cm. for pure sols[14]. Table 3 gives the c. v. of H_2 — Pt sols of various concentrations after the addition of a quantity of NaOH corresponding to the minimum of conductivity.

Table 3

$t = 25°$

Concentration of sol (mgr./litre)	$\varkappa_{sol} \times 10^6$	$\varkappa_{sup.\ liq.} \times 10^6$	u μ/sec. per V/cm.	ζ mV
112	0.93	1.01	6.7	125
115	1.09	0.98	6.7	125
460	1.83	2.00	6.7	125

The ζ-potential was calculated by the relation:

$$\zeta = \frac{6\pi\eta u}{D}.$$

Table 4

$t = 25°$ C

Concentration of sol (mgr. litre Pt.)	$\varkappa_{sol} \times 10^6$	$\varkappa_{sup.\ liq.} \times 10^6$	u μ/sec. per V/cm.	ζ mV
112	0.80	0.75	3.3	63
460	1.38	1.53	3.3	63
460	1.39	1.60	3.5	63

[14] The particles of the H_2 — Pt sol move towards the anode, so that both cataphoretic velocity and ζ-potential should be noted with a negative sign. However, as we consider throughout this paper only this one type of sol, the negative sign has been omitted for convenience, it being understood that all the values ot u, ζ and σ are negative.

The coefficient was taken equal to 6 and not 4, since we are dealing here with particles whose dimensions are small in comparison with the thickness of the double layer[15].

The c. v. at the minimum of conductivity of H_2 — Pt sols titrated with $Ba(OH)_2$ is lower than the c. v. of the initial sol, as can be seen from Table 4.

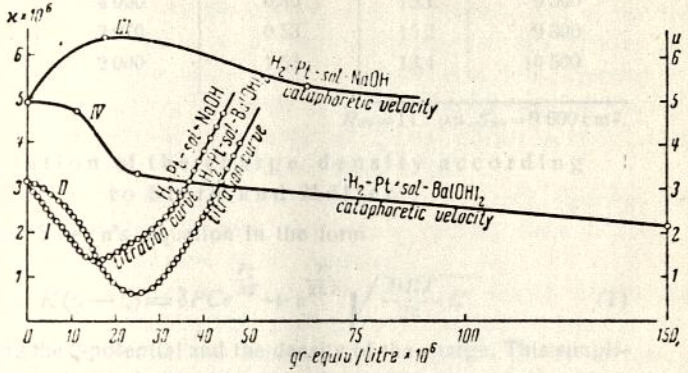

Fig. 7.

During the measuremnet of the c. v. of the initial H_2 — Pt sol, the boundary moving towards the positive pole became sharper, whilst the boundary moving from the negative pole became more diffuse. In the case of H_2 — Pt sols reduced to minimum conductivity by addition of alkali, the picture is reversed.

The course of the relation between the c. v. and the addition of alkali is shown in Fig. 7 which, for comparison, also gives the curves of conductometric titration with NaOH and $Ba(OH)_2$.

Determination of the average radius of the particles

The count of the platinum particles by means of the immersion slit ultramicroscope in an optically limited volume of liquid (8.79×10^{-10} cm.^{3}) was made after the H_2 — Pt sol had been protected from coagulation by gelatin. The amount of gelatin added was 0.05 gr./litre for a sol of 120 mgr./litre Pt and 0.20 gr./litre for 480 mgr./litre Pt. The results are given in Table 5.

[15] P. Debye a. E. Hückel, Physik. Z., **25**, 49, 204 (1924). D. C. Henry, l. c.[8].

Table 5

Concentration of sol (mgr./litre)	Dilution of the sol for the counting of particles	Average number of particles in 8.79×10^{-10} cm.^{3}	Average radius of particles $\mu\mu$	Total area of particles for 100 mgr./litre Pt (cm.^{2})
120	524	0.67	15.2	9 300
480	4 000	0.40	15.1	9 300
480	2 670	0.53	15.2	9 300
480	2 000	1.53	13.4	10 500

$R_{av} = 14.7\ \mu\mu$, $S_{av} = 9\,600$ cm^2.

Calculation of the charge density according to Stern and Müller

We used Stern's equation in the form

$$K(\varphi - \zeta) = \delta F C e^{\frac{F\zeta}{RT}} + e^{\frac{F\zeta}{2RT}} \sqrt{\frac{DRT}{2\pi} C} \qquad (1)$$

for calculating the ζ-potential and the density of the charge. This simplified form is applicable in the absence of specific adsorption, at low concentrations of electrolytes and at high values of ζ, which corresponds to our experimental data. The actual value of ζ was determined from equation (1) by the method of successive approximations.

For this calculations it is necessary to know the total potential difference and the capacity of the double layer. Assuming these values to be the same at the surface of the colloidal platinum particles and on platinized platinum electrodes, φ and k can be taken, as will be seen further, equal to 0.810 V and 20 μF respectively; further, $\delta = 3 \times 10^{-8}$ cm. is the thickness of the Helmholz part of the double layer; $R = 8.32 \times 10^7$ ergs; $D = 80$; $F = 2.94 \times \times 10^{14}$ e. s. u., $T = 291°$ and $C = 10^{-8}$ moles per cm.^{3} [16].

Substituting these values, we obtain $\zeta = 300$ mV., whereas the highest value for ζ as calculated from our values of the cataphoretic velocity was equal to 125 mV.

[16] There is some uncertainty in the choice of the value for C, since we do not know exactly what foreign electrolytes determine the conductivity of the sol minus that of the colloid itself. Considering the value of the conductivity at its minimum, C may be taken equal to 10^{-8}. This is confirmed by the fact that addition of univalent ions in such an amount does not appreciably affect the structure of the double layer.

Substitution of $\zeta = 300$ mV. and of the values for δ, R, F, C, T in the expressions:

$$\eta_1 = \delta F C e^{\frac{F\zeta}{RT}}, \quad (2)$$

$$\eta_2 = e^{\frac{F\zeta}{2RT}} \sqrt{\frac{DRT}{2\pi} C} \quad (3)$$

gives the density of the charge of the Helmholz part of the double layer $\eta_1 = 14\,000$ e. s. u. and the density of the charge of the diffuse part $\eta_2 = 22\,000$ e. s. u., whence the total density of the charge $\eta_1 + \eta_2 = \eta_0 = 36\,000$ e. s. u. Substituting in the expressions (2) and (3) 125 mV. for ζ, we obtain $\eta_1 = 13$ e. s. u. and $\eta_2 = 675$ e. s. u., or $\eta_0 = 688$ e. s. u.

It has already been mentioned that Stern's equation could not be expected to give satisfactory results, since it does not consider the curvature of the particles.

We calculated the relation between the density of the charge and the curvature by means of Müller's method of integral curves, according to which the density of the charge σ of the diffuse part of the double layer is given by the equation:

$$\sigma = \frac{DkT}{4\pi\varepsilon} \cdot y_0^2 \left(\frac{d\chi}{dy}\right)_0. \quad (4)$$

In this expression $\chi = \frac{\varepsilon\zeta}{RT}$ and $y = \frac{\lambda}{R}$; R is the radius of the particle, $\lambda = \sqrt{\frac{DkT}{4\pi\varepsilon^2 \nu \Sigma c_i}}$ is the known measure of the thickness of the double layer.

The values for the density of the charge calculated for various radii at $\zeta = 100$ mV. and $\zeta = 125$ mV. are given in Table 6.

Table 6

$\zeta = 100$ mV.		$\zeta = 125$ mV.	
$R \times 10^7$ cm.	σ e. s. u.	$R \times 10^7$ cm.	σ e. s. u.
1.7	12 700	1.34	19 600
3.6	6 100	2.9	9 400
7.7	3 000	6.0	4 900
15.3	1 700	12.5	2 600
19.2	1 400	16.1	2 200
33.3	450	29.0	1 400

The variation of the charge density with the radius of the particles is shown in Fig. 8, where curve *I* corresponds to $\chi = 4$ ($\zeta = 100$ mV.) and curve *II* to $\chi = 5$ ($\zeta = 125$ mV.).

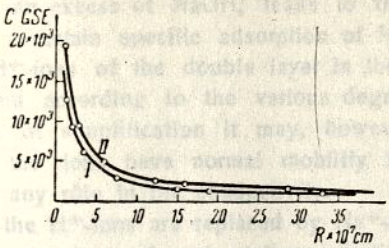

Fig. 8.

Discussion

The data given in Tables 1 and 2 and Fig. 3 confirm the view-point expressed by Bach and Rakov[2] that the conductivity of the colloid, due to the mobility of the H^+-ions of the double layer and to the mobility of the Pt-particles bearing a negative charge, constitutes the main part of the conductivity of the sol. In this respect our H_2—Pt sols differ from the platinum sols described earlier by Beans and Eastlack[17], Pennycuick[18], Pauli and Shield[19] and Pauli and Baczewski[12], since the conductivity of the latter is mostly due to the presence of foreign electrolytes.

Titration with NaOH of the liquid obtained after freezing out the H_2—Pt sol (Fig. 5) shows that it has acid properties. This may be due partly to incomplete coagulation of the sol (golden opalescence of the liquid) and partly to the presence of acid electrolytes.

The characteristic course of the curves for the titration of H_2—Pt sols by NaOH (Fig. 4) may be attributed to the fact that not all the H^+-ions of the outer sheet are linked to the surface with the same strength. Part of the H^+-ions are easily replaced by Na^+-ions; the sol titrates to minimum conductivity practically as a strong acid, as seen when comparing with the titration curve of

[17] H. T. Beans a. H. E. Eastlack, J. Am. Chem. Soc., **37**, 2667 (1915).
[18] S. W. Pennycuick, J. Chem. Soc., London, **1927**, 2600.
[19] W. Pauli a. Schield, Koll. Z., **72**, 165 (1935).

H_2SO_4 at the same concentration (curve *VI* Fig. 4). The bond between the H^+-ions and the surface is purely electrostatic. The behaviour of the other part of the H^+-ions, which are substituted only in presence of an excess of NaOH, leads to the assumption that there must be a certain specific adsorption of H^+-ions. The participation of the H^+-ions of the double layer in the conductivity of the sol is different according to the various degrees of their linkage. For the sake of simplification it may, however, be assumed that one part of the ions have normal mobility whilst the other part do not play any rôle in the conductivity.

As the H^+-ions are replaced by Na^+-ions the potential of the gas electrode, *i. e.*, of each platinum particle, becomes more negative so that more H^+-ions are sent into the solution. The form of the conductometric titration curve with NaOH solution is typical not only for H_2 — Pt sols, but also for other pure acidoid sols such as hydroxyplatinum sols[12], silver iodide sols[20] and hydrophilic sols of gum arabic. In a recent paper, de Bruyn and Overbeek[20] assume that this form of the curve is due, in the case of AgJ, to the presence of foreign ions, *e. g.*, Zn^{++} and Cu^{++}, accumulating in the sol during the electrodecantation. Since we did not apply electrodecantation for the preparation of our H_2 — Pt sols, this explanation cannot hold in all cases, and we consider that this characteristic form of the titration curve is actually due to the structure of the double layer in pure acidoid systems.

The form of the titration curve of H_2 — Pt sols with $Ba(OH)_2$ (Fig. 6) differs considerably from that with NaOH. The initial slow decrease in the conductivity corresponds to the substitution of Ba^{++}-ions for H^+-ions in the deeper parts of the outer sheet of the double layer, Ba^{++}-ions coming closer to the surface than Na^+-ons owing to their higher charge. Upon further addition of $Ba(OH)_2$, H^+-ions taking greater part in the conductivity are replaced. The diffuse minimum is characteristic not only for H_2 — Pt sols, but for other acidoid sols as well, even non-metallic[13].

A comparison of the conductance titration curves of NaOH and $Ba(OH)_2$ allows of evaluating the number of H^+-ions corresponding to the surface charge.

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[20] H. de Bruyn a. Th. G. Overbeek, Koll. Z., **84**, 186 (1938).

Titration curves of the same sol (400 mgr./litre) with NaOH and $Ba(OH)_2$ are compared in Fig. 9. If all the H^+-ions had been replaced by Na^+-ions at the point L of curve I, the rise of the conductivity would be linear from that point onwards. Actually this rapid rise begins only after N'. An amount of NaOH corresponding to $NN' = LL'$ is necessary in addition to OM for the replacement of all the H^+-ions of the double layer by Na^+-ions. The total charge of the surface is given by OM', and the excess $M'P$ of NaOH necessary to achieve the substitution of all the H^+-ions is equal to 6.6×10^{-6} gr. equiv./litre of NaOH for this sol. This concentration of free alkali corresponds to pH = 8.8.

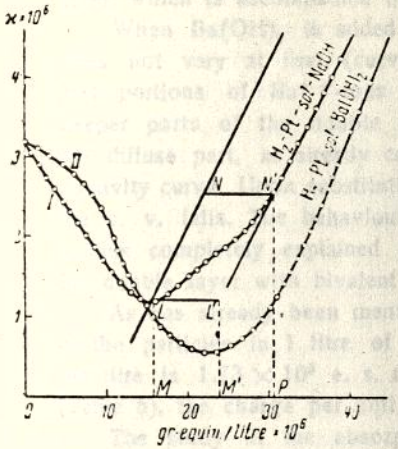

Fig. 9.

The abscissa of L' is in good agreement with the abscissa of the minimum of the $Ba(OH)_2$ titration curve. The total surface charge is equal to 6×10^{-6} gr. equiv. or 1.73×10^9 e. s. u. for every 100 mgr. of Pt in one litre of sol.

It can be seen from Fig. 7 that the rapid change of the cataphoretic velocity and its passage through a maximum corresponds to the substitution of Na^+-ions for H^+-ions, *i. e.*, to a significant change of the double layer structure.

The question whether the maximum of c. v. at low concentrations of electrolytes is related to a maximum of the ζ-potential is still unsettled. Bickermann[21] and Hermans[8] have shown that the relaxation effect in the diffuse double layer can give rise to a maximum of c. v. even when the variation of ζ is monotone. It seems to us, however, that in the case of H_2—Pt sols, it is

[21] J. J. Bickermann, Z. physik. Chem., **171**, 209 (1934).

more natural to assume that the change of the structure of the double layer due to the substitution of Na^+-ions for H^+-ions is accompanied by a rise of the ζ-potential. When all the H^+-ions are replaced, further addition of NaOH leads only to a compression of the double layer, which is accompanied by a slow decrease in the potential.

When $Ba(OH)_2$ is added to the sol, the cataphoretic velocity does not vary at first (curve *II*, Fig. 9). This confirms that the first portions of Ba^{++}-ions displace only the H^+-ions from the deeper parts of the double layer, without notable alteration of the diffuse part, as already concluded from the course of the conductivity curve. Upon substitution of H^+-ions from the diffuse part, the c. v. falls. The behaviour of the sol in presence of $Ba(OH)_2$ is thus completely explained by consideration of the structure of the double layer with bivalent cations in the outer sheet.

As has already been mentioned, the charge of the total surface of the particles in 1 litre of sol containing 100 mgr. of platinum per litre is 1.73×10^9 e. s. u. With a surface equal to 9600 $cm.^2$ (Table 5), the charge per unit surface is equal to 1.8×10^5 e. s. u.

The study of the absorption of alkali on platinized platinum electrodes in relation to the potential of the electrode[22] has shown that the point of zero charge of the H_2-platinum electrode is $+0.3$ V. as referred to the normal hydrogen potential. Knowing the position of the zero charge point we can determine, for any concentration of H^+-ions, the total p. d. in the double layer. In the case of our H_2—Pt sols, the charge density 1.8×10^5 e. s. u. corresponds to a pH value of 8.8, whence the total p. d. $\varphi = 0.058 \times 8.8 + 0.3 = 0.81$ V.

Measurements on mercury[23], lead[24] and smooth platinum[25] show that the capacity of the pure surface of these metals is about 18—20 μF. For our calculations, we took the capacity of the surface of platinum equal to 20 μF. In 1 *N* solution to which these measurements refer, the corresponding charge of the surface is equal to 20 $\mu F \times 0.81$ V. $= 1.62 \times 10^{-5}$ coulombs $= 4.86 \times 10^4$

[22] Unpublished data by A. Platonov, see A. Frumkin a. Šlygin, Acta Physicochimica URSS, **5**, 819 (1936).
[23] T. Borissowa a. M. Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936).
[24] B. Kabanov a. S. Joffa, Acta Physicochimica URSS, **10**, 317 (1939).
[25] Unpublished data by P. Dolin (Karpov Institute).

e. s. u. The surface charge is lower in dilute solutions owing to the capacity being smaller because the double layer is more diffuse. The value of the charge may in this case be determined by Stern's equation. It is equal to the potential drop $\varphi - \zeta$ in the Helmholtz part of the double layer multiplied by its capacity which may be taken equal to the capacity in a concentrated solution. The value for the ζ-potential calculated from our data according to Stern is 300 mV., whence

$$\eta = 20 \times 10^{-6}(0.81-0.3) = 1.04 \times 10^{-5} \text{ coulombs} = \\ = 3.06 \times 10^{4} \text{ e. s. u.}$$

This value is 5, 9 times smaller than the charge per unit surface determined on colloidal platinum particles.

All the known properties of platinum sols lead to the conclusion that there is no difference between the behaviour of the surface of platinum sol particles and that of platinized platinum electrodes. The charge density can be determined from the capacity of the platinum electrode with much greater accuracy then from the ultramicroscopic count of sol particles; in the latter case all the experimental errors lead to a diminished value of the surface, *i. e.*, to an exaggerated value for the charge per unit surface. Assuming the latter to be 30 600 e. s. u. on the surface of the particles of H_2 — Pt sols, we can calculate the corresponding radius; R is found to be 2.5 $\mu\mu$. This value may be compared to that which we obtained according to Müller from the density of the charge in the diffuse double layer, using our experimental data on the conductivity of the sol at various points of the titration curve and the corresponding values for ζ.

Assuming that the conductivity of the sol, less the initial conductivity of the water, is due only to the presence of the platinum particles and the H^+-ions of the double layer, and that the latter possess normal mobility, the concentration C of H^+-ions in the ionic atmosphere may be calculated using the equation:

$$\varkappa_{sol} - \varkappa_{H_2O} = CF(V_{H^+} + u_{Pt}),$$

where V_{H^+} is the mobility of the H^+-ions and u_{Pt} — the cataphoretic mobility of the particles.

At 25° C, $\varkappa_{sol} - \varkappa_{H_2O} = 0.8 \times 10^{-6}\,\Omega^{-1}$ cm.$^{-1}$ for a sol containing 100 mgr./litre, $V_{H^+} = 36.2$ μ/sec. per V./cm. $u_{Pt} = 5.0$ μ/sec. per V./cm., whence $C = 2.0 \times 0.10^{-6}$ gr. equiv./litre, *i. e.*, it may be

considered that one third of the H^+-ions corresponding to the total charge of the surface, and one half of those corresponding to the minimum of the curve for conductance titration, participate with normal mobility in the conductivity of the sol. In the platinum sols studied by Pauli and Pennycuick, there is no noticeable divergence between the number of H^+-ions calculated from the conductivity and that found by titration. This comes probably from the conductivity of these sols being chiefly due to the presence of foreign electrolytes.

If it be assumed that only the ions of the diffuse part of the double layer participate in the conductivity, then the charge of the diffuse part corresponding to unit surface must be 10 200 e. s. u. According to Müller this charge density would conform at $\zeta = 100$ mV. (see Table 6 and Fig. 8) to a radius of 2.5 μμ. Calculating in the same manner the concentration of Na^+-ions corresponding to the conductivity at the minimum of the titration curve, we obtain for 100 mgr./litre $C = 2.7 \times 10^{-6}$ gr. equiv./litre, *i. e.*, only 45% of the Na^+-ions necessary for complete replacement of H^+-ions participate in the conductivity with normal mobility.

The charge density falling upon the diffuse part would therefore be 13 770 e. s. u. According to Müller this charge density at $\zeta = 125$ mV. corresponds to a radius of 2.0 μμ. Thus the value for the radius of the particles calculated according to Müller for various ζ-potentials and charge densities is close to that calculated from the capacity of the platinized platinum electrode. This confirms that the radius of the particles as determined from ultramicroscopic counts is markedly larger than the actual value[26].

This more detailed investigation of the structure of the double layer at the surface of colloidal platinum particles has thus allowed of bridging the discrepancy which existed up to the present between the charge of the particles calculated from electrokinetic characteristics of sols and that obtained from conductivity data.

We wish to express our sincere gratitude to Prof. A. Frumkin for the valuable advice he has given us in the course of this work.

[26] The determination of the radius of the particles which is now being carried out by a somewhat modified method leads to values for the charge density which are much closer to the results obtained from the capacity. The results will be published shortly.

Summary

1. The conductivity of H_2—Pt sols is due for the greater part to the conductivity of the colloid itself and is proportional to the platinum content of the sol.

2. The H_2—Pt sol is a genuine acidoid sol in which every particle of platinum behaves as a hydrogen gas electrode.

3. The conductance titration curves of the H_2—Pt sols with NaOH and $Ba(OH)_2$ solutions differ in form; this corresponds to differences in the structure of the double layer in the case of uni- and bi-valent cations. The total surface charge of the particles in 1 litre of sol with a platinum content of 100 mgr./litre is equal to 6×10^{-6} gr. equiv. or 1.73×10^9 e. s. u. When H^+-ions are being replaced by Na^+-ions, complete replacement takes place at pH = 8.8.

4. The cataphoretic velocity of the H_2—Pt sols does not depend upon their concentration, and for the pure sols equals 5.0 μ/sec. per V./cm. ($\zeta = 100$ mV.). The maximum c. v. corresponds to the conductivity minimum of the NaOH titration curve and equals 6.7 μ/sec. per V./cm. ($\zeta = 125$ mV.). At the conductivity minimum of the $Ba(OH)_2$ titration curve the c. v. is equal to 3.4 μ/sec. per V./cm. ($\zeta = 64$ mV.).

5. The concentration of H^+-ions calculated from the conductivity of the initial sol, assuming that the ions possess normal mobility, is equal to $^1/_3$ of the total number of H^+-ions that can be replaced by Na^+. The concentration of the Na^+-ions calculated from the conductivity at the minimum of the titration curve equals 45% of all the Na^+-ions substituted for H^+-ions.

6. The average radius of the platinum particles determined from the ultramicroscopic count of the particles is equal to 14.7 μμ.

7. The charge density calculated from the particle radius 14 μμ and the total charge 1.73×10^9 e. s. u. is equal to 1.8×10^5 e. s. u. per cm.^{2} whilst the charge density calculated using the zero charge point as determined from adsorption data on platinized platinum electrodes, is equal to 3.1×10^4 e. s. u.

8. The radius of 2.5 μμ calculated form the data on adsorption is in good agreement with that calculated according to Müller from the experimental value of ζ (100 mV. and 125 mV.) and the number of ions participating in the conductivity.

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