Chemistry. — *Flow potentials, electro-endosmosis and electrophoresis with platinum.* By H. R. KRUYT and J. OOSTERMAN.

(Communicated at the meeting of March 26, 1938.)

In previous communications [1]) we described how the measuring of the flow potential on a platinum capillary is complicated by occurring polarization phenomena but that ultimately it appeared that the potential in the flow cell became zero if the flowing liquid was composed of 10^{-4} n.HCl + + 1 $^0/_{00}$ quinhydrone. The question presents itself what the electrokinesis of platinum will be like on examination of electro-endosmosis or electrophoresis.

Electro-endosmosis with platinum plugs.

A platinum plug is to be preferred to a single capillary, since the quantity of liquid replaced electro-endosmotically in the first case is much larger than in the second, which highly benefits the accuracy of the measurements.

Fig. 1 reproduces the employed apparatus.

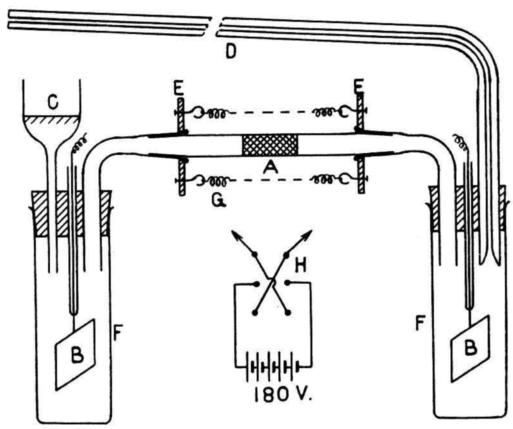

Fig. 1.

The plug *A* is pressed into a glass tubs of 0.6 cm diameter which via rectangularly bent small tubes with normal ground-in stoppers (held together

[1]) Proc. Royal Acad. Amsterdam, **40**, 404 (1937). Doctoral thesis of J. OOSTERMAN (Utrecht 1937) and an elaborate article of the two of us to be published soon in Koll. Beihefte.

by means of the coil-springs G fastened to the ebonite flanges E) is connected with vessels F (flocculation glasses closed with carefully boiled rubber stoppers) in which are situated the strongly platinized platinum electrodes B. In our experiments these were connected via a commutator H with a cell of 180 V. Formation of gas on these electrodes was never observed. The funnel C serves, by adding drops of liquid, to bring the meniscus in the capillary D to a suitable point for reading. The shifting of the meniscus was observed by means of a telescope.

We tested the usefulness of the apparatus by first placing a plug of cotton wool in it; this was first boiled in distilled water. The electro-endosmotic water transport now was so large that within 8 sec. the meniscus in D shifted along 10 divisions of the scale on the telescope (27 divisions = 5 mm.). Since the meniscus in equilibrium in 100 sec. showed no greater shift than 0.4 division of the scale, an electro-endosmotic water transport may certainly be indicated which amounts to 1 % of that observed with the plug of cotton wool.

The preparation of the platinum plugs took place as follows: Platinum remnants were dissolved in nitrohydrochloric acid. The solution thus obtained was dried by evaporation, dissolved in hydrochloric acid and filtered, after which treatment the platinum was reduced in alkali with formaldehyde. The platinum then separates as a very fine black powder, which after filtration was successively boiled with dilute HCl, distilled water, dilute HNO_3, distilled water. Subsequently it was thoroughly rinsed with hot distilled water.

In the central glass tube of the apparatus a strong platinum wire was fastened by fusion, perpendicular to the length of the tube. On this was brought successively a small plug of platinum gauze, the finely divided platinum forming the actual plug, and another small plug of gauze to shut it off.

The platinum plug was made in various ways. Successively we prepared and examined:

a. a very strongly compressed plug of the extremely fine platinum black;

b. a very loosely compressed plug of the exceedingly fine platinum black;

c. a very strongly compressed plug of platinum sponge (for this purpose the platinum black was intimately mixed in an agate mortar with NH_4Cl and annealed in a tube of Pyrex glass till all NH_4Cl was sublimated. Thus we obtained a highly porous platinum mass which we boiled with HCl and distilled water);

d. a very loosely compressed plug of the same platinum sponge.

On application of a voltage up to 180 Volts the result of these experiments was perfectly negative. An eventual electro-endosmotic transport with platinum sponge consequently is certainly less than 1 % of that with cotton wool.

Electrophoresis with platinum sols.

Platinum sols were prepared according to BREDIG's method of dispersion. The measurements were taken by the method of KRUYT and VAN GILS [1]).

The previous history of the measured sols was the following:

Two sols, I and II, were prepared by dispersion of *Pt*-electrodes in twice distilled water. To portions of these sols were added equal volumes of solutions, in such a way that I*a* and II*a* contained 10^{-4} n.HCl as final concentration and I*b* and II*b* 10^{-4} n.HCl + 1 ‰ quinhydrone. In a similar way sol IIc was prepared, which contained no HCl but 1 ‰ quinhydrone.

Further, two sols, III and IV, were prepared by electrical dispersion in 10^{-4} n.HCl. Part of these sols again obtained a final concentration of 10^{-4} n.HCl + 1 ‰ quinhydrone, III*a* by dissolving the calculated amount of quinhydrone in the sol, IV*a* by diluting with an equal volume of a solution of 10^{-4} HCl + 2 ‰ quinhydrone [2]).

In the table the results have been given. The electrophoretic velocity E.V. is given in μ per volt. cm. sec.

No.	Dispersed in	Final concentration	E.V.	No.	Dispersed in	Final concentration	E.V.
I	water	0	2.75	II	water	0	2.62
I*a*	,,	10^{-4} n. HCl	0.73	II*a*	,,	10^{-4} n. HCl	1.07
I*b*	,,	10^{-4} n. HCl + 1‰ quinh.	2.52	II*b*	,,	10^{-4} n. HCl + 1‰ quinh.	2.94
				IIc	,,	1‰ quinh.	3.04
III	10^{-4} n. HCl	10^{-4} n. HCl	2 12	IV	10^{-4} n. HCl	10^{-4} n. HCl	1.60
III*a*	,,	10^{-4} n. HCl + 1‰ quinh.	2 50	IV*a*	,,	10^{-4} n. HCl + 1‰ quinh.	2.54

The following should be observed here.

The sols I*a* and II*a* with their low E.V. are unstable; after 24 hours they are completely flocculated. If, however, to part of sol I*a* the calculated amount of quinhydrone is added, so that a final concentration of 1 ‰ is attained, the E.V is raised. After 30 minutes it is 1.59, the next day 2.32, and the sol is perfectly stable.

[1]) H. R. KRUYT and G. E. VAN GILS, Koll. Beih. **45**, 60 (1936).

[2]) The sols I*a* and I*b* consequently have half the sol concentration of sol I, similarly II*a*, II*b* and IIc half the sol concentration of sol II, and IV*a* that of IV. However, III*a* has the same sol concentration as III.

Discussion of the results.

The following questions have to be answered:

1. Why is the electrokinesis zero in measurements of electro-endosmosis on metal capillaries, and in measurements of flow potentials on metal capillaries, when polarization is excluded, while it becomes clearly manifest in case of glass capillaries?
2. Why does electrokinesis become manifest in case of electrophoresis of platinum sols, but not in measurements of flow potentials and electro-endosmosis on platinum capillaries?
3. Why has in case of electrophoresis of the sol the polarization no disturbing influence, while it has this effect on measurements of flow potentials?

The answers to these questions may be easily found if we try of form a picture of the lines of electric force in the system.

In fig. 2 the course is reproduced of the lines of electric force in case of a practically non-conductive capillary: they go through the tube and consequently the potential difference may set the opposite ions of the double layer into motion, which occasions electro-endosmosis. In fig. 3

Fig. 2.

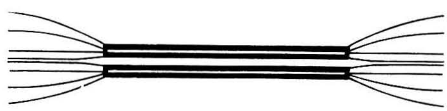

Fig. 3.

the lines of electric force are given for a metal capillary, whose resistance is far smaller than that of the flowing liquid. Although the double layer is present, it cannot give rise to electro-endosmosis.

With the flow potential measurements the opposite ions are carried along by the hydrodynamic flow and a tension is formed between the two electrodes; but this E.M.F. causes a flow of the electricity in opposite direction. This, however, follows the reproduced lines of electric force: the conduction in the liquid takes place by means of ions, which must discharge at the ends of the capillary, causing a tension of poralization. If we prevent this from being formed by the presence of quinhydrone and hydrochloric acid, the flow potential according to the formula of VON SMOLUCHOWSKI [1]) appears to be immeasurably small.

The lines of electric force in the case of electrophoresis of highly conductive particles have been drawn in fig. 4, those for isolating particles in fig. 5. However different the course may be, in both cases the potential may attack the double layer and consequently electrophoresis will set in; at any rate if the atmosphere of the opposite ions is not entirely compressed

[1]) See the lit. cited under [1]) p. 370.

in the immovable part of the double layer. This case was approximated with the sols Ia and IIa by the addition of 10^{-4} n.HCl to the formed sol.

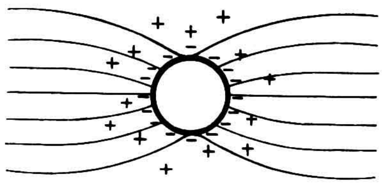

Fig. 4.

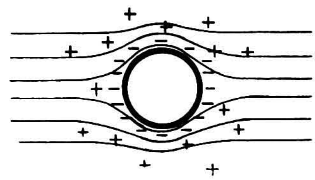

Fig. 5.

If, however, quinhydrone is added to this system, the ε-potential at the phase boundary platinumwater is radically modified and thus ζ is raised. That is why the sols I*b* and II*b* are much stabler than I*a* and II*a* respectivly. Finally soll II*c* contains quinhydrone but no HCl and is in the most favourable condition with the greatest E.V.

That the sols dispersed in 10^{-4} n. HCl are stable, in contrast with the sols I*a* and II*a*, is due to the different constitution of the double layer; in all probability they contain chlor-platinum complexes as inner covering of the double layer.

Polarisation occurs no doubt at both sides of an electrophoretically migrating metal particle; but the demensions of the colloidal particle are too small that this phenomenon causes an appreciable effect on the migration. If it were possible to prepare a platinum sol with long needle shaped particles, such an effect of retardation would no doubt appear.

Utrecht, VAN 'T HOFF-*Laboratory of the State University.*