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THE ADSORPTION OF CALCIUM BY GUM ARABIC. MINERAL ELECTRODES. III.

BY

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The determination of Ca concentrations from measurements of the e.m.f. of cells gives rise to difficulties, which one is generally not able to overcome. As shown by Corten and Estermann [1]) it is possible to use electrodes of the third order; they found a linear relationship between the e.m.f. of the cell and the -log Ca between 0.1 and 0.001 normal. However Le Blanc and Harnapp [2]) could not reproduce their results completely. The use of calcium amalgam electrodes is too complicated to be suitable. As a matter of fact there may be complications when one uses an electrode of the third order, and it would be of advantage to have an electrode for the determination of Ca concentrations like the glass elctrode for the measurement of the H concentrations. No foreign substances have to be introduced into the solutions under investigation containing calcium if such an electrode is available.

Preliminary researches [3]) showed that glass and some minerals could function as a calcium electrode. Amongst a great number of minerals fluorite, CaF_2, proved to be, up till now, the best. The construction of the electrode has been described elsewhere [4]). Some fifty electrodes have been studied and it has been found, that marked differences may occur, which must be ascribed to differences in the surfaces of the CaF_2-plates. One day five electrodes were made; the same liquid ($CaCl_2$ containing 14.78 gram calcium per liter) was placed inside the glass tube and they were used at the same temperature, 18°, in the same solutions of calcium nitrate and calcium chloride. The electrodes were all different. One of them showed a peculiar behaviour; there was no relationship between e.m.f. of the cell and pCa. This electrode was ground with emery paper, rinsed with water and used again: it became a splendid electrode.

When not in use the electrodes were placed in distilled water. It happened that a good electrode became a bad one after some days. Afterwards the electrodes were placed in a saturated solution of calcium fluoride. After each measurement the electrode was washed with this solution. It was found that by this treatment the electrodes showed a more constant behaviour. It is necessary to standardize the

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[1]) Z. physik. Chem. 136, 228 (1928). [2]) ibid. 166, 321 (1933).
[3]) Proc. Akad. Wetenschappen Amsterdam 37, 212 (1934); 38, 434 (1935).
[4]) c.f. [3]).

electrode with solutions of a calcium salt of known concentrations before measurements are done.

With the CaF_2-electrode cells are build up of the type:Ag-AgCl-$CaCl_2$-CaF_2-solution of calcium salt-saturated KNO_3 bridge-0.1 Calomel electrode.

The e.m.f. is measured potentiometrically, using vacuum tubes as amplifiers (Philips 4060 and B 405), according to a scheme given by Janssen [5]). The sensitivity of the measurements is 0.5 millivolt, the reproducibility, using the same electrode, is about 2 millivolt.

If the e.m.f. of the cells is plotted against the -log[Ca] = pCa a straight line results. The CaF_2-electrode is negative.

Solutions of calcium nitrate, calcium chloride and calcium acetate were made; their concentration was determined by oxidimetric titration of the precipitated calcium oxalate. These solutions had different pH; however it was found, that the acidity had no influence upon the e.m.f. of the cell as may be seen from table 1.

Table I.

Mixture	E. m. f. (electrode 124)
100 cm³ Ca acetate 1.076 normal 90 cm³ distilled water	64 millivolt
10 cm³ Ca acetate 1.076 normal 10 cm³ acetic acid 1.055 „ 80 cm³ distilled water	64 „
10 cm³ Ca acetate 1.076 „ 40 cm³ acetic acid 1.055 „ 50 cm³ distilled water	64 „

In table 2 the results are tabulated obtained with electrode No. 124 in dilutions of the standard solutions; fig. 1 shows a graphical representation.

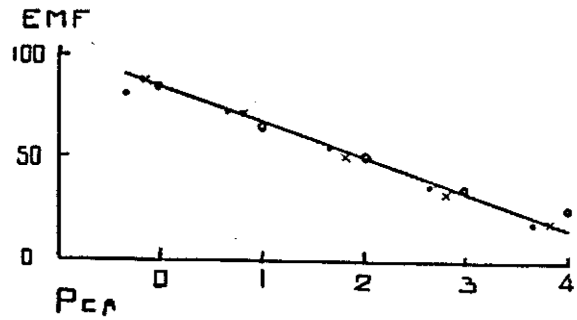

Fig. 1.

[5]) L. W. Janssen, Diss. Utrecht, 1933.

Table II.

$Ca(NO_3)_2$	$-\log(Ca) = pCa$	e.m.f. in milli Volt
$C_1 = 2.2082$ N	-0.34	81.5
$C_2 = 2.2082\ 10^{-1}$	0,66	72.5
$C_3 = 2.2082\ 10^{-2}$	1.66	56.5
$C_4 = 2.2082\ 10^{-3}$	2.66	36.5
$C_5 = 2.2082\ 10^{-4}$	3.66	19.0
$CaCl_2$		
$C_1 = 1.4788$ N	-0.17	87.5
$C_2 = 1.4788\ 10^{-1}$	0.83	71,0
$C_3 = 1.4788\ 10^{-2}$	1.83	50.5
$C_4 = 1.4788\ 10^{-3}$	2.83	31.5
$C_5 = 1.4788\ 10^{-4}$	3.83	15.5
Ca acetate		
$C_1 = 1.0760$ N	-0.03	83.0
$C_2 = 1.0760\ 10^{-1}$	0.97	65.0
$C_3 = 1.0760\ 10^{-2}$	1.97	49.5
$C_4 = 1.0760\ 10^{-3}$	2.97	36.5
$C_5 = 1.0760\ 10^{-4}$	3.97	25.0

The CaF_2-electrode has been used to study the adsorption of calcium by gelatine and milk [6]). Also the adsorption by gum arabic has been studied.

A 4 % solution of gum arabic was made in the ordinary way [7]). Dilutions were made to 3 %, 2 % and 1 %. The e.m.f. of the cell: Ag-AgCl-$CaCl_2$-CaF_2-gum arabic-saturated KNO_3 bridge-0.1 calomel electrode was for these dilutions 42 millivolt.

The gum arabic contains 0.87 % calcium. From fig. 1 it follows that 42 millivolt correspond to pCa 2.4. Assuming the calcium in the gum arabic to be in true solution the pCa calculated in table 3 result for the dilutions mentioned. From the pCa measured and mentioned in column 5 of table 3 it follows, that part of the calcium is adsorbed and that the amount adsorbed is highest in the most concentrated solution; they behave as calcium buffers.

Table III.

Gum arabic	g Ca per liter	Normality of calcium	pCa calc.	pCa exp.
4 %	0.348	0.017	1.8	2.4
3 „	0.261	0.013	1.9	2.4
2 „	0.174	0.009	2.0	2.4
1 „	0.087	0.004	2.4	2.4

The adsorption may be seen also from the measurements to be described now.

Solutions of calcium nitrate of different concentrations were mixed

6) J. Biol. Chem. 113, 333 (1936).
7) Kolloid Beihefte 29, 396 (1928).

with an equal volume of water, resp. 4 % gum arabic solution, the pCa of which was measured. Then an equal volume of water was added to the solution containing gum arabic so that the concentration of the gum became 1 $^1/_3$ %. In Table 4 the results are tabulated; the first column gives the pCa of the solutions without gum arabic, the second column the pCa of the mixtures containing the gum arabic of 2 %, resp. 1 $^1/_3$ %.

Table IV.

pCa of calcium nitrate solution	pCa of mixture containing gum arabic 2 %
— 0.04	0.25
0.2	0.5
0.9	1.0
1.2	1.4
1.6	1.8
1.9	2.0
	gum arabic 1$^1/_3$ %
0.1	0.4
0.4	0.5
1.1	1.2
1.4	1.5

(The pCa of the calcium nitrate solutions was calculated from the concentrations.)

The figures show that gum arabic adsorbs calcium; unfortunately however measurements in smaller concentrations are impossible, using calcium fluorite electrodes. The researches are to be continued with other mineral electrodes.

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