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## ELECTROCHEMICAL RESEARCHES ON PARAFFIN MEMBRANES I.

The specificity of special paraffin membranes as  
calcium-ion electrodes

BY

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A membrane consisting of a mixture of pure paraffin of low melting point, a calcium salt of low solubility in water and a non-ionogenic detergent can be used as an electrode for the determination of calcium-ion concentrations, viz. pCa. Investigations are here reported on solutions of single salts.

Since the introduction of the glass electrode as a means of measuring pH by *Haber and Kłemensiewicz* in 1909<sup>1)</sup> its use has generally been accepted. Measurements of the pH of solutions are so simple, taking the necessary precautions, that it is tempting to investigate whether it would be possible to find membranes for the determination of the concentrations, viz. activities, of other ions.

*Farrington Daniels*<sup>2)</sup> wrote:

"There is a need for electrodes capable of measuring ion activities of calcium, sodium, and potassium as distinguished from the concentration of the salts."

The use of  $\text{CaF}_2$  electrodes for estimating concentrations of calcium in solution has been investigated<sup>3)</sup> and criticized by *Anderson*<sup>4)</sup> and *Greenberg and Larson*<sup>5)</sup>. *Mrost and Arnold*<sup>6)</sup> also using fluorite membranes found that they were suitable for calcium and magnesium ions. In their paper they wrote (pg. 5): "These results appear to be

<sup>1)</sup> *F. Haber and Z. Kłemensiewicz*, Z. physik. Chem. **67**, 385 (1909).

<sup>2)</sup> *Farrington Daniels*, "Outlines of physical chemistry" (1948), pg. 463.

<sup>3)</sup> *H. J. C. Tendeloo*, J. Biol. Chem. **113**, 333 (1936).

<sup>4)</sup> *Rubert S. Anderson*, J. Biol. Chem. **115**, 323 (1936).

<sup>5)</sup> *David M. Greenberg and Clarence E. Larson*, J. Biol. Chem. **115**, 769 (1936).

<sup>6)</sup> *M. Mrost and R. Arnold*, Joernaal van die Suid-Afrikaanse Chemise Instituut **4**, 1 (1951).

substantially in agreement with those of *Tendeloo*, especially in so far as the differences in the e.m.f. obtained with the membrane in solutions of different concentrations are concerned. The differences in the absolute values are due in part to the fact that *Tendeloo* used a normal calomel electrode whereas a saturated calomel electrode was used in the above determinations."

Many papers have been published on membrane potentials in electrolytic cells. It may suffice here to point to reviews<sup>7)</sup>.

According to our own experience, fluorite electrodes are not always attractive, therefore we began a few years ago to investigate glasses of varying composition as membranes for the determination of calcium-ion concentrations. About 30 different glasses have been made, but all of them showed a preponderant sensitivity for hydrogen ions. We did not succeed in finding a dependence of the potentials of membranes made from these glasses on the concentration, *viz.* activity, of calcium or other ions at concentrations below 0.1 molar.

We investigated a great number of membranes of rather different composition as electrodes. As they gave no reliable results we omit any further details.

As we received, however, a sample of paraffin, highly purified and free from acids, for which we have to thank the directors of Koninklijke/Shell Laboratories at Amsterdam, we started a series of new experiments which gave better results. A description of these experiments is given here.

#### Electrodes.

The electrodes consisted of glass tubes, inside diameter 10 mm. (Fig. 1).

On one side a cotton gauze was fitted by means of a rubber ring. The glass tubes were immersed in molten paraffin without closing the side not-provided with the gauze. A thin membrane is formed in the gauze after solidification.

Having thus prepared the membranes the tubes were placed, open sides down, in a beaker containing a layer of water about 3 cm deep. The tubes remained during 24 to 48 hours in this position. Leaking membranes could be easily detected.

We determined also the electrical resistance of a number of the electrodes which was about  $10^7$  ohm or higher for about 1.13 cm<sup>2</sup>.

As membranes we used

- a) pure paraffin melting point 51.5° C;
- b) a mixture of pure paraffin and a detergent;

<sup>7)</sup> Ann. Rev. Phys. Chem. 3, 124 (1952); 4, 384 (1953); 4, 387 (1953); 5, 431 (1954); 7, 159 (1956).

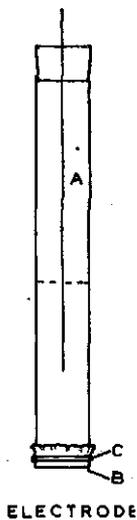


Fig. 1.

- A Glass tube, inner solution, and inner electrode
- B Membrane
- C Rubber ring
- ∅ 10 mm, length 110 mm

- c) a mixture of pure paraffin, a detergent and a calcium salt of low solubility in water.

The electrodes were completed by introducing into the tube either a solution of  $\text{CaCl}_2$  or  $\text{KCl}$  and a silver-silver chloride wire, or a solution of  $\text{CaCl}_2$ , saturated with silver oxalate and calcium oxalate, and a silver wire, solid silver oxalate and calcium oxalate being present.

The electrode was combined with a saturated calomel electrode, and the e.m.f. of the cell, using different salt solutions, as mentioned in the tables, was measured with a Philips pH-meter GM 4491 at room temperature.

### Measurements.

Solutions of  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  were made by diluting the most concentrated solution which was analyzed by precipitation as calcium oxalate and titration with  $\text{KMnO}_4$ . Solutions of  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{KNO}_3$  and  $\text{NaNO}_3$  were made by weighing the exact amount of the *pro analysi* salts to make 1 liter of a 1 molar solution which was diluted to obtain the more dilute solutions.

#### a. Electrodes of pure paraffin.

The e.m.f. of the following cells was measured at room temperature.

- 1)  $\text{Ag}/\text{AgCl}$  — solution of — paraffin — salt solution — sat. calomel electrode  
a chloride membrane

The saturated calomel electrode was always negative.

The solution of a chloride was either  $\text{CaCl}_2$  or  $\text{KCl}$ . It will be mentioned as "inner solution" in the tables; the salt solutions of different concentrations are the "outer solutions" in the tables.

To be able to compare the results easily we eliminated differences between the

electrodes by assigning to the e.m.f. of the cells with the highest concentration of the "outer solution" the value of 30 millivolts. If e.g. the experimental values for  $c_1$ ,  $c_2$ ,  $c_3$  were respectively, 100, 105, 112 mV, we publish the values 30, 35, 42.

To illustrate the differences between *identical* electrodes the e.m.f. of cells with electrodes  $P_1'$ ,  $P_2'$ , OxPA1 and OxPA2, in solutions of  $\text{CaCl}_2$ , have been tabulated in Table I.

Table I.  
Differences between identical electrodes.

Molar conc. $\text{CaCl}_2$	1	0.5	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
Electrode										
$P_1'$	—	—	110	116	124	130	136	139	143	145
$P_2'$	—	—	103	107	114	120	126	129	134	136
OxPA1	57	61	68	74	80	88	94	100	105	108
OxPA2	53	58	64	70	75	83	89	95	100	104

In table II the results are mentioned obtained with electrodes  $P_1'$  and  $P_2'$  both consisting of  $\text{Ag}/\text{AgCl}$ -0.001 *N*-solution of  $\text{CaCl}_2$ -paraffin membrane.

Table II.  
E.M.F. of cells with electrodes  $P_1'$  and  $P_2'$  in mV.

Outer solution $\text{CaCl}_2$ of molar concentration	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
$P_1'$	30	36	44	50	56	59	63	65
$P_2'$	30	34	41	47	53	56	61	63
$\text{Ca}(\text{NO}_3)_2$ of molar concentration	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
$P_1'$	30	34	39	45	51	56	60	61
$P_2'$	30	34	39	45	50	54	57	59

Electrode  $P_2$ , inner solution 0.1 *N*  $\text{CaCl}_2$ , does not respond to varying concentrations of  $\text{KCl}$  or  $\text{NaNO}_3$  in the outer solution, whereas electrode  $P_3$ , inner solution

Table III.  
E.M.F. of cells with electrodes  $P_2$  and  $P_3$  in mV.

Outer solution molar concentration	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
Electrode								
$\text{CaCl}_2$ $P_2$	30	35	41	48	54	57	59	59
$\text{KCl}$ "	30	30	31	31	32	32	29	27
$\text{NaNO}_3$ "	30	28	30	31	31	30	27	24
$\text{CaCl}_2$ $P_3$	30	35	39	44	47	46	43	34
$\text{KCl}$ "	30	28	25	20	13	4	-10	-18
$\text{NaCl}$ "	30	30	31	27	21	15	6	-2

0.1 N KCl, responds less to varying concentrations of calcium ions in the outer solutions (Table III), but does respond to varying concentrations of potassium and sodium ions.

We also found, that a paraffin membrane did not respond to pH. We made buffer solutions of 0.2 M acetic acid and 0.2 M sodium acetate, and of 1/15 M  $\text{KH}_2\text{PO}_4$  and 1/15 M  $\text{Na}_2\text{HPO}_4$ . Electrode  $P_1$  did not respond to pH (Table IV). The inner solution of electrode  $P_1$  was 0.1 N  $\text{CaCl}_2$ .

Table IV.

E.M.F. of cells with electrode  $P_1$  in buffer solutions in mV.

Buffer solution	pH	4.89	5.10	5.25	5.47				
$\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$	E.M.F.	44	44	45	45				
$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	pH	5.47	5.74	6.05	6.16	6.44	6.57	6.76	
	E.M.F.	51	51	52	54	55	56	56	

**5. Electrodes of pure paraffin and a detergent.**

A mixture of 3 g paraffin and 12.5 mg Arlacel 85, i.e. sorbitan tri-oleate of Atlas Powder Company, was melted and used as membrane material.

Electrode  $PA_1$  had an inner solution of 0.1 N  $\text{CaCl}_2$ , saturated with and containing solid Ca-oxalate and Ag-oxalate, and a silver-electrode.

Electrode  $PA_2$  had an inner solution of 0.1 N KCl and an Ag-AgCl-electrode.

Table V gives the results of the measurements.

Table V.

E.M.F. of cells with electrodes  $PA_1$  and  $PA_2$  in mV.

Outer solution	Electrode	Molar concentration							
		0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
$\text{CaCl}_2$ $\text{Ca}(\text{NO}_3)_2$ KCl NaCl $\text{MgSO}_4$ $\text{KNO}_3$ $\text{NaNO}_3$	$PA_1$	30	36	43	50	55	57	59	59
		30	34	40	46	51	55	58	60
		30	30	30	32	35	35	31	30
		30	31	34	34	33	31	27	25
		30	31	34	36	38	39	39	40
		30	30	33	37	39	41	44	45
		30	30	34	38	39	41	42	43
$\text{CaCl}_2$ KCl NaCl $\text{KNO}_3$ $\text{NaNO}_3$ $\text{MgSO}_4$	$PA_2$	30	33	37	40	43	42	40	36
		30	29	28	24	21	16	5	*1
		30	31	31	31	27	23	16	10
		30	28	26	22	17	11	1	5
		30	30	30	28	24	19	9	3
		30	30	30	30	29	27	24	22

Electrodes  $PA_1$  and  $PA_2$  did not respond to pH-differences. Electrode  $PA_2$  is identical with  $PA_1$ ;  $PA_1$  had an inner solution of 0.1 N  $\text{CaCl}_2$  and an Ag-AgCl-electrode. Electrode  $PA_3$  had an inner solution of 0.1 N KCl and an Ag-AgCl-electrode.

Table VI gives the results of the measurements.

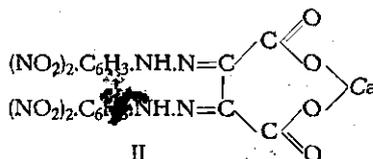
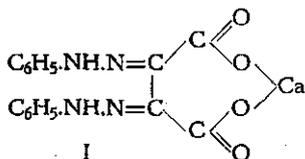
Table VI.  
E.M.F. of cells with electrodes PA<sub>3</sub>, PA<sub>4</sub> and PA<sub>5</sub> in mV.

Outer Solution	Electrode	Molar concentration							
		0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
CaCl <sub>2</sub> Ca(NO <sub>3</sub> ) <sub>2</sub> KNO <sub>3</sub> NaNO <sub>3</sub>	PA <sub>3</sub>	30	33	39	45	50	55	59	61
		30	35	41	47	52	57	60	62
		30	30	31	35	39	41	42	44
		30	30	32	36	40	41	42	43
CaCl <sub>2</sub> Ca(NO <sub>3</sub> ) <sub>2</sub> KNO <sub>3</sub> NaNO <sub>3</sub>	PA <sub>4</sub>	30	33	39	45	51	55	59	63
		30	33	38	45	50	55	60	62
		30	32	34	38	41	44	47	50
		30	31	33	38	42	45	48	49
KCl KNO <sub>3</sub>	PA <sub>5</sub>	30	29	28	26	23	19	14	
		30	29	27	24	21	16	8	

c. Electrodes of pure paraffin, a detergent and a calcium salt.

From these measurements it follows that the greatest differences between the e.m.f. of the highest and the lowest concentration of the outer solutions are found in those cases where the inner and the outer solutions contain calcium-ions, and where the inner solutions contain potassium ions and the outer solution either potassium or sodium ions. The different behaviour of uni- and bi-valent ions is, however, not clear.

We tried now to increase the selectivity for calcium ions by incorporating in the membranes calcium salts of low solubility in water, viz. calcium oxalate, the calcium salt of the osazone of dihydroxytartaric acid<sup>8)</sup> (I), and the calcium salt of the 2,4-dinitrophenylosazone of dihydroxytartaric acid<sup>9)</sup> (II)



The electrodes were made of a mixture of

Pure paraffin	3 g
Arlacel 85	12.5 mg
Calcium salt	75 mg.

On heating, a suspension of the calcium salt in molten paraffin was formed which was homogenized as far as possible by stirring and rubbing with a glass rod.

The activity coefficients of the outer solutions mentioned in the following tables

<sup>8)</sup> C.f. Fritz Feigl, "Qualitative analysis by spot tests" (1947) pg. 170.

<sup>9)</sup> Synthesized by Dr. F. W. Broekman, Lab. of Physical and Colloid Chemistry, Wageningen.

<sup>10)</sup> Wendell M. Latimer, "The oxidation states of the elements and their potentials in aqueous solutions", Second edition (1952).

are from Table 86 in *Latimer's book "Oxidation potentials"*<sup>10</sup>). The concentrations are in molalities (mol./1000 g solvent). For our calculations, it does not make an appreciable difference if we use these activity coefficients for molar concentrations of the same value.

In Table VII and Table VIII we limit ourselves to measurements on solutions of  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  and electrodes:

OxPA 1:	membrane containing calcium oxalate,	inner solution	0.01 N- $\text{CaCl}_2$
OxPA 2:	" " " " " "	" "	0.01 N- "
OxPA 3:	" " " " " "	" "	0.1 N- $\text{CaCl}_2$ + Ca and Ag oxalate
OPA 6:	" " calcium osazone I,	" "	0.1 N- $\text{CaCl}_2$
OPA 8:	" " " " I,	" "	0.1 N- $\text{CaCl}_2$ + Ca and Ag oxalate
OPA 9:	" " " " I,	" "	0.001 N- $\text{CaCl}_2$
NOPA 1:	" " " " II,	" "	0.001 N- $\text{CaCl}_2$
NOPA 1:	" " " " II,	" "	0.1 N- $\text{CaCl}_2$
NOPA 3:	" " " " II,	" "	0.001 N-KCl

Table VII.

 E.M.F. of cells with electrodes OxPA, OPA and NOPA in  $\text{CaCl}_2$ .

Outer solution ↓ $\text{CaCl}_2$	Molar concentration $c \rightarrow$	1	0.5	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001	0.0005	0.0002
	Act. coeff. — <sup>10</sup> log $f_c$	0.71 0.15	0.52 0.59	0.48 1.02	0.52 1.29	0.57 1.54	0.66 1.88	0.73 2.14	0.79 2.41	0.85 2.77	0.89 3.05	— 3.3*	— 3.7*
Electrode mV OxPA1	30	35	42	49	56	63	69	75	80	83	—	—	
	30	34	41	47	53	61	67	73	78	81	—	—	
	30	35	41	47	52	60	66	72	77	81	82	83	
OxPA2 OxPA3	30	34	40	46	52	59	66	71	78	81	85	89	
	30	34	40	46	52	59	66	71	78	81	85	89	
Electrode mV OPA 6 OPA 8 OPA 9	30	35	42	47	54	62	68	73	80	83	86	92	
	30	35	41	47	53	60	66	70	76	78	80	83	
	30	33	38	43	49	57	63	69	74	77	79	82	
NOPA 1 NOPA 2 NOPA 3	30	33	40	47	53	60	66	71	77	79	—	—	
	30	35	42	48	54	62	68	73	78	81	83	85	
	30	33	40	46	52	60	65	70	75	77	78	79	
OxPA OPA NOPA	Mean values												
	30	35	41	47	53	61	67	73	78	81	84	86	
	30	34	40	46	52	60	66	71	77	79	82	86	
	30	34	41	47	53	61	66	71	77	79	80	82	

 \*) i.e. —<sup>10</sup>log  $c$ .



There are differences between the electrodes. In general, the dependence on the activity of calcium ions is evident. It is perhaps not necessary to tabulate the measurements of all the electrodes with other solutions. They do not respond to differences in pH.

**Table IX.**

E.M.F. of cells with electrodes OxPA, OPA and NOPA in solutions of KCl, NaNO<sub>3</sub> and MgSO<sub>4</sub>.

Outer solution	Molar concentration $c \rightarrow$	1	0.5	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
KCl	Electrode mV										
	OxPA2	30	30	31	31	32	32	29	27	26	27
	OPA8	30	32	33	33	35	36	38	39	40	41
	NOPA3	30	31	31	30	29	29	28	27	25	23
NaNO <sub>3</sub>	OxPA2	30	31	33	34	35	34	33	31	—	—
	OPA8	30	31	32	33	35	36	38	40	—	—
	NOPA3	30	31	32	33	34	32	31	30	—	—
MgSO <sub>4</sub>	OxPA11 <sub>1</sub>	30	29	28	28	29	29	30	31	—	—
	OPA12	30	29	28	28	29	30	30	31	30	29
	NOPA3	30	30	30	31	32	34	35	36	37	36

To illustrate the behaviour of these electrodes in solutions of a potassium, sodium, and magnesium salt only, some results are tabulated in Table IX, from which it is clear that these electrodes respond not at all or only slightly to differences in concentrations of the solutions. The behaviour of these electrodes in mixtures of electrolytes will be investigated in the near future.

The same ideas have led us to investigate other electrodes more or less specific for other ions, but these researches are not yet finished.

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