ELECTROCHEMICAL RESEARCHES ON PARAFFIN MEMBRANES II.

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 mixtures of $CaCl_2$ and KCl, or $MgCl_2$.

In the previous communication [1]) we reported the results of investigations with membrane-electrodes consisting of pure paraffin of low melting point, a calcium salt of low solubility in water, and a non-ionogenic detergent. These membrane-electrodes behave as specific calcium-ion electrodes in solutions of single salts and they do not respond to pH-differences.

The researches to be described now concern measurements in solutions of *mixtures* of salts.

The e.m.f. of the following cells was measured at room temperature with a Philips pH-meter GM 4491:

Ag/AgCl – solution of – membrane – salt solution – sat. calomel
         0.01 m $CaCl_2$ containing   electrode
                       Ca-oxalate

The mean values of two or three series of measurements of each of the solutions as specified are compiled in Table I.

The mean values of the measurements of the same solution with these electrodes are in Table II.

The membranes containing the calcium-salts of the osazone of

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[1]) *H. J. C. Tendeloo* and Miss *A. Krips*, Rec. trav. chim. **76**, 703 (1957)

dihydroxy-tartaric acid and of 2,4-dinitrophenylosazone of dihydroxy-
tartaric acid [2]) behave similarly.

From the figures of both tables it may be concluded that the elec-
trodes have a fairly acceptable specificity for calcium ions.

In the last line of Table II we give the mean values of all mixtures.
These values together with those of the solutions of $CaCl_2$, i.e. the third
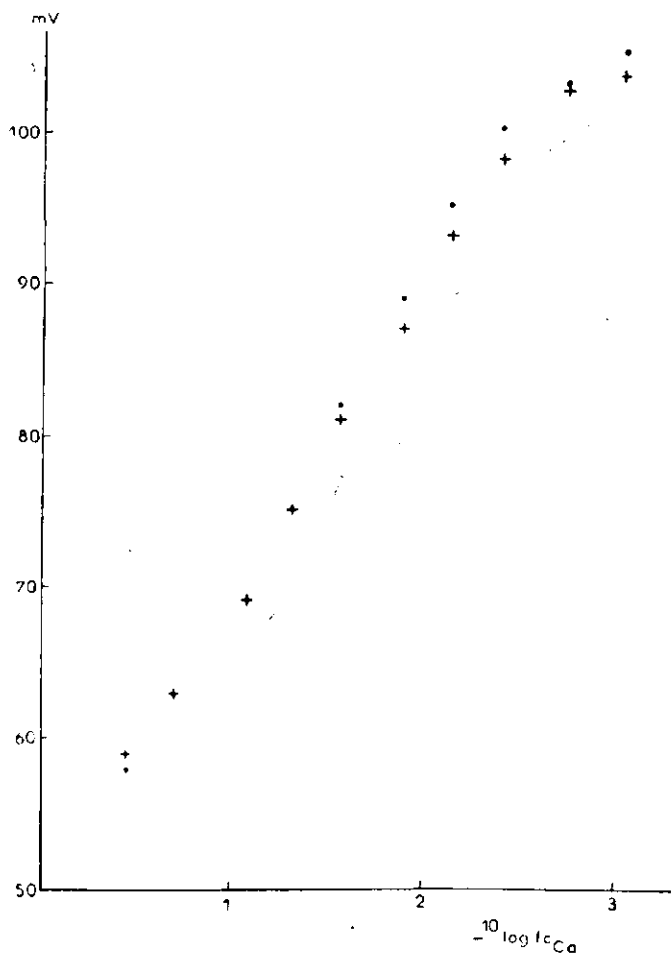line of Table II, are graphically represented as a function of $-^{10}\log fc_{Ca}$
in Fig. 1.

Fig. 1. Function of $-^{10}$ log fc_{Ca} of solutions of $CaCl_2$·, of mixed
solutions +, and mean values of mV of cells with electrodes
OxPA 4, 5, and 6 (cf. Table II).

[2]) Cf. 1.

For concentrations of $CaCl_2$ between 1.0 and 0.005 molar there is a fairly acceptable specificity for calcium ions.

Table I.

Electrode
OxPA 4

			1.0	0.5	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
$CaCl_2$ molar conc.												
,,		mV	58	63	70	76	83	91	97	102	106	106
,,	+ KCl 0.01 M	,,	58	61	69	76	83	89	94	98	101	103
,,	+ KCl 0.005 M	,,	60	63	69	74	81	88	94	98	100	103
,,	+ KCl 0.001 M	,,	62	65	72	77	85	90	97	100	102	—
,,	+ $MgCl_2$ 0.01 M	,,	60	63	68	74	80	85	90	97	95	95
,,	+ $MgCl_2$ 0.005 M	,,	60	63	68	74	79	85	89	94	96	97
,,	+ $MgCl_2$ 0.001 M	,,	60	63	67	74	77	83	89	93	96	99

OxPA 5

$CaCl_2$		mV	58	62	69	74	80	87	92	97	100	103
,,	+ KCl 0.01 M	,,	60	63	70	75	81	88	94	100	102	103
,,	+ KCl 0.005 M	,,	59	64	71	77	83	90	95	99	102	103
,,	+ KCl 0.001 M	,,	59	62	68	73	78	84	89	92	96	98
,,	+ $MgCl_2$ 0.01 M	,,	60	64	70	77	82	88	92	98	99	98
,,	+ $MgCl_2$ 0.005 M	,,	60	63	71	77	83	90	94	98	100	100
,,	+ $MgCl_2$ 0.001 M	,,	59	63	69	76	80	88	92	96	100	100

OxPA 6

$CaCl_2$		mV	57	63	69	76	83	90	96	100	104	105
,,	+ KCl 0.01 M	,,	58	62	68	72	78	85	90	95	97	98
,,	+ KCl 0.005 M	,,	58	62	68	75	81	87	93	98	101	102
,,	+ KCl 0.001 M	,,	58	62	69	75	82	89	96	100	104	104
,,	+ $MgCl_2$ 0.01 M	,,	58	62	69	74	80	87	92	99	97	97
,,	+ $MgCl_2$ 0.005 M	,,	58	62	68	74	80	86	91	96	98	99
,,	+ $MgCl_2$ 0.001 M	,,	59	63	68	75	81	87	94	99	102	103

Table II.

Mean values for electrodes OxPA 4, 5, and 6.

			1.0	0.5	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
$CaCl_2$ M			1.0	0.5	0.2	0.1	0.05	0.02	0.01	0.005	0.002	0.001
$-^{10}\log f_{Ca}$			0.46	0.72	1.08	1.32	1.57	1.90	2.15	2.41	2.77	3.06
$CaCl_2$		mV	58	63	69	75	82	89	95	100	103	105
,,	+ KCl 0.01 M	,,	59	62	69	74	81	87	93	98	100	101
,,	+ KCl 0.005 M	,,	59	63	69	75	82	88	94	98	101	103
,,	+ KCl 0.001 M	,,	60	63	70	75	82	88	94	97	101	101
,,	+ $MgCl_2$ 0.01 M	,,	59	63	69	75	81	87	91	98	96	97
,,	+ $MgCl_2$ 0.005 M	,,	59	63	69	75	81	87	91	96	98	99
,,	+ $MgCl_2$ 0.001 M	,,	59	63	68	75	79	86	92	96	99	101
Mean values of mixtures		,,	59	63	69	75	81	87	93	98	100	101

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