

THE EFFECT OF CHANGES IN HYDRODYNAMIC CONDITIONS ON THE RESPONSE OF CALCIUM-SELECTIVE MEMBRANE ELECTRODES WITH A MACROCYCLIC CARRIER

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Shifts of the potentials of a calcium ion-selective electrode based on the complex of 7,19-dibenzyl-2,2,3,3-tetramethyl-7,19-diaza-1,4,10,13,16-pentaoxacycloheneicosane-6,20-dione with calcium tetra(4-chlorophenyl)borate in various membrane solvents caused by changes in hydrodynamic conditions in the measured solution were examined. The use of 2-fluoro-2'-nitrodiphenyl ether as a membrane solvent combined with substitution of benzyl groups with octyl ones in the neutral carrier eliminates this unfavourable phenomenon while preserving the selectivity parameters of the electrode.

Ternary complexes of some macrocyclic polyether diamides with calcium and tetra(4-chlorophenyl)borate ions represent one type of active components of membranes of calcium ion-selective electrodes^{1,2}. The complex of 7,19-dibenzyl-2,2,3,3-tetramethyl-7,19-diaza-1,4,10,13,16-pentaoxacycloheneicosane-6,20-dione (*I*) ranks among those which possess the highest selectivity for calcium. When this compound was applied in plasticized poly(vinyl chloride) electrode membranes, the membrane potential was found to be sensitive to changes in hydrodynamic conditions in the measured solution². This phenomenon restricts applicability of the electrode in some analytical applications. Preliminary experiments showed that the magnitude of a change in the potential of the electrode due to stirring of the measured solution is affected by the membrane solvent used. In this study a route is suggested for elimination of the effect of changes of hydrodynamic conditions on the membrane potential using new membrane solvents in connection with a change in the structure of a neutral carrier.

EXPERIMENTAL

Chemicals

Complexes of cyclic diamides *I* and *II* with calcium tetra(4-chlorophenyl)borate have been described earlier^{1,2}.

in the measured solution. The steady-state potential obtained after immersing the electrode into solution is shifted to more negative values when the solution is set in motion, *e.g.*, by stirring. The potential reaches gradually a new approximately constant value (Fig. 1, curve 1). On switching off the stirring the potential is shifted back again and limits to its original value. Changes in the potential smaller by an order of magnitude occur if the electrode is repeatedly immersed several times into

TABLE I

Selectivity coefficients of the complex of poly(etherdiamide) *II* with calcium tetra(4-chlorophenyl)-borate in various membrane solvents expressed as $-\log k_{Ca,M}$

Membrane solvent	ϵ_r	Ion M							
		Mg ²⁺	Sr ²⁺	Ba ²⁺	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
NPOE	24	3.88	0.75	1.49	1.53	3.23	3.36	3.64	3.88
FPOE ^a	6	4.03	0.70	1.50	0.08	2.68	3.15	3.33	3.45
CIPOE ^a	6	4.09	0.73	1.53	0.00	2.57	3.12	3.23	3.39
NPBE	27	3.88	0.77	1.47	1.14	3.29	3.29	3.36	3.00
NDPE	29	4.19	0.79	1.48	1.13	3.44	3.58	3.74	3.66
CIPBE	7	4.06	0.74	1.40	0.28	3.17	3.69	3.74	3.74
FNDPE	50	4.00	0.80	1.66	1.51	3.22	3.31	3.37	3.36

^a Solvent sweats out from the membrane.

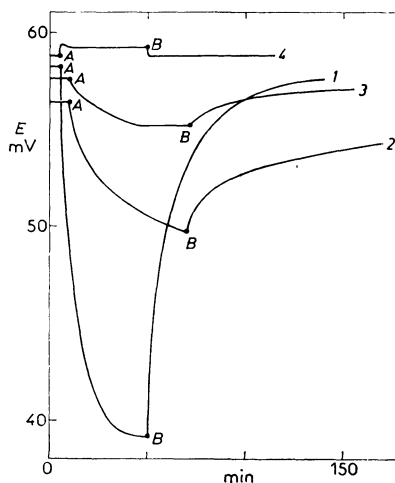


FIG. 1

Effect of stirring on the potential of calcium sensors with various compositions of the membrane. 1 Diamide *I* complex-2-nitrophenyl octyl ether; 2 diamide *I* complex - 2-fluoro-2'-nitrodiphenyl ether; 3 diamide *I* complex - 2-chlorophenyl benzyl ether; 4 diamide *II* complex - 2-nitrophenyl octyl ether. The 10^{-3} mol/l CaCl₂ solution used in the measurement was vigorously stirred in the time interval \overline{AB}

unstirred solution and also have a relaxation character. These shifts of several tenths of millivolt may displace repeated calibration curves to more negative values. Both effects render application of the membrane sensor in automatic systems with through-flow cells virtually impossible, especially in those cases where air-segmented flow is used during the cleaning period. A shift of the potentials to more negative values was observed by Fedotov and coworkers⁵ with the valinomycin potassium electrode in measurements in the through-flow cell at high flow rates. The phenomenon described by these authors also has a relaxation character and is explained by an orientation of complex compounds in the polymeric matrix in the direction of acting mechanical forces.

Experiments with membranes containing other solvents showed that the extent of the observed effect of stirring on the calcium sensor might be affected by the solvent used, as illustrated by Fig. 1. Curves 2 and 3 demonstrate the decrease in this effect under identical experimental conditions if 2-fluoro-2'-nitrodiphenyl ether and 2-chlorophenyl benzyl ether are used. No solvent could be found, however, in which stirring would induce no change of potential at all. Only in electrodes with poly(etherdiamide) *II* where benzyl groups on amide nitrogen atoms have been replaced with more lipophilic octyl groups the above effect disappears. In the stirred solution there is an instantaneous shift by several tenths of millivolt in the direction of more positive values (*cf.* Fig. 1, curve 4). The shift is independent of the time of stirring, and the potential resumes its original value immediately after switching off the stirring. Octyl groups, probably due to their long aliphatic chain, screen the ligand molecule in the complex, thus decreasing the possibilities of interactions with the surrounding medium caused by changes in hydrodynamic conditions. At the same time, the change in the ligand structure reduces changes in the potential caused by repeated immersion of the electrodes in the case of membranes with 2-nitrophenyloctyl ether and with the other solvents used in this study. The optimal electrode behaviour was observed with membranes plasticized with 2-fluoro-2'-nitrodiphenyl ether where also this effect was completely eliminated.

For the complex with more lipophilic poly(etherdiamide) containing octyl groups (*II*) we also investigated the effect of membrane solvents on selectivity. The values of selectivity coefficients along with those of dielectric constants ϵ_r of the solvents used are summarized in Table I. Selectivity for calcium with respect to the other alkali earth metals remains the same in all cases, unaffected by the structure or polarity of the solvent. As regards selectivity for calcium with respect to alkali metals, some rather pronounced changes occur only with lithium in halogenated solvents with a low dielectric constant. In these solvents selectivity for calcium with respect to lithium is lower by as much as an order of magnitude. With the other alkali metals the theoretically expected decrease in selectivity for calcium accompanying a decrease in the dielectric constant of the solvent⁶ does not take place, obviously due to the tetraphenylborate component of the complex. The presence of the nitro

group in the molecule leads to a rise in the dielectric constant which reaches its highest value with 2-fluoro-2'-nitrodiphenyl ether. In membranes containing these solvents the selectivity coefficients for all ions are comparable with results measured with the commonly used membrane solvent, *i.e.*, 2-nitrophenyl octyl ether.

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