Effect of Plasticizer on the Selectivity of Potassium-selective PVC Membrane Electrodes Based on Bis(crown ether)s

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Synopsis. Potassium-selective PVC membrane electrodes based on bis(crown ether)s containing benzo-15-crown-5 moiety were prepared, *o*-nitrophenyl octyl ether (NPOE) or dipentyl phthalate (DPP) being used as a plasticizer. Selectivity coefficients for various monovalent ions were measured. The preference of potassium over sodium in the bis(crown ether) (I; $n=5$)–NPOE electrode system is close to that in the valinomycin system.

Neutral carrier type ion-selective electrodes have been remarkably developed, attempts being made to prepare electrodes based on valinomycin and macrocyclic polyethers.[1,2] A report was given on the preparation of potassium-selective PVC membrane electrodes based on bis- and poly(benzo-15-crown-5)s.[3] However, the electrodes of poly(crown ether)s were impractical due to the poor response to activity change of potassium ion and the long response time, whereas the bis(crown ether)s were found to be high-selective active components.

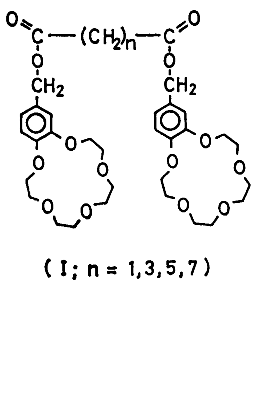
In this note, we would like to report on the effect of plasticizers upon the selectivity of potassium-selective PVC membrane electrodes based on bis(benzo-15-crown-5)s.

Experimental

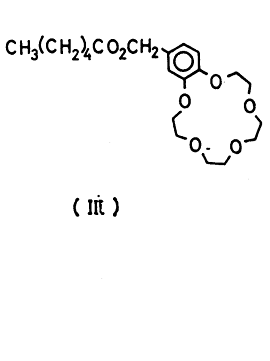
Chemicals. The syntheses of crown ether derivatives (I, II) were reported.[3] (Hexanoyloxymethyl)benzo-15-crown-5 (III) was synthesized from 4-hydroxymethyl-15-crown-5 and hexanoyl chloride in chloroform in the presence of triethylamine, and purified by recrystallization from petroleum ether. The plasticizers, NPOE and DPP were prepared according to reported methods.[4,5]

Electrode. The PVC membrane electrode was prepared as reported.[3] The electrochemical cell can be represented as follows: Ag, AgCl/0.001 M KCl/PVC membrane/measured solution/0.1 M NH_4NO_3/KCl (sat.)/Hg_2Cl_2 (s), Hg.

Measurements. All the measurements of e.m.f. were made at 25±0.1 °C using Corning pH meter 130. Standard potassium solutions for calibration plots were obtained by gradual dilution of 1 M potassium chloride solution. Selectivity coefficient k_{KM} was calculated by FIM (fixed interference method).[6] The constant concentrations of Na^+, Rb^+, Cs^+, and NH_4^+ are 1×10^{-1}, 1×10^{-3}, 1×10^{-3}, and 1×10^{-2} M, respectively.



(I; n = 1,3,5,7)



(III)

Results and Discussion

In order to elucidate the effect of plasticizer upon the electrode property, potassium-selective PVC membrane electrodes based on bis(crown ether)s (I; $n=1$, 3, 5, 7) were prepared with use of NPOE or DPP as the plasticizer. For comparison, benzo-15-crown-5 II, (hexanoyloxymethyl)benzo-15-crown-5 (III), and valinomycin (IV) were also employed as a neutral carrier. The electrode properties are sumarized in Table 1.

The electrodes of bis(crown ethers) (I; $n=1$, 3, 5, 7) showed a linear response to the activity of potassium chloride in the range 10^{-5}—10^{-1} M (1 M=1 mol dm^{-3}). The slopes of calibration plots were 55—59 mV per decade of activity change at 25 °C. These electrodes showed the same tendency in selectivity coefficients as reported.[3] The electrode of bis(crown ether) (I; $n=5$) showed the highest selectivity, which might be partly due to dependence of the chain length connecting two crown ether moieties upon the complex formation constant.[7]

The electrodes of monomeric analogs, II and III, also showed a linear response with a near-Nernstian slope in the activity range 10^{-5}—10^{-1} or -3×10^{-1} M KCl. However, the potassium-selectivity of the electrodes of I surpasses that of II about one to two order of magnitude, reflecting the high extractability of bis(benzo-15-crown-5) for potassium as compared to the monomeric analog.[8,9] Modification by a lipophilic chain such as III improves the potassium selectivity of benzo-15-crown-5.

It should be noted that the selectivity coefficients of the NPOE systems are generally much smaller than those of the DPP systems in the crown ether-based electrodes. The DPP systems are nearly equal in the selectivity coefficient to the dibutyl phthalate systems. NPOE was found to be the best plasticizer of the three in our PVC membrane electrode systems. Partition of cation to membrane should affect the selectivity of electrode, which depends on dielectric constant of plasticizer. NPOE which has a higher dielectric constant than DPP is considered to increase the selectivity of electrode.

Thus, the selectivity coefficient of potassium over sodium (k_{KNa}) for the bis(crown ether) (I; $n=5$)–NPOE system is close to that for the valinomycin system. In the selectivity coefficients of potassium over other interfering ions, this system is also superior to the valinomycin system. Our potassium-selective electrodes can be compared favorably with the electrode based on valinomycin in the selectivity, electrode response, and response time (within 10 s). Moreover, they have an advantage over valinomycin-based electrodes since the

Table 1. Electrode properties of PVC membranes containing crown ether derivatives

Crown ether	Plasticizer	Maximal slope (mV/decade)	Range pK^+	k_{KM}			
				Na^+	Rb^+	Cs^+	NH_4^+
Bis(crown ether) (I; $n=1$)	NPOE[a)]	56	4.5—1	4×10^{-4}	1×10^{-1}	2×10^{-2}	1×10^{-2}
Bis(crown ether) (I; $n=3$)	NPOE	58	5—1	5×10^{-4}	1×10^{-1}	2×10^{-2}	1×10^{-2}
Bis(crown ether) (I; $n=5$)	NPOE	58	5—1	3×10^{-4}	2×10^{-1}	1×10^{-2}	1×10^{-2}
Bis(crown ether) (I; $n=7$)	NPOE	57	5—1	4×10^{-4}	1×10^{-1}	1×10^{-2}	1×10^{-2}
Monocyclic crown ether (II)	NPOE	57	5—0.5	2×10^{-3}	1	3×10^{-1}	8×10^{-2}
Monocyclic crown ether (III)	NPOE	58	5—1	1×10^{-3}	7×10^{-1}	1×10^{-1}	5×10^{-2}
Valinomycin (IV)	NPOE	59	4.5—1	2×10^{-4}	1.4	3×10^{-1}	1×10^{-1}
Bis(crown ether) (I; $n=1$)	DPP[b)]	59	5—1	5×10^{-4}	2×10^{-1}	2×10^{-2}	8×10^{-3}
Bis(crown ether) (I; $n=3$)	DPP	55	5—1	2×10^{-3}	2×10^{-1}	2×10^{-2}	1×10^{-2}
Bis(crown ether) (I; $n=5$)	DPP	56	5—1	7×10^{-4}	2×10^{-1}	1×10^{-2}	9×10^{-3}
Bis(crown ether) (I; $n=7$)	DPP	58	5—1	9×10^{-4}	2×10^{-1}	1×10^{-2}	1×10^{-2}
Monocyclic crown ether (II)	DPP	58	5—0.5	1×10^{-2}	5×10^{-1}	5×10^{-1}	1×10^{-1}
Monocyclic crown ether (III)	DPP	58	5—1	4×10^{-3}	9×10^{-1}	3×10^{-1}	8×10^{-2}
Valinomycin (IV)	DPP	59	5—1	9×10^{-5}	2.1	5×10^{-1}	2×10^{-2}

a) *o*-Nitrophenyl octyl ether. b) Dipentyl phthalate.

bis(crown ether)s can be synthesized more easily than valinomycin.

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