Sensor molecules for silver(I)-selective membranes based on mono- to quadri-dentate podands

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A series of podands containing nitrogen and sulfur atoms are utilized as sensing components to prepare Ag^+-selective polymeric membrane electrodes whose characteristics are dependent on the structure of each podand used.

Crown ether type synthetic molecules have been employed in polymeric sensors as ionophores for the determination of metallic ions (Li^+, Na^+, K^+, Ca^{2+}).[1–3] Nitrogen- and oxygen-containing cryptands have also been used for the measurement of Zn^{2+} and other heavy-metal ions.[4,5] A group of polythiacrown ethers and acyclic polythia compounds have been exploited for the measurement of Ag^+.[6,7] Recently podand structures, acyclic oligoethers, have also been shown to be valuable additions to the above chemical species for ionophores.[8,9] Obtained simply and cheaply, the podand structures containing oxygen and sulfur as the binding sites have been studied in conjunction with the extraction and detection of precious metal ions such as Ag^+.[9,10] Soft coordination sites like sulfur of the thia compounds seem to generate great affinity toward the d^{10} transition-metal ions such as Ag^+ and Hg^{2+}.

It would be interesting to compare the relationship between molecular structure and electrochemical properties for ionophore-based membrane sensors. Employing similarly structured thioethers, Teixidor *et al*. have reported that any molecule with thioether group(s) could be highly selective towards silver(I).[6] The present report may provide an exception to this hypothesis.

Here we report on sensors based on a series of multiarmed podands that have essentially the same type but different numbers of arms (Fig. 1). All the podand structures were prepared as reported previously.[11] PVC-based ion-selective electrode (ISE) membranes were prepared by the method of Simon and coworkers.[12] The membrane compositions in the present work are listed in Table 1. Cell potentials were measured at ambient temperature (18 °C). The potentiometric cell used was as follows: Ag/AgCl(s)/4 M KCl saturated with AgCl/tris buffer/sample solution/ion-selective membrane/1 mM $AgNO_3$/AgCl(s)/Ag. A tris buffer solution consisting of 0.05 M tris(hydroxymethyl)aminomethane (Trizma Base) adjusted with HNO_3 solution to pH 9.0 was used as the working buffer for the potentiometric measurements. Selectivity coefficients, $k^{pot}_{Ag/X}$, were obtained by using the separate solution method.[13]

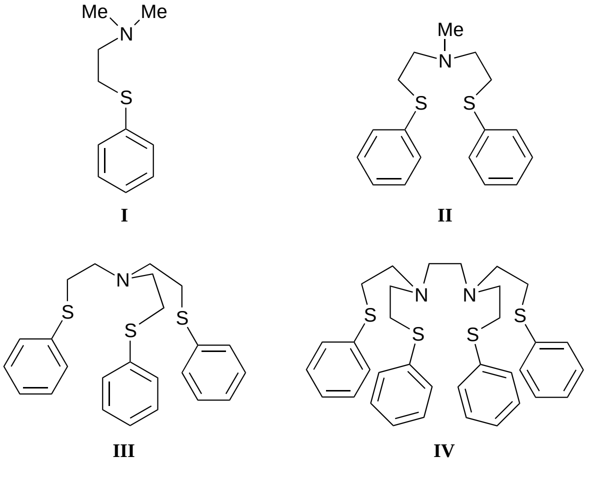

Fig. 1 Structures of some podand-type ionophores used in the preparation of Ag^+-selective membrane electrodes

Table 1 Formulation and electrochemical properties of podand-based Ag^+-selective membrane electrodes

Electrode	Podand[a,b]	PVC[a]	DIDA[a]	Detection limit/M[c]	Slope/mV decade^{-1} [c,d]
E1	4.0, **I**	32.0	64.0	N/A	N/A
E2	4.0, **II**	32.0	64.0	1.6×10^{-5}	45.5
E3	6.0, **III**	32.0	62.0	0.8×10^{-6}	58.0
E4	4.0, **III**	32.0	64.0	0.8×10^{-6}	58.5
E5	2.0, **III**	32.0	66.0	0.9×10^{-6}	57.0
E6	1.0, **III**	32.0	67.0	1.4×10^{-6}	47.2
E7	4.0, **IV**	32.0	64.0	1.0×10^{-6}	58.5
E8	Ag_2S			0.8×10^{-6}	59.1

[a] Numbers indicate mass%. [b] Bold roman characters indicate the podands in Fig. 1. [c] E1–E7, average of three membranes; E8 is a Ag_2S-based solid-state electrode. [d] Between detection limit and 1 mM.

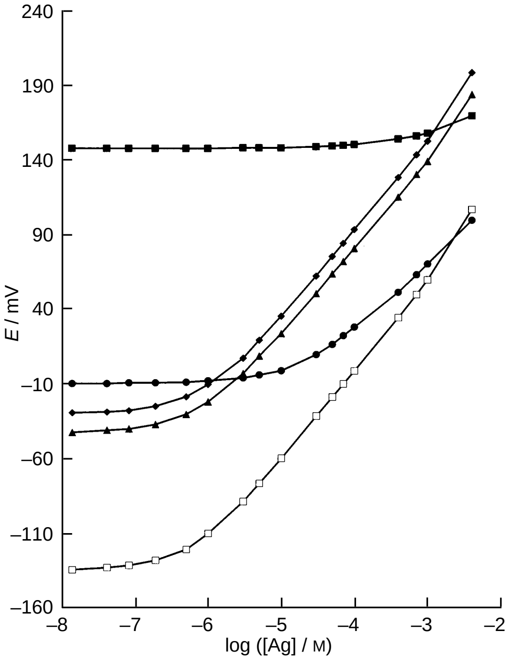

Fig. 2 Typical potentiometric Ag^+ ion responses of the podand-based PVC membrane electrodes: (■) E1, (●) E2, (▲) E4, (◆) E7 and (□) E8 in Table 1. Measurements were made in 0.05 M tris buffer, pH 9.0.

The equilibrium potentiometric responses of the new podand-based PVC membrane electrodes in the concentration range of 0–10 mm are shown in Fig. 2. As summarized in Table 1, almost Nernstian slopes are observed in podand **III**- and **IV**-based membrane electrodes. On the other hand, podand **I**- and **II**-based electrodes give negligible and small response slopes, respectively. The response time of each electrode is short; the time required to reach 90% of the equilibrium mV values was < 2 s. In terms of the lifetime of the PVC membrane electrodes, response stability was observed for over a month.

Table 2 lists the potentiometric selectivity coefficient data of some podand-based PVC membrane electrodes for the interfering cations relative to Ag^+.

Among thiapodands, NS_3 and N_2S_4 donor set podands (**III** and **IV** in Fig. 1) seem to show the best response and selectivity to Ag^+. Values of log $k_{Ag/X}$ range from -3.5 for K^+ to -5.1 for Ba^{2+}, Ca^{2+} and Mg^{2+}. The high selectivity toward Ag^+ is due to the high affinity of sulfur atoms in the ionophores. It is well known that $Ag^+(d^{10})$ exhibits a strong affinity towards sulfur-derived ligands and shows a remarkable preference for linear coordination.[7] For the Hg^{2+} ion, the selectivity coefficient (log $k_{Ag/Hg}$) was -4.0. Compared to that of an Ag_2S-based electrode, the relative selectivity toward Ag^+ over Hg^{2+} is much improved.

Table 2 Static-mode potentiometric selectivity coefficients,[a] log $k^{pot}_{Ag/x}$, of the podand-based membrane electrodes[b]

	Electrode[c]			
Cation	E2 (**II**)	E4 (**III**)	E7 (**IV**)	E8 (Ag_2S)
Ag^+	0	0	0	0
NH_4^+	-1.8	-3.7	-3.5	-4.0
Na^+	-1.8	-3.7	-3.5	-4.0
K^+	-1.8	-3.7	-3.5	-4.0
Ba^{2+}	-3.1	-5.1	-4.9	-5.2
Ca^{2+}	-3.1	-5.1	-4.9	-5.2
Mg^{2+}	-3.2	-5.1	-4.9	-5.2
Cu^{2+}	-3.2	-5.0	-4.8	-4.7
Cd^{2+}	-2.6	-4.9	-4.7	-5.1
Co^{2+}	-2.4	-5.0	-4.5	-5.1
Pb^{2+}	-2.9	-4.9	-4.8	-5.2
Ni^{2+}	-2.9	-5.0	-4.8	-5.2
Hg^{2+}	-2.9	-4.0	-4.0	-2.1

[a] Measured by the separate solution method at 1 mm cation concentrations in 0.05 m tris–nitric acid, pH 9.0. [b] Membrane compositions (E1–E8) listed in Table 1. [c] Bold roman characters in parentheses indicate the podands in Fig. 1.

In our previous study,[11] it was found that all of the podands tested in this study form 1 : 1 stoichiometric complexes with Ag^+ in methanol. The sequence of stability constants, log K, of complexes was found to be **IV** (12.43 ± 0.22) > **III** (9.29 ± 0.16) > **II** (7.02 ± 0.12) > **I** (3.4 ± 0.3) (assuming the stoichiometry for **I**–Ag^+ system is 1 : 1). In the same study, it was also revealed that the complex stability of the podands is mainly enthalpic in origin. From Ag^+-induced chemical shift measurements, it was also found that nitrogen atoms behave as strong donors for Ag^+ as do sulfur atoms.[11] Because of no or lower selective affinity of nitrogen for soft cations including Ag^+, both the total number of nitrogen/sulfur and the fraction of sulfur in a podand system seem to be related to the total response and selectivity of the membrane sensors toward Ag^+. The present study shows that the simple hypothesis of Teixidor *et al.*,[6] has exceptions for complex molecules including our nitrogen–sulfur containing podands.

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Footnote

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