Simple Sensor Molecules for Detection of Silver(I) based on Monothioethers

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Polyvinyl chloride (PVC) membrane all solid-state electrodes based on the thioethers diethyl sulfide, ethyl phenyl sulfide or diphenyl sulfide have been developed exhibiting high selectivity for silver(I), with low detection limits and short response times.

There has recently been great interest in the development of sensor molecules for detection of Ag^I, mainly for ISE[1–4] or ISFET[5] devices. The variety of molecular structures used is notable, most of them being based on macrocyclic thioethers.[1–5] The relative fit of the ligand cavity to the metal ion radius was considered the reason as to why the thioether macrocycles were capable of discriminating between closely related heavy-metal ions.[6–8] We have systematically studied a series of di- and tri-thioether xylyl containing sensor molecules.[3] High selectivity for Ag^I and excellent electrode properties were found, being superior to those reported previously and to that of conventional Ag_2S-based solid-state electrodes. Even though their general behaviour towards Ag^I was similar, conformational analysis indicated a great contrast of coordinating motifs.[9] This systematic search led to the hypothesis that the macrocyclic nature or the cavity size of these or other thioether ligands was not the main basis for good selectivity towards Ag^I, but rather simply the existence of the thioether group in the sensor molecule.

Table 1 Electrode characteristics

Sensor	EtSEt	PhSEt	PhSPh	L
Detection limit (mol dm^{-3})	6.6×10^{-7}	4.0×10^{-7}	4.6×10^{-7}	6.7×10^{-7}
Slope (mV per decade)	62	62	62	56
Time response(s)	<10	<5	<6	<5
pH interval	1.7–8.0	1.7–8.3	1.7–8.3	1.8–8.5
Lifetime (month)	>9	>9	>9	>9

Table 2 Logarithm of selectivity coefficients ($\log K^{pot}_{Ag/M}$)

	EtSEt	PhSEt	PhSPh	L
Na^+	−4.8	−4.9	−4.9	−5.1
Ca^{2+}	−5.4	−5.4	−5.3	−5.4
Cu^{2+}	−5.0	−4.2	−4.2	−5.0
Ni^{2+}	−5.5	−5.6	−5.5	−5.3
Co^{2+}	−5.6	−5.9	−5.9	−4.9
Pb^{2+}	−5.4	−6.0	−5.8	−5.2
Zn^{2+}	−5.7	−5.5	−5.4	−5.4
Cd^{2+}	−5.6	−5.6	−5.5	−5.0

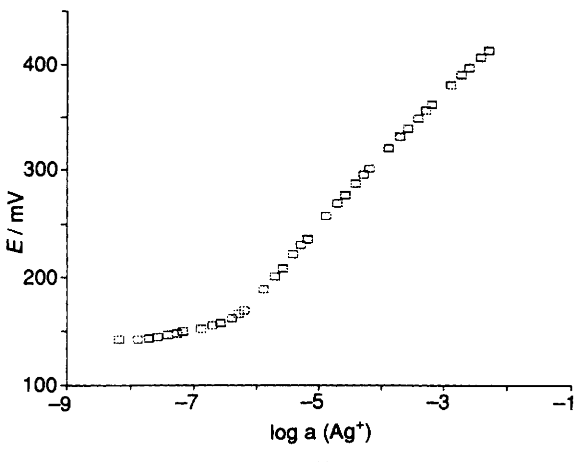

Fig. 1 Electrode response for silver(I)-selective electrode based on PhSEt. Ag–AgCl double-junction reference electrode (Orion 90-02-00) was used.

To prove this assumption we have used as sensor molecules common lab-shelf chemicals containing a thioether group, examining the influence of the moities (alkyl and/or aryl) directly attached to the sulfur, *viz.*, EtSEt, PhSEt and PhSPh. The results reported here confirm the hypothesis that it is the thioether group presence in the sensor molecule, rather than cavity fitting, that leads to the high sensing response towards Ag^I.

The three thioethers have been tested as sensor molecules in PVC-based all-solid-state electrodes. All display a Nernstian response for silver(I) and show similar selectivity and response properties to the best previously reported silver-ion selective electrode.[3]

The ion-selective electrodes were prepared and assembled as previously described.[10–12] The membrane composition was as follows: thioether (10 mg, 7%), bis(2-ethylhexyl)phthalate (44.2 mg, 31%), PVC (88.6 mg, 62%). The potentiometric selectivity coefficients ($K^{pot}_{Ag/M}$) were determined by the fixed interference method (FIM).[13] The constant background concentration was 0.1 mol dm^{-3} for all interferent ions.

Electrode characteristics and selectivity coefficients for Ag^I with respect to other cations are summarized in Tables 1 and 2, respectively. Fig. 1 shows a typical calibration graph obtained with PhSEt, which is similar to those obtained with EtSEt or PhSPh. All three thioethers exhibit similar selectivity and response parameters thus showing the absence of an influence of the nature of the moieties attached to sulfur. Tables 1 and 2 also contain data related to the macrocycle 3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene[3] (L) for comparison. The selectivity coefficients for all the interferent ions tested are equal or lower than those of L except for Cu^{II}. As to Ag^I detection, these results demonstrate that it is not necessary to specially design the ligand in order to discriminate between different metal ions. Any molecule, even with a sole thioether group, provided that it has adequate lipophilicity and solubility characteristics, is expected to be highly selective towards Ag^I and display similar selectivity coefficients to those reported here.

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