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Silver(I) Ion Selective Electrode Based on Dithiamacrocycles

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Poly(vinyl chloride) membrane all solid state electrode based on the macrocyclic polythiaether 6-oxa-3,9-dithiabicycle[9,3,1]-pentadeca-1(15)-11,13-triene, has been developped. The electrode exhibits a Nernstian linear response to silver(I) ion from 10^{-6} to 10^{-1} M, good selectivity (no response for Hg(II)) and short response time (<10 s).

Macrocyclic polythiaethers have the ability to form complexes with transition metal cations. We have experimented the 15-aza-6-oxa-3,9-dithiabicycle[9,3,1]pentadeca-1(15)-11-13-triene,[1] as a neutral carrier for copper(II) ion-selective membrane electrode. This azadithiaether macrocycle is relatively soluble in the common mediator solvents used. We have improved its characteristics by changing the pyridine moiety by a benzene group, so reducing its polarity and solubility in water. The resulting dithiaether macrocycle 6-oxa-3,9-dithiabicycle[9,3,1]pentadeca-1(15)-11,13- triene (MAO) (Fig. 1) is an excellent neutral carrier for silver(I) ion-selective membrane electrodes with no response for Hg(II) ion.

Synthesis of the reagent is as follows. Under nitrogen atmosphere and high dilution conditions (3 mL/h), solution A (KOH, 0.04 mol; 2-mercaptoethyl ether, 0.02 mol; degassed 1-butanol, 50 mL) and solution B (α, α'-dichloro-m-xylene, 0.02 mol; 1-butanol, 50 mL) were mixed over 1-butanol (1.5 L). The KCl formed was eliminated and the resulting solution was evaporated to dryness. The oily material was extracted with benzene (150 mL), washed with Na_2CO_3 and H_2O and dried (Na_2SO_4, 8 h). The material was dissolved in benzene (5 mL) and chromatographed over neutral Al_2O_3. The fraction eluted with benzene was separated and carried to dryness. The resulting oily material was poured onto petroleum ether (40-60 °C, 50 mL) and a crystalline compound appeared. Elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR and MS confirmed the structure proposed in Fig. 1.

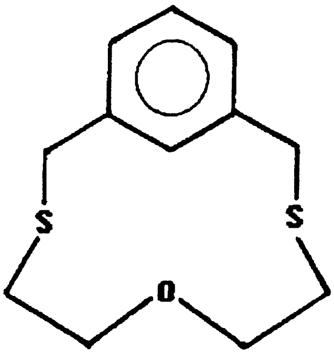

Fig. 1.

The constructed ion-selective electrodes were of conductive polymer composite-substrate all-solid-state PVC matrix membrane type. The sensor membranes were prepared and assembled as previously described.[2,3] The sensor material (MAO, 7%, 5 mg) with dioctylphtalate (31%, 22 mg) as plasticizer and poly(vinyl chloride) (62%, 44.3 mg) were dissolved in THF (2 mL). The conductive polymer composite (graphite-loaded epoxy resin) used as solid internal contact has been described previously.[2,3] Best results were obtained by conditioning the electrode before use by soaking for 24 h in a 10^{-1} M $AgNO_3$ solution. The electrochemical cell is as follows: solid internal contact/sensor membrane/working solution/reference electrode. The emf (at 25 ± 0.1 °C) was measured relative to Ag-AgCl double junction reference electrode (Orion 90-02-00) with the outer chamber filled with 10^{-1} M KNO_3 solution. A Crison (Barcelona) digital potentiometer (±0.1 mV) was used.

A typical calibration curve exhibits Nernstian linear response within an activity range of 10^{-1} M to 10^{-6} M. The properties of the electrodes are summarized in Table 1. The MAO macrocycle was found to be a useful sensor material for silver(I) ion. No response towards more common, monovalent and divalent metal ions has been found, even for Hg(II) ion. Some sensor materials have been reported for Ag(I). Currently, however, Hg(II) is an interferent ion for them.4) Recently, M. Oue et al.5,6) have reported several thiacrown ether derivatives as neutral silver-ion selective carriers, their best selectivities toward Hg(II) are comparables with that reported here (Selectivity coefficients are in the range, 6.5×10^{-3}--3.4×10^{-2})

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Table 1. Response characteristics of Ag(I)-membrane electrodes based on the MAO

Detection limit for Ag^+ (M)	3×10^{-7}	Slope (mV/decade)	59
Response Time (s)	< 10	Effective pH range a)	2.5-8.5
Life time (month)	> 4		

Selectivity coefficients $K^{pot}_{Ag/M}$ b)

M = Mg(II)	4.9×10^{-6};	M = Na(I)	1.3×10^{-5};	M = Ca(II)	1.1×10^{-5}
M = Co(II)	2.5×10^{-6};	M = Sr(II)	1.0×10^{-5};	M = Pb(II)	1.2×10^{-5}
M = Zn(II)	2.7×10^{-6};	M = Ni(II)	4.5×10^{-5};	M = K (I)	1.7×10^{-5}
M = Cd(II)	3.9×10^{-6};	M = Cu(II)	1.3×10^{-5};	M = Hg(II)	5.0×10^{-3}

a) 10^{-3} M $AgNO_3$ solution. b) Obtained by the mixed solution method (Fixed interference method). Background concentrations were 10^{-1} M for all ions, except for Hg^{2+}, 10^{-5} M.

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