

Chemically modified field-effect transistors; potentiometric Ag^+ selectivity of PVC membranes based on macrocyclic thioethers

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(Received 17th June 1992)

Abstract

A chemically modified field-effect transistor (CHEMFET) with satisfactory Ag^+ selectivity is described. The potentiometric Ag^+ selectivities of CHEMFETs with plasticized PVC membranes based on macrocyclic thioethers have been determined. All the macrocyclic thioethers tested showed silver response and a selectivity towards Ag^+ and Hg^{2+} versus other interfering cations. The highest Ag^+ selectivity was obtained for a 14-membered cyclic tetrathioether with an exocyclic methylene group.

Keywords: Ion-selective electrodes, Potentiometry, CHEMFETs, Macrocyclic thioethers, PVC membranes, Silver

Macrocyclic thioethers have the ability to discriminate between closely related heavy metal ions based on the relative fit of the ligand cavity size to the metal ionic radius [1]. Taking advantage of their ion-discriminating ability, macrocyclic thioethers have been used as neutral carriers in ion-selective electrodes (ISE), especially for silver [2–5] and mercury [3,6]. However, there is no report of Ag^+ -selective sensors based on chemically modified field-effect transistor (CHEMFET) devices. A CHEMFET combines the principle of detection by a membrane ISE with the solid-state integrated-circuit (IC) technology [7–11]. We have developed a CHEMFET technology based on a chemically attached poly(2-hydroxyethyl methacrylate) (polyHEMA)

hydrogel interlayer between a hydrophobic membrane and the ISFET gate oxide insulator layer. This solves the problem of the thermodynamically ill-defined membrane/gate oxide interface and suppresses interference from carbon dioxide [10].

In this study, we have determined the potentiometric Ag^+ selectivities of CHEMFETs with plasticized PVC membranes containing macrocyclic thioethers. The effects of the membrane matrix, e.g. type of ionophore, amount of lipophilic salt, and different plasticizers have been investigated in detail. The structures of the ionophores used are depicted in Fig 1.

EXPERIMENTAL

Chemicals

High-molecular-weight PVC, bis(2-ethylhexyl)-phthalate (DOP), *o*-nitrophenyl octyl ether (*o*-

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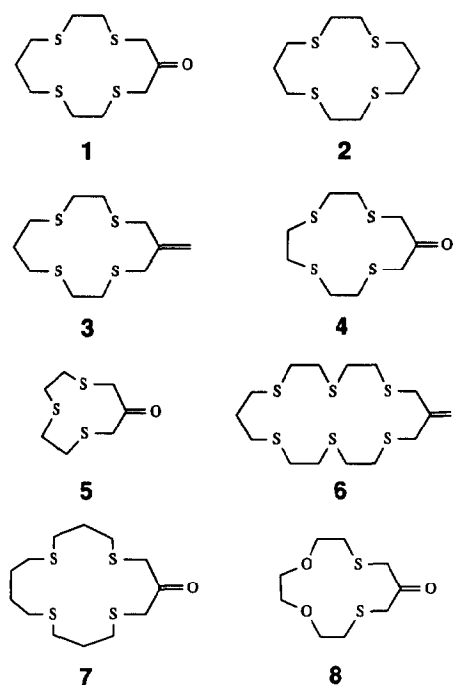


Fig. 1 Structures of the macrocyclic thioethers (ionophores 1–8)

NPOE) and potassium tetrakis(4-chlorophenyl)-borate (KTPCIPB) were obtained from Fluka. Tetrahydrofuran (THF) was freshly distilled from benzophenone–sodium before use. The nitrates of cadmium, calcium, copper, lead, mercury, potassium and silver used were of analytical-reagent grade (Merck). All solutions were made with doubly distilled and deionized water. Compounds 1, 4, 5, 7, 8 [12,13] and 2, 3, 6 [14] were prepared according to literature methods.

CHEMFETs

The ISFETs were fabricated as described previously [8]. The CHEMFETs used in this study contain an intermediate hydrogel layer of poly-HEMA between the gate oxide and the sensing membrane. The polyHEMA layer was anchored chemically to the gate oxide as described before [10,15]. CHEMFETs were encapsulated with epoxy resin (Hysol). Subsequently, the hydrogel layer was conditioned by immersion in buffered (pH 4) 0.1 M aqueous silver nitrate solution for 3–6 h prior to solvent casting. The membranes

were made by solvent casting of a mixture of 33 mg of PVC, 65 mg DOP or *o*-NPOE, 2 mg of ionophore and 0.1–2 mg of KTPCIPB (10–100 mol% with respect to the ionophore) in 1 ml of THF on mounted CHEMFETs and the THF was allowed to evaporate overnight. Before the measurements were started the membranes had been conditioned in 0.1 M aqueous silver nitrate solution for one night.

CHEMFET measurements

The CHEMFETs were measured in a constant drain-current mode ($I_d = 100 \mu\text{A}$), with a constant drain-source potential ($V_{ds} = 0.5 \text{ V}$) [16]. This was achieved using a source-drain follower type ISFET amplifier. The developed membrane potential was compensated by an equal and opposite potential (ΔV_{gs}) via the reference electrode. A saturated calomel electrode (SCE) was used as reference with a double junction containing 1.0 M potassium nitrate. Four CHEMFETs were monitored simultaneously and the data were collected and analyzed using an Apple IIe micro-computer. All experiments were performed in a dark and grounded metal box to eliminate interference by static and photosensitivity of the CHEMFETs. The potentiometric selectivity coefficients, $K_{i,j}^{\text{pot}}$, were determined by the Fixed Interference Method (FIM) [17]. The constant background concentrations of all interfering ions were 0.01 M at a constant pH 4. All concentrations were converted to activities using the extended Debye–Hückel equation [18]. The obtained response characteristics were analyzed according to the Nicolsky–Eisenman equation [19]

$$E = E^{\circ} + S \log \left[a_i + \sum K_{i,j}^{\text{pot}} a_j^{z_i/z_j} \right],$$

$$S = 2.303 RT/z_i F$$

where all the symbols have their conventional meanings.

RESULTS AND DISCUSSION

The “real” blank membranes (only plasticizer and PVC) showed no selectivity at all for the ions used for interference studies. Two plasticizers

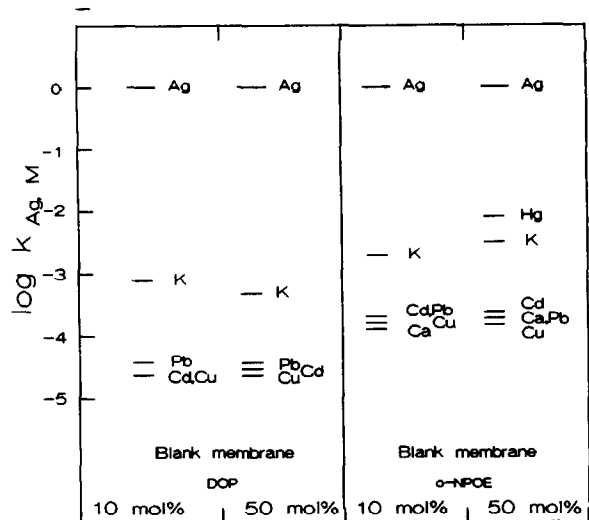


Fig 2 Selectivity coefficients, $\log K_{Ag,M}$, of blank membranes with different plasticizers and amounts of $KTpCIPB$

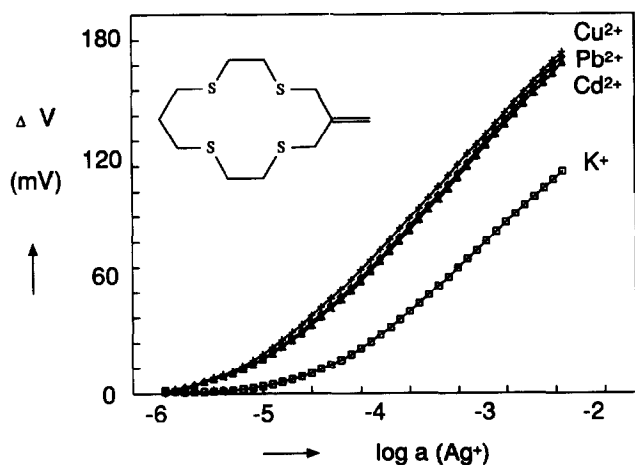
were tested the less polar di(2-ethylhexyl)-phthalate (DOP) and more polar *o*-nitrophenyl octyl ether (*o*-NPOE). Both types of membranes showed anionic response in case of Hg^{2+} titration with slopes of about 20 and 10 mV, respectively.

Blank (without ionophore) membranes but with lipophilic salt [potassium tetrakis(*p*-chlorophenyl)borate] gave good Ag^+ selectivity (Fig 2). The selectivities versus divalent cations are al-

most the same for all membranes with different amounts of $KTpCIPB$ salt. The highest Ag^+ selectivities were found for membranes with the less polar plasticizer (DOP), because this will favour the extraction of monovalent rather than divalent cations. The CHEMFET responses were linear over about 1 decade (DOP) or 2 decades (*o*-NPOE) of silver activity with slopes of around 25–30 and 34–45 mV, respectively.

All tested macrocyclic thioethers showed silver response and a selectivity towards Ag^+ and Hg^{2+} versus other interfering cations. A typical silver response of a CHEMFET with a PVC membrane containing a 14-membered macrocyclic tetra-thioether (3) is given in Fig 3.

The size of the macrocyclic ring influences the Ag^+ selectivity although this effect is moderate. Based on the three thioethers with a carbonyl group in the ring, the small 10-membered trithioether (5) showed the highest Ag^+ selectivity versus all tested cations (Fig 4). This conclusion is still preliminary because the number of sulphur atoms in the rings is different. Casabo et al [4] have presented impressive Ag^+ selectivities of membrane ISE for Ag^+ versus Hg^{2+} with small macrocyclic thioethers in the membrane. A 17-membered tetrathioether (7) showed responses only for membranes with 50 mol% $KTpCIPB$ and even then its Ag^+ selectivity was only slightly better than of the 14-membered macrocy-



potentiometric selectivity

$\log K_{i,j}$	
K^+ 0.01	-3.2
Ca^{2+} 0.01	-4.5
Cu^{2+} 0.01	-4.8
Cd^{2+} 0.01	-4.8
Pb^{2+} 0.01	-4.7

Fig 3 Ag^+ -response curves of CHEMFET based on a plasticized PVC membrane containing 14-membered thioether 3 with respect to different interfering cations

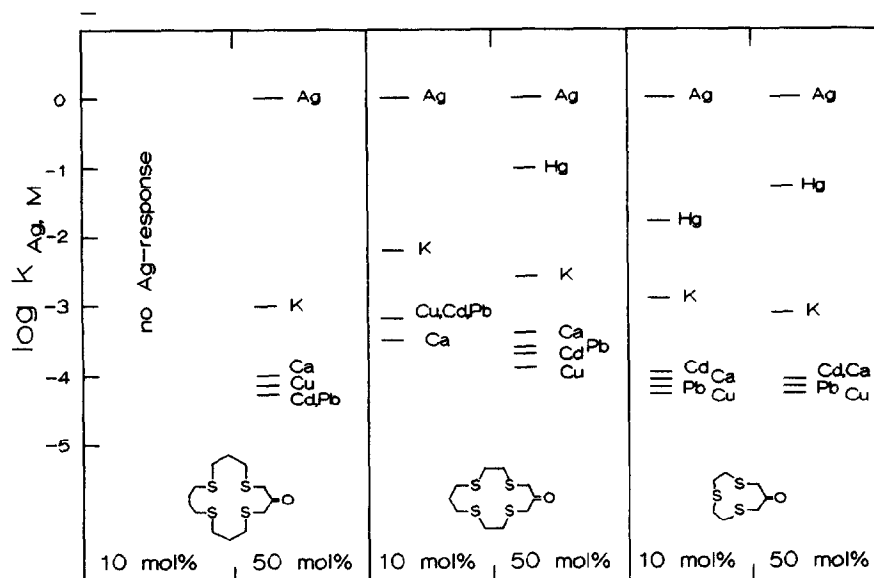


Fig 4 Selectivity coefficients $\log K_{Ag,M}$, of membranes based on macrocyclic thioethers with various ring size (ionophores 1, 5, and 7) and different amounts of KTpCIPB

cle (1) The 13-membered ionophore (4) gave better Ag^+ selectivity versus tested cations, apart from potassium (Fig 5), than the 14-membered macrocyclic (1)

Ionophores with a carbonyl group exhibited preference for Ag^+ over Hg^{2+} , but introduction of a carbonyl group lowers Ag^+ selectivity with respect to all the tested cations (Fig 5) The

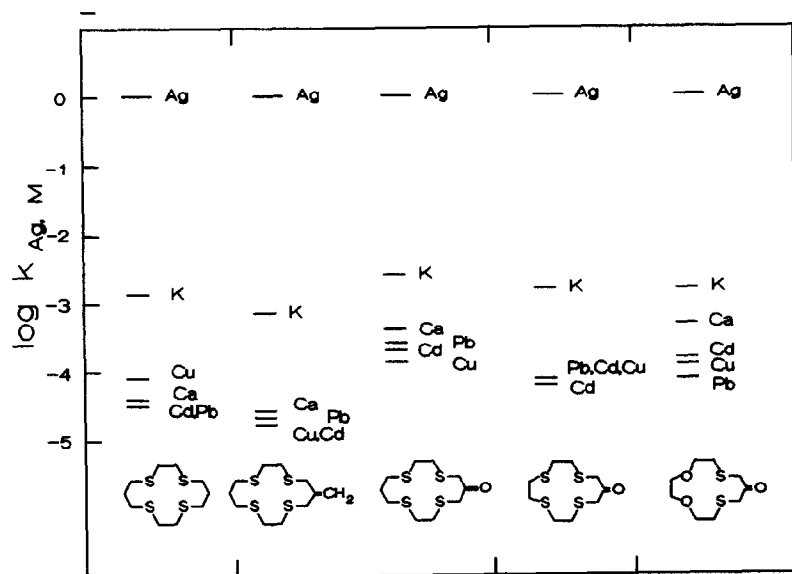


Fig 5 Selectivity coefficients, $\log K_{Ag,M}$, of membranes based on macrocyclic thioethers 1, 2, 3, 4 and 8 Membranes with 50 mol% of KTpCIPB

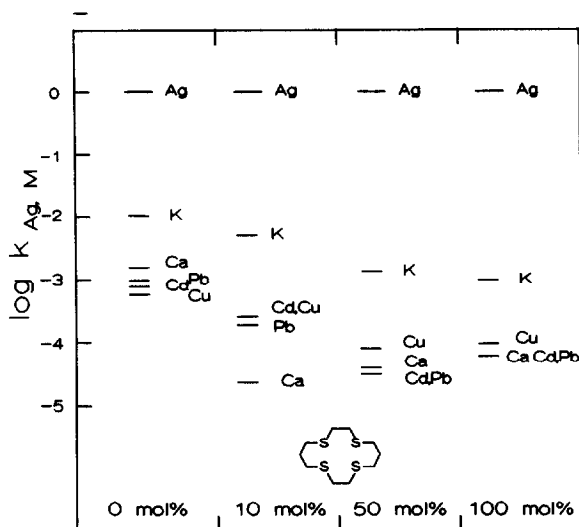


Fig 6 Selectivity coefficients, $\log K_{Ag,M}$, of membranes based on macrocyclic thioether 2 with different amounts of KTP-CIPB

highest Ag⁺ selectivity was obtained for the 14-membered tetrathioether (3) with an exocyclic methylene group. This group seems to cause the superior selectivity but an explanation for this phenomenon would need more variation in the macrocyclic thioether structures.

Substitution of two sulphur atoms in the ring by oxygen changes the behaviour of the ionophore significantly. The Ag⁺ selectivity of ionophore 8 (Fig 5) becomes worse, especially versus calcium, which has a preference for harder basic oxygen atoms.

Optimal CHEMFET composition

The amounts of lipophilic salt in the membranes does not have a significant influence on the Ag⁺ selectivity (except for potassium), but it has a beneficial effect on the stability of the CHEMFET response. The membranes with 50 mol% of KTPCIPB showed stable response values in measurements over 9 h contrary to the membranes containing 10 mol%. This indicates that the lipophilic salt is leaching from the membrane. It appears that the amount of lipophilic salt does not influence the Ag⁺/Hg²⁺ selectivities.

In order to find the optimal membrane composition we have tested membranes with the 14-

membered tetrathioether (2) in DOP and with different amounts of KTPCIPB (0, 10, 50, 100 mol% with respect to the ionophore). The selectivity coefficients $\log K_{Ag,M}$, are presented in Fig 6. The best values were obtained with membranes that contain 50 mol% of KTPCIPB.

Conclusions

Satisfactory Ag⁺-selective CHEMFETs based on PVC membranes and macrocyclic thioethers have been realized. All tested macrocyclic thioethers show good Ag⁺ sensitivity but not always a Nernstian response to the activity changes of Ag⁺. An important role of lipophilic salt in the membrane with respect to its Ag⁺ selectivity was observed. The presented macrocyclic thioethers are still insufficiently lipophilic for long term applications of the designed sensors.

The authors thank the Technology Foundation (STW), Technical Science Branch of the Netherlands Organization for Advanced and Pure Research (NWO) for the financial support.

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