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# Lead selective electrodes based on thioamide functionalized calix[4]arenes as ionophores

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## Abstract

Lead selective electrodes based on a di- and tetrathioamide functionalized calix[4]arene as ionophores were investigated. The Pb(II)-response functions exhibited almost theoretical Nernstian slopes in the activity range  $10^{-6}$ – $10^{-2}$  M of lead ions. For both ionophores a preference for lead over other cations was observed. The best results were obtained for membranes containing the tetrathioamide derivative (ionophore **1**), potassium tetrakis(4-chlorophenyl)borate and *o*-nitrophenyl octyl ether as a plasticizer. This electrode showed greatly improved selectivity over copper, zinc and cadmium ions as compared with commercial solid-state lead selective electrodes.

**Keywords:** Calix[4]arenes; Lead selective electrodes; Thioamide

## 1. Introduction

There is an increasing interest in the development of lead(II) ion-selective electrodes. Many compounds, either organic or inorganic, have been used as electroactive materials. The sulfide, oxide, selenide, and other salts of lead together with silver sulfide provide the active phase of solid-state electrodes [1–9]. For these electrodes other cations which form insoluble salts, e.g., cadmium, copper, mercury and silver interfere strongly with the electrode response towards lead(II), the influence of alkali and alkaline earth cations is negligible. Also, a chalcogenide glass electrode reported by Vlasov [10] exhibits the interference of copper and silver ions but the selectivity towards lead versus cadmium is improved.

The use of complexing agents offers the possibility of designing ligands with a wide range of functional groups, and consequently different abilities to complex cations. Several neutral compounds with oxygen, nitrogen and sulphur donor atoms have been examined as ionophores for lead selective electrodes [11–13]. The selectivity of dibenzo-18-crown-6 and its derivatives for lead in the presence of transition, alkali and alkaline earth metal ions has been investigated and values of  $\log k_{\text{Pb,M}}$  as high as  $-2.8$  were found. Silver, potassium and copper showed the highest interference. Electrodes based on acyclic oxamides [14,15] have shown good selectivity for lead(II) ions in the presence of some transition, alkali and alkaline earth metal ions ( $\log k_{\text{Pb,M}} < -3$ ). It has been also described [16] that the incorporation in a membrane of macrocyclic oxamides induces a pronounced preference for lead over some

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transition and alkaline earth metal ions. However, the selectivity against monovalent ions was lower than that observed for the acyclic oxamides, and is depended on the number, the distribution of oxygen donor atoms and the ring size. Podands with antipyrilaminomethine groups as ionophores have been reported by Pyatova et al. [17]. The logarithmic selectivity coefficients were more negative than  $-3$  except for potassium ( $-2.2$ ), copper ( $-1.5$ ) and silver ( $-0.3$ ). Poly(hydroxamic acid) in silicone rubber as supporting material has been proposed for lead selective electrode [18]. Nickel, mercury and copper ions interfere strongly but for other cations values  $\log k_{\text{pb},\text{M}} > -1.6$  were reported. Kamata and Onoyama [19,20] have reported several acyclic dithiocarbamate ionophores. In all cases copper ions interfered strongly ( $\log k_{\text{pb},\text{M}} > 0$ ). Also the interference of sodium and potassium ions was significant.

Recently we have synthesized acyclic oxamides [21] and oxamide and thioamide derivatives of calix[4]arene which show good selectivities towards lead over other ions tested in CHEMFETs measurements [22].

In this paper we report on lead selective electrodes based on lipophilic thioamide functionalized calix[4]arenes **1** and **2** as receptor molecules.

## 2. Experimental

### 2.1. Chemicals

All salts employed were of analytical grade and were purchased from POCH (Gliwice, Poland). The standard stock solutions (0.1 M) of metal nitrates were prepared in redistilled water; working solutions were obtained by dilution of the stock solution with redistilled water. The pH was adjusted by the addition of nitric acid, sodium hydroxide or ammonia solution.

### 2.2. Ionophores and membrane materials

The synthesis of ligands used has been described previously [22]. High molecular weight poly(vinyl chloride) (PVC), potassium tetrakis(*p*-chlorophenyl) borate (KTpClPB), *o*-nitrophenyl octyl ether (*o*-NPOE) and bis(butylpentyl) adipate (BBPA) were obtained from Fluka (Buchs, Switzerland). As a sol-

vent for membrane components, freshly distilled tetrahydrofuran (THF) p.a. (POCH) was used.

### 2.3. Membrane and electrode preparation

The membrane contained 1 wt% ionophore, 75 mol% KTpClPB (relative to the ionophore), 65–66 wt% plasticizer, and 33 wt% PVC. The membrane components, 200 mg in total, were dissolved in 2 ml of freshly distilled THF. This solution was placed in a glass ring of 24 mm i.d. resting on a glass plate. After overnight solvent evaporation, the resulting membrane was peeled off from the glass mould and discs of 7 mm i.d. were cut out. Membrane discs were mounted in electrode bodies (Type IS 561; Philips, Eindhoven, Netherlands) for electromotive force (EMF) measurements. As internal filling solution, a 0.005 M solution of  $\text{PbCl}_2$  was used. The electrodes were subsequently conditioned overnight in a solution of 0.01 M  $\text{Pb}(\text{NO}_3)_2$ . For each membrane composition two electrodes were prepared.

### 2.4. EMF measurements

All measurements were carried out at 20°C with cells of the following type: Ag; AgCl; KCl (0.1 M)/0.1 M  $\text{KNO}_3$ /sample solution//sensor membrane//internal filling solution; AgCl; Ag.

The EMF values were measured using a custom made 16-channel electrode monitor. Details of this equipment are described in [23]. Potentiometric selectivity coefficients,  $k_{\text{pb},\text{M}}$  were determined by the fixed interference method [24,25] with increasing the activity of primary ion in the solution in steps of  $0.5 \log a_{\text{pb}}$  and/or, for hard interfering ions, by the separate solution method using 0.01 M solutions of metal nitrates at a constant pH of 4 (for mercury pH 2). In this case for calculations the experimentally obtained slope was used. The activities of metal ions in aqueous solutions were calculated according to the Debye-Hückel approximation [26]. The performance of the electrodes was examined by measuring EMFs of the primary ion solutions in the  $10^{-7}$ – $10^{-1}$  M concentration range in solutions stirred with a magnetic stirrer.

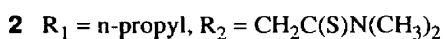
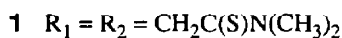
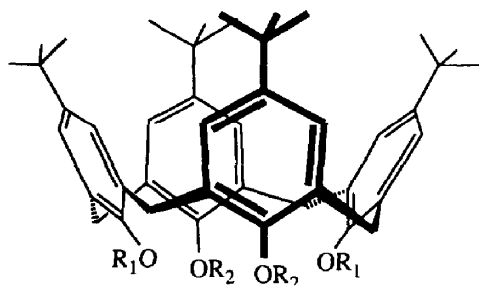


Fig. 1. Structures of ionophores.

### 3. Results and discussion

Structures of the examined ligands **1** and **2** are presented in Fig. 1.

The Pb(II)-response functions of membranes with **1** and **2** exhibited a nearly theoretical Nernstian slope for divalent cations and were linear to at least  $10^{-6}$  (1) or  $10^{-5}$  m (2)  $\text{Pb}(\text{NO}_3)_2$ . The calibration graphs in the presence of some interfering cations for **1** based electrodes are displayed in Fig. 2a and b.

The logarithmic values of the selectivity coefficients (expressed as  $\log k_{\text{Pb},\text{M}}$ ) are presented in Fig. 3a. For both ionophores a preference for lead over the other cations tested was observed. The Pb selectivity is higher for the tetrathioamide (ionophore **1**) than for

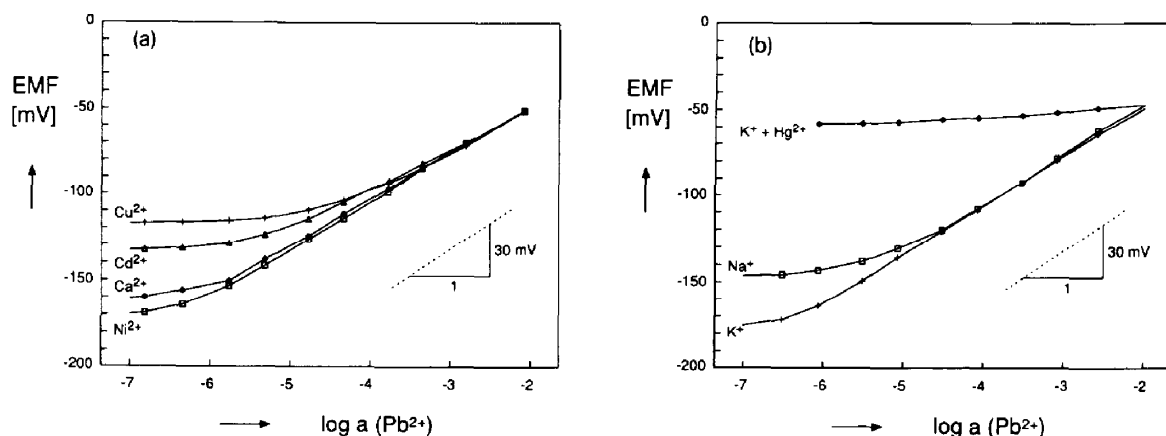


Fig. 2. Selectivity coefficients,  $\log k_{\text{Pb},\text{M}}$ , for PVC membranes with *o*-nitrophenyl octyl ether or bis(1-butylpentyl) adipate as plasticizer and with potassium tetrakis(4-chlorophenyl)borate (75 mol%). Membranes containing ionophore **1** or **2** (a) are compared with the “blank membranes” (b) [0.1 M solutions of nitrates, pH 4, internal electrolyte: 0.005 M  $\text{PbCl}_2$ ].

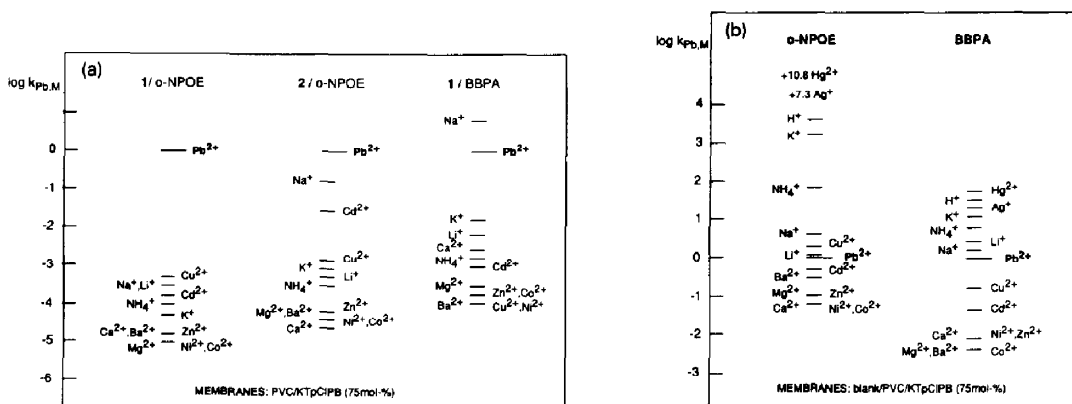


Fig. 3. Pb response of electrodes containing calix[4]arce ionophore **1** in the presence of 0.1 M of the chosen cations.

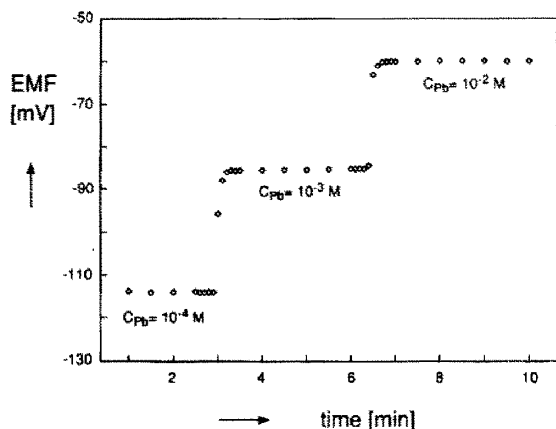


Fig. 4. Response time of electrodes containing calix[4]arene ionophore 1 in the presence of 0.1 M  $\text{KNO}_3$ .

the dithioamide (ionophore 2) derivative of calix[4]arene. The smallest difference ( $< 0.6$  units) was found for calcium, barium, magnesium, zinc, copper, nickel, cobalt, lithium and ammonium ions while for cadmium, potassium and sodium ions this difference was even higher than 2 units. This leads to the conclusion that four thioamide groups are a prerequisite in a calix[4]arene based ionophore for selective complexation of lead(II) ions.

The incorporation of ligand 1 or 2 in *o*-NPOE plasticized membranes (in the presence of lipophilic anion sites) substantially affects the selectivity of the membranes as compared with the "blank membrane" (cf. Fig. 3a and Fig. 3b). Without ionophore only a slight selectivity towards divalent cations was observed (with the exception of copper and mercury). The examination of the influence of the KTpCIPB concentration showed that membranes with ligands 1 and 2 but without KTpCIPB do not induce selectivity towards lead ions. The observation that certain ligands behave as carriers only when lipophilic anionic sites are present in the membrane is well known [27]. An increased ratio of KTpCIPB to ionophore improves the selectivity for lead(II) ions over monovalent cations and increases the linear range of electrode response in the higher concentration range of lead ions. We found that a ratio of ligand to KTpCIPB of 1:0.75 is sufficient to exclude the sample anions influence and to obtain satisfactory selectivities for lead ions. With this composition further experiments were carried out.

It was found that for both electrodes, based on 1 and 2, mercury ions did interfere. When the membrane with

ionophore 2 came in contact with these ions the electrode was poisoned and did not show previous lead performance even after long conditioning in the lead nitrate solution. In the case of ionophore 1, the electrode regained almost its lead response. The poisoning by mercury(II) ions has been mentioned by Kamata and Onoyama [19] for electrodes based on bis(diisobutyl-dithiocarbamate) neutral carrier with *o*-NPOE as a plasticizer.

The comparison of the selectivity data for "blank membranes" with *o*-NPOE and BBPA, suggests that the use BBPA as a plasticizer could reduce this effect. In the case of membranes based on BBPA plasticized PVC containing ionophore 1 the poisoning did not occur but the electrodes were affected by silver(I) and mercury(II) ions. The following selectivity coefficients, determined by a separate solution method for  $10^{-2}$  M solutions of cations (pH 4 for lead and silver, and pH 2 for mercury), were obtained:  $\log k_{\text{Pb,Hg}} = +0.6$  and  $\log k_{\text{Pb,Ag}} = +1.5$ . The selectivity coefficients versus other cations tested are shown in Fig. 3a. A change of the plasticizer for BBPA leads to a decrease of the selectivity towards lead ions over the cations tested, especially for alkali metal ions. The exception was copper(II). In this case  $\log k_{\text{Pb,Cu}}$  was lower (0.6) than for *o*-NPOE membranes plasticized.

The following properties of electrodes were tested: the selectivity, lead(II) response (slope, detection limit), pH dependence and response time. The electrode properties are summarized in Table 1.

The response time ( $t_{95\%}$ ) of the electrodes was tested by measuring the time required to achieve a 95% value

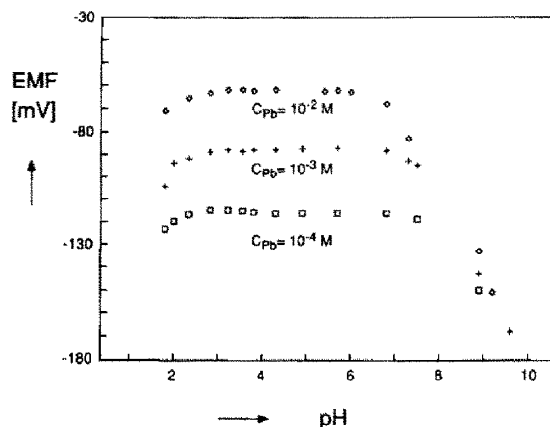


Fig. 5. pH response of electrodes containing calix[4]arene ionophore 1 in the presence of 0.1 M  $\text{KNO}_3$ .

Table 1

Properties of Pb-selective membrane electrodes based on tetra- and dithioamide calix[4]arenes **1** and **2** (PVC, *o*-NPOE, 75 mol%, KTpCIPB)

Ionophore	Fresh membrane		After six weeks	
	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>
Slope (mV/dec)	28.7	28.8	24.0	25.4
Response time $t_{95\%}$ (s)	< 10	< 8	< 20	< 10
Linear range (log $a$ )	< -1.8	< -1.8	< -2.0	< -1.8
Detection limit	-6.5	-5.5	-6.0	-5.0
pH range	3–6	4–6		
Stability, 0.01 M Pb (mV/min), $t = 25$ min	< -0.01	-0.02	0.03	-0.04
Drift <sup>a</sup> (mV/day)			-1.5	-1.6

<sup>a</sup> Drift of measured potential for 0.01 M Pb(NO<sub>3</sub>)<sub>2</sub> solutions.

of steady potential for a 10<sup>-2</sup> M solution, when Pb(II) concentration was rapidly increased from 10<sup>-3</sup> to 10<sup>-2</sup> M and similarly for a change of Pb(II) concentration from 10<sup>-4</sup> to 10<sup>-3</sup> M. The results obtained for the electrode based on ligand **1** are presented in Fig. 4. In both cases (for **1** and **2**) the response time was less than 10 s.

The pH dependence of the electrode response was examined using 10<sup>-4</sup>, 10<sup>-3</sup> and 10<sup>-2</sup> M Pb(NO<sub>3</sub>)<sub>2</sub> solutions adjusted with nitric acid and ammonia. An electrode based on ionophore **1** showed an EMF plateau between pH 3 and 6 (Fig. 5), but based on **2** in a smaller pH range (4–6). The decrease of the potential in alkaline media can be explained by the formation of lead hydroxide in the solution, and at lower pH by the ionophore protonation.

#### 4. Conclusions

The present results regarding the selectivity, electrode response, linear range, pH dependence and response time suggest that ligands tested can be used as ionophores for lead selective electrodes. The best results were obtained with membranes containing the tetrathioamide functionalized calix[4]arene (ionophore **1**), KTpCIPB and *o*-NPOE as a plasticizer. For this membrane composition the slope is close to the theoretical for divalent ions in a wide range of lead(II) concentrations. The selectivity towards copper, zinc and cadmium ions is greatly improved as compared with commercial solid-state lead selective electrodes [28]. Moreover, for alkali metal ions the selectivity is

higher than that of other lead selective liquid membrane electrodes [11–19].

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