



## Azothia- and Azoxythiacrown Ethers as Ion Carriers. Part I. Cationic Response of Membrane Electrodes

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### Abstract

13-Membered azothia- and azoxythiacrown ethers have been applied as ion carriers in ion-selective membrane electrodes. Their sensitivity and selectivity were studied towards alkali, alkaline earth, transition and heavy metal cations. It was found that membranes doped with the azoxythiacrown ether (**A**) show higher affinity towards  $\text{Pb}^{2+}$  than  $\text{Cu}^{2+}$  ( $\log K_{\text{Cu,Pb}}^{\text{pot}} = 1.7$ ), whereas membranes with the azothiacrown ether (**B**) are more selective towards  $\text{Cu}^{2+}$  than  $\text{Pb}^{2+}$  ( $\log K_{\text{Cu,Pb}}^{\text{pot}} = -2.4$ ). The discrimination of alkali and alkaline earth cations was found to be greater for **B** than for **A**. Electrodes with both ionophores suffered from strong interference by  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ . The relation between the carrier structure and electrode properties has been discussed.

### Introduction

Antibiotics, crown ethers and some podands are widely used as ion-carriers in ion-selective membrane electrodes [1]. Azo- and azoxycrown ethers in membrane electrodes show high sodium or potassium selectivity dependent on the size of the macrocyclic unit. 13-Membered azoxycrown ethers **I** cause sodium over potassium selectivity of the respective membranes. Even more selective are azocrown carriers **II** [2–4]. These crown ethers form complexes with metal cations engaging lone electron pairs of the oxygen atoms of oxyethylene units and one nitrogen atom of the azo group in the case of azocrowns, and the nitrogen or oxygen atom of the azoxy group in the case of azoxycrown ethers. For a qualitative correlation of complex structures and membrane electrode selectivity cf., [5]. However, both classes of these compounds showed higher silver selectivity [2–4]. Replacing oxygen for a sulfur atom in the macroring of crown ethers increases their susceptibility towards heavy metal cations with a simultaneous decrease of affinity to form complexes with “hard” cations [6]. Recently we published the synthesis of thia analogs of compounds **I** and **II**, namely the thiaazo- and thiaazoxycrown ethers [7]. Preliminary studies evaluated their high sensitivity towards silver cations. The aim of this paper is detailed evaluation of the properties of azoxythiacrown **A** and azothiacrown ether **B** as cation carriers in membrane electrodes. Structures of the azo- and

azoxycrown ethers and their thia analogs are presented in Figure 1.

### Experimental

High molecular weight poly(vinyl chloride) (PVC), potassium tetrakis(4-chlorophenyl) borate (KTPCIPB), 2-nitrophenyl octyl ether (NPOE) and tetrahydrofuran (THF, distilled prior to use) were purchased from Fluka (Ronkonkoma, NY). All aqueous solutions were prepared with salts of p.a. purity using distilled-deionized water.

Compounds **A** and **B** were obtained as described earlier [7].

#### Membrane preparation

In general, the polymeric membranes evaluated for ion response contained 1 wt% ionophore (**A** or **B**), 30–33 wt% PVC, 66–67 wt% *o*-NPOE and various amounts of lipophilic anionic additives (for details see the Results and Discussion section). The membrane components, total 200 mg, were dissolved in 2 mL of freshly distilled THF. This solution was placed in a glass ring (24 mm i.d.) over a glass plate. After evaporation of the solvent overnight, the resulting membrane was peeled from the glass mould and discs of 7 mm i.d. were cut out. Membrane discs were mounted in conventional ISE electrode bodies (Type IS 561; Philips, Eindhoven, The Netherlands) for electromotive force (EMF) measurements.

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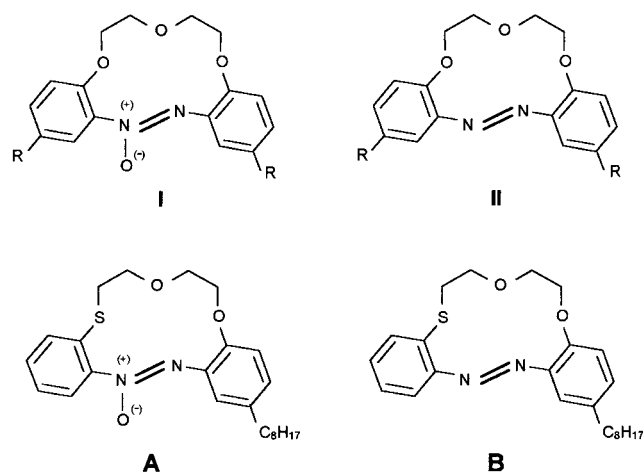


Figure 1. Structures of azoxy- and azocrown ethers (**I** and **II**) and their thia analogs (**A** and **B**).

### Potentiometric measurements

All measurements were performed at ambient temperature ( $22 \pm 1$  °C) using a galvanic cell of the following type:

Ag/AgCl<sub>(s)</sub> / 3 M KCl / bridge electrolyte / sample // ion-selective membrane / internal electrolyte / AgCl<sub>(s)</sub>/Ag.

The bridge electrolyte consisted of 1 M lithium acetate. Unless otherwise stated, 0.01 M NaCl solution was used as the internal filling solution for the assembled electrodes. Electrodes were conditioned in 0.01 M NaNO<sub>3</sub> solution overnight before measurement.

The EMF values were measured using a custom made 16-channel electrode monitor. Details of this equipment were described previously [8].

### Selectivity coefficients

Potentiometric selectivity coefficients were determined by the separate solution method (SSM), according to a procedure established by Bakker [9]. Selectivity coefficients were calculated according to equation 1, by using the EMF values for the highest measured ion activities that belongs to the linear response range for a given ion (unless otherwise indicated).

$$\log K_{1,J}^{\text{pot}} = \frac{z_I F (E_J - E_I)}{2.303 RT} + \log \left( \frac{a_I}{a_J^{z_I/z_J}} \right) \quad (1)$$

Activity coefficients were calculated according to Debye-Hückel approximation [10].

## Results and discussion

It is well known that a carrier incorporated into a plasticized polymeric membrane defines the selectivity of ion-selective electrodes. The selectivity coefficients reflect both the selectivity of the carrier and the ion-exchange process that occurs between the uncomplexed primary and interfering

ions in the sample and organic phase of the polymeric membrane [11]. However, for a polymeric matrix containing the same plasticizer, the differences in the selectivity pattern observed for different carriers are related to their ability to form complexes with cations.

Figure 1 shows the structures of the examined 13-membered thiacycrown ethers. In compound **A** the macrocycle contains the —N(O)=N— group, while compound **B** contains the —N=N— group. The carrier properties of compounds **A** and **B** have been tested using ion-selective electrodes with plasticized PVC membranes (PVC/*o*-NPOE = 1 : 2).

The selectivity is one of the most important characteristics of a sensor. Very recently, a new procedure of selectivity coefficient determination was published by Bakker [9]. This procedure involves conditioning the electrode membrane in discriminated ion solutions before measurements and ensures response even for significantly discriminated ions and allows determination of unbiased selectivity coefficients. This method was chosen for the evaluation of the selectivity pattern in our studies.

In a preliminary experiment the sequence of cations (starting from the most discriminated one) for more detailed selectivity studies have been investigated. The solutions of nitrate salts of Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cs<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup> ions were examined. It was found that Li<sup>+</sup>, Ca<sup>2+</sup> and Na<sup>+</sup> ions belong to the group of ions most discriminated by the studied crown ethers. 0.01 M solutions of sodium salts have been chosen to prepare the conditioning and inner filling solutions. The examined electrodes responded toward ions in the 10<sup>-4</sup>–10<sup>-2</sup> M concentration range with slopes of 24–28 mV/dec for divalent and 48–51 mV/dec for monovalent cations, except for Li<sup>+</sup> (33 mV/dec at 10<sup>-3</sup>–10<sup>-1</sup> M range).

It has been shown that for membranes based on neutral carriers the addition of anionic additives is beneficial in many respects, including the selectivity-modifying influence due to differences in the stoichiometry of the complexes formed by the ionophore with primary and interfering cations and their charge [12, 13]. It was found that no significant changes in selectivity values were observed for membranes containing carrier **A** or **B** and 15–70 mol% or 17–90 mol% (relative to ionophore) of borates, respectively. At higher concentrations ( $\geq 120$  mol% for **A** and 180 mol% for **B**) of anionic additives, the membranes behave as a pure cation-exchange system with the preference for more lipophilic over hydrophilic cations ([11]; see also column 1 in Figure 2). This implies that for ionophore **A** the predominant Pb<sup>2+</sup>-ionophore complex stoichiometry can be assessed as 1 : 2 while for ionophore **B** complexes Cu<sup>2+</sup> : ionophore of 1 : 1 stoichiometry may be also considered. For further selectivity studies membranes containing 1 wt% of ionophore and 20 or 40 mol% (relative to ionophore **A** or **B**, respectively) of lipophilic anionic additives (KTpCIPB) were prepared. Values of the selectivity coefficients determined for the membrane of chosen compositions roughly reflect the complexation selectivity of the ion carriers because in these cases a sufficient excess of ligand molecules is available in

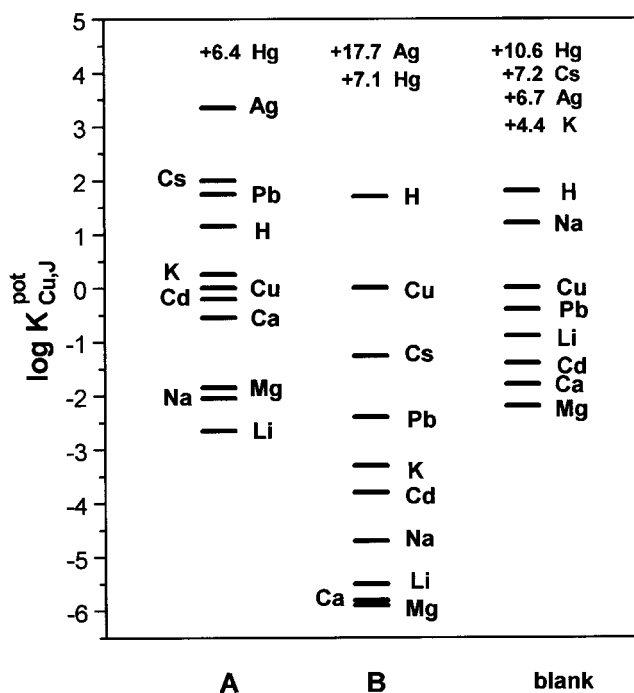


Figure 2. Selectivity coefficients,  $\log K_{I,J}^{\text{pot}}$ , of plasticized poly(vinyl chloride) membranes containing as a carrier azoxythiacrown ether **A** or azothiacrown ether **B** and/or ion-exchanger KTpCIPB; PVC/*o*-NPOE (1 : 2) membranes with: 1 wt% **A** and 20 mol% KTpCIPB (column 1); 1 wt% **B** and 40 mol% KTpCIPB (column 2); 1 wt% KTpCIPB (column 3). Membranes were conditioned in a discriminated ion solution (0.01 M  $\text{NaNO}_3$ ) before measurements.

the membrane for divalent as well as for the monovalent ions independently of the stoichiometry of the complexes formed.

The potentiometric ion selectivities (given as  $\log K_{I,J}^{\text{pot}}$ , where I stands for  $\text{Pb}^{2+}$  or  $\text{Cu}^{2+}$  for ionophore **A** or **B**, respectively, and J stands for an interfering ion) are presented in columns 1 and 2 in Figure 2. Column 3 in Figure 2 represents the selectivity for electrodes with PVC/*o*-NPOE-based membranes without ionophore and containing the cation exchanger KTpCIPB (blank membrane).

A comparison of the selectivities of membranes based on azoxy- (**A**) and azo- (**B**) derivatives with those based on a classical cation exchanger indicates that both crown ethers induce selectivities that are dramatically different from the selectivity based on the hydrophobicity of cations (columns 1 and 2 as compared with 3 in Figure 2). Moreover, it can be seen from Figure 2 that the incorporation of an azoxy group instead of an azo group leads to dramatic changes in the complexation properties of the molecule. Membranes doped with the azoxythiacrown ether (**A**) show higher affinity towards  $\text{Pb}^{2+}$  than  $\text{Cu}^{2+}$  ( $\log K_{\text{Cu,Pb}}^{\text{pot}} = 1.7$ ), whereas membranes with the azothiacrown ether (**B**) are more selective towards  $\text{Cu}^{2+}$  than  $\text{Pb}^{2+}$  ( $\log K_{\text{Cu,Pb}}^{\text{pot}} = -2.4$ ). Both ionophores discriminate alkali and alkaline earth cations but this discrimination is greater for **B** than for **A**. The wider range of selectivity coefficient values for membranes based on the azo- derivative than for the azoxy- compound may suggest greater differences in the stability constants for complexes with **B** than with **A**.

Electrodes reported in the literature as  $\text{Pb}^{2+}$ - or  $\text{Cu}^{2+}$ -selective suffer very often from strong interference by  $\text{Ag}^+$  or  $\text{Hg}^{2+}$  [1, 14]. The evaluation of crown ethers **A** and **B** has been extended for these ions in independent experiments, using fresh membranes. Sets of calibrations for  $\text{Na}^+$ ,  $\text{I}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Na}^+$ ,  $\text{I}^{2+}$ ,  $\text{Ag}^+$  were carried out for **A** ( $\text{I}^{2+} = \text{Pb}^{2+}$ ) and **B** ( $\text{I}^{2+} = \text{Cu}^{2+}$ ). The results obtained revealed that  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  ions are extremely preferred ions by both ionophores. However, selectivity coefficients determined for the azoxy- derivative **A** with  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  are lower by several orders of magnitude than for the azo- derivative **B**. Moreover, the azothiacrown ether **B** shows stronger affinity for silver than for mercury ion, while a significant preference for mercury over silver ion can be noticed for **A**.

The observed changes in selectivity pattern, induced by ligands that differ only in the presence of an azo- or azoxy-group in the ring, can be explained by Pearson's Hard-Soft Acid-Base theory [15]. According to this principle, it could be expected that replacing a hard oxygen donor atom by a soft sulfur donor atom in azo or azoxycrown ethers might lead to increased selectivity towards softer cations. Indeed, it has been already reported [2] that 13-membered azocrown ethers exhibit sodium selectivity. Selectivity coefficients ( $\log K_{\text{Na},J}^{\text{pot}}$ ) for other alkali, alkaline earth,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions were found to be lower than  $-2$ . Their azoxy-derivatives behaved similarly, however, a pronounced increase of selectivity coefficient values was observed for  $\text{Cs}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  ions. It should be noticed that these compounds showed similar, high  $\text{Ag}^+$  selectivity ( $\log K_{\text{Na,Ag}}^{\text{pot}} \sim +3$ ), although the softness of the azo- group is greater than that of the azoxy unit. In addition, the azoxy unit could bind a cation *via* the nitrogen or oxygen atom [5, 16].

In our case the inverted selectivity pattern for  $\text{Cu}^{2+}$  vs.  $\text{Pb}^{2+}$  ion ( $\text{Cu}^{2+}$  is a softer acid than  $\text{Pb}^{2+}$ ) and, to some extent for  $\text{Ag}^+$  vs.  $\text{Hg}^{2+}$ , was observed depending on whether the harder  $-\text{N}(\text{O})=\text{N}-$  (**A**) or softer  $-\text{N}=\text{N}-$  (**B**) electron donor is present in the macrocycle.

As expected, conditioning of membrane electrodes in solutions containing highly preferred ions can change the electrode performance. The temporal changes in potentiometric response of electrodes toward the examined cations are presented in Figures 3a-c and 4a-c for ionophores **A** and **B**, respectively. As can be seen from the calibration curves obtained during the very first contact with the preferred ion (curves 1 in Figures 3 and 4), all electrodes exhibited the intermediate super-Nernstian response that can be explained as due to a discrepancy between ion activities in the bulk and at the phase boundary [9]. Electrodes start to show Nernstian response toward a given cation at relatively high concentrations. The magnitude of the EMF change (jump) at the depletion zone and the concentration when an electrode starts to respond in a Nernstian fashion depends on the cation and ionophore used.

When electrodes were left overnight in the solution of highest concentration of measured ion used for their calibration, substantial long-term drifts were observed for all electrodes with membranes containing azothiacrown ether **B** and membranes with azoxythiacrown ether **A** conditioned in

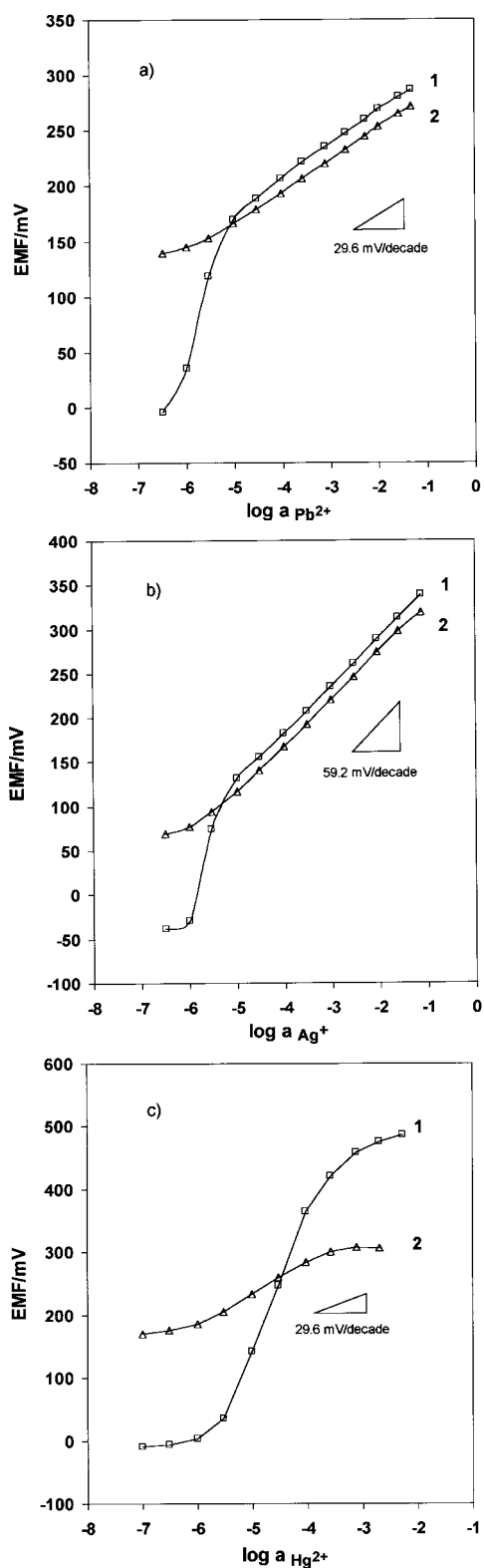


Figure 3. Potentiometric response of ion-selective electrodes based on azoxythiacrown ether A as neutral carrier towards: (a)  $\text{Pb}^{2+}$  ion, (b)  $\text{Ag}^{+}$  ion and (c)  $\text{Hg}^{2+}$  ion. Curves 1 – the very first contact with a given ion, curves 2 – after the conditioning of electrodes in a given ion solution.

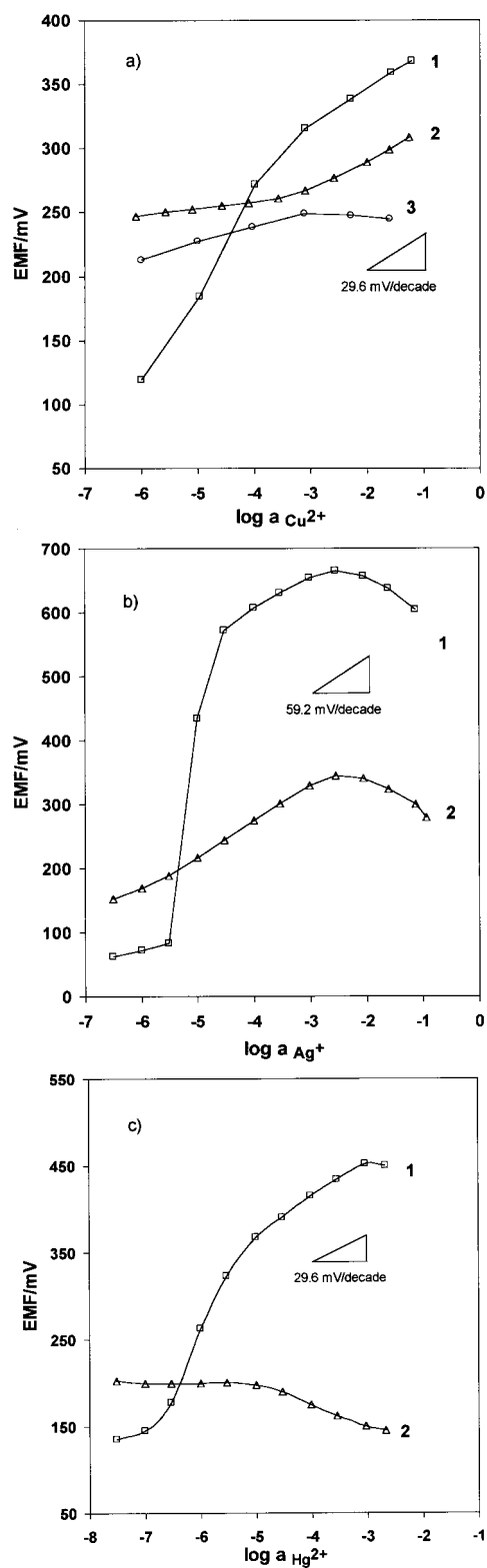


Figure 4. Potentiometric response of ion-selective electrodes based on azoxythiacrown ether B as neutral carrier towards: (a)  $\text{Cu}^{2+}$  ion, (b)  $\text{Ag}^{+}$  ion and (c)  $\text{Hg}^{2+}$  ion. Curves 1 – the very first contact with a given ion, curves 2 – after the conditioning of electrodes in a given ion solution, curve 3 in (a) – after 5 days contact with 0.1 M  $\text{Cu}(\text{NO}_3)_2$  solution.

Hg(NO<sub>3</sub>)<sub>2</sub> solution. Such drifts originate from primary ions diffusing across the membrane to the membrane-inner electrolyte interface, where they displace the initially contained discriminated ion from the membrane [9]. The results are summarized in Table 1.

Table 1. The influence of the equilibration in preferred ion solutions on the performance of electrodes with membranes based on azoxythiacrown ether (A) or azothiacycrown ether (B)

Ionophore	Ion	First contact with a highly preferred ion		After the equilibration with a highly preferred ion	
		Beginning of linear response (log a)	Slope (mV/dec)	Linear range (log a)	Slope (mV/dec)
A	Pb <sup>2+</sup>	> -4.5	+29.2	> -5.5	+28.6
A	Ag <sup>+</sup>	> -5	+56.8	-5.5 ÷ -1.5	+56.4
A	Hg <sup>2+</sup>			-5.5 ÷ -3.5	+49.1
B	Cu <sup>2+</sup>	> -3	+28.0	> -3.0*	+25.6
B	Ag <sup>+</sup>	> -4.5	+57.2	-5.5 ÷ -3.0	+56.8
B	Hg <sup>2+</sup>	> -4.5	+46.5	No cationic response	

\* After 24 hours of continuous contact with Cu(NO<sub>3</sub>)<sub>2</sub> solution; no response after several days in Cu(NO<sub>3</sub>)<sub>2</sub> solution.

As shown in Figures 3 and 4, electrodes exhibited activity-independent potentials for low concentrations of the nitrate salts of examined cations after 24 hours of membrane equilibration with the preferred ion solution (curves 2). The release of the preferred ion from the membrane is responsible for the increase of the low detection limit of electrodes [17].

It should be pointed out that the values of selectivity coefficients, determined according to Bakker's procedure and measured after equilibration of membranes containing azoxythiacrown ether A with Pb<sup>2+</sup> or Ag<sup>+</sup> solutions, have not been changed significantly. These electrodes still exhibited typical cationic response in a wide range of ion concentration (see Figure 3 a, b). Moreover, the response time was found to be shorter than 20 s.

In other cases (Ag-B, Hg-B, Cu-B and Hg-A), electrodes have not recognized strongly discriminated cations after the conditioning of membranes in the highly preferred ion solutions. The measured values of log K<sub>Cu,Pb</sub><sup>Pot</sup> reflected rather a low detection limit of the electrode than true selectivity of the membrane. Electrodes with membranes containing ionophore A or B and soaked in Hg<sup>2+</sup> or Ag<sup>+</sup> solutions, respectively, showed cationic response only in a low concentration range (see Figures 3c and 4b). For high concentrations of the examined cations anionic response due to a coextraction process of the primary cations and interfering anions from the sample to the ion-selective membrane phase was recorded (so-called Donnan failure) [11, 18]. Such behavior can be observed for very strong cation-carrier complexes. The further investigation of the influence of various anions on the performance of studied electrodes is presented in reference [19].

Cationic response, observed initially for electrodes based on ionophore B, has almost completely disappeared after several days exposure of the electrodes to Cu(NO<sub>3</sub>)<sub>2</sub> solution (curve 3 in Figure 4a). This might be a result of e.g.,

kinetic limitations but anion interference might also play a role. Electrodes based on ionophore B after 24 hours contact with Hg(NO<sub>3</sub>)<sub>2</sub> solution showed anionic response towards the nitrate ion.

Based on the results presented above it can be concluded that azothiacycrown ether (B) forms much stronger complexes with soft transition metals than azoxythiacrown ether (A). Although for azothiacycrown ether (B) the highest values of selectivity coefficients were obtained for Ag<sup>+</sup>, it seems that ionophore B binds to Cu<sup>2+</sup> and Hg<sup>2+</sup> ion too tightly to exhibit reversible response towards these cations, or the electrode performance is governed by kinetic limitations. Their response became anionic rather than cationic, particularly when nitrates of previously discriminated cations were tested.

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## References

- P. Bühlmann, E. Pretsch and E. Bakker: *Chem. Rev.* **98**, 1593 (1998).
- E. Luboch, J. F. Biernat, E. Muszalska and R. Bilewicz: *Supramol. Chem.* **5**, 201 (1995).
- J. F. Biernat, E. Luboch, A. Skwierawska, R. Bilewicz and E. Muszalska: *Biocyb. Biomed. Eng.* **16**, 125 (1996).
- E. Luboch, J. F. Biernat, Yu. A. Simonov, A. A. Dvorkin and V. K. Bel'skii: *Tetrahedron* **54**, 4977 (1998).
- E. Luboch, J. F. Biernat, Yu. A. Simonov, V. Ch. Kravtsov and V. K. Bel'skii: *Supramol. Chem.* **11**, 109 (1999).
- J. S. Bradshaw, R. M. Izatt, A. V. Bordunov, C. Y. Zhu and J. K. Hathaway: In: J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle (eds), *Comprehensive Supramolecular Chemistry*, Pergamon, United Kingdom 1996, Vol. 1, p. 71; H. K. Frensdorff: *J. Am. Chem. Soc.* **93**, 600 (1971).
- J. Szczygelska-Tao, J. F. Biernat, V. Ch. Kravtsov and Yu. A. Simonov: *Tetrahedron* **55**, 8433 (1999).
- Z. Brzózka: *Pomiary, Automatyka, Kontrola (Warsaw)* **9**, 197 (1988); *Chem. Abstr.* **112**, 15643q.
- E. Bakker: *Anal. Chem.* **69**, 1061 (1997).
- P. C. Meier: *Anal. Chim. Acta* **136**, 363 (1982).
- E. Bakker, P. Bühlmann and E. Pretsch: *Chem. Rev.* **97**, 3083 (1997).
- P. C. Meier, W. E. Morf, M. Laubli and W. Simon: *Anal. Chim. Acta* **156**, 1 (1984).
- R. Eugster, P. M. Gehrig, W. E. Morf, U. E. Spichiger and W. Simon: *Anal. Chem.* **63**, 2285 (1991).
- Y. Umezawa: *CRC Handbook of Ion-Selective Electrodes: Selectivity Coefficients*; CRC Press: Boca Raton, Ann Arbor, Boston, (1990).
- R. G. Pearson: *J. Am. Chem. Soc.* **85**, 3533 (1963).
- E. Luboch, J. F. Biernat and V. Kessler: *XXIV-th International Symposium on Macrocyclic Compounds*, Barcelona 1999, Proceedings, PS1-42.
- P. Bühlmann, S. Yajima, K. Tohda, K. Umezawa, S. Nishizawa and Y. Umezawa: *Electroanalysis* **7**, 811 (1995).
- W. E. Morf, D. Ammann and W. Simon: *Chimia* **28**, 65 (1974).
- K. Wyglądacz, E. Malinowska, J. Szczygelska-Tao and J. F. Biernat: *J. Incl. Phenom.* **39**, 309-314.

