

Studies on 16-Membered Azothia- and Azoxythiacrown Ethers as Ion Carriers in Ion Selective Membranes

JOLANTA SZCZYGELSKA-TAO,¹ JAN F. BIERNAT,^{1*} ŁUKASZ GÓRSKI² and ELŻBIETA MALINOWSKA²

¹Department of Chemical Technology, Technical University of Gdańsk, 80-952 Gdańsk, Poland; ²Department of Analytical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

(Received: 15 July 2003; in final form: 16 November 2003)

Key words: azothiacrown, azoxythiacrown, cation carrier, complex formation constants, membrane electrodes, segmented sandwich membranes, selectivity

Abstract

16-Membered azothia- and azoxythiacrown ethers have been studied as ion carriers in ion-selective membranes. Their selectivities towards alkali, alkaline earth, transition and heavy metal cations were evaluated. The complex formation constants for these compounds with chosen cations have been determined using segmented sandwich membranes method.

Introduction

Neutral carrier type ion-selective electrodes have been developed mainly with respect to alkali and alkaline earth metal cations, however, interest in recognition of heavy or transition metal ions is still not as large as expected. It was shown that 13-membered azo- and azoxycrown ethers in membrane electrodes show high sodium selectivity, whereas 16-membered compounds are highly potassium selective [1, 2]. These crown ethers form complexes with metal cations engaging besides lone electron pairs of oxygen atoms of oxyethylene units and one nitrogen atom of the azo group (in the case of azocrown), or nitrogen or oxygen atom of the azoxy group in the case of azoxy-crown ethers. However, both classes of these compounds show prevailing silver selectivity [1–3]. Replacing oxygen by sulfur atoms in a macroring of crown ethers increases their receptivity towards heavy metal cations and decreases their affinity to ‘hard’ cations [4].

Recently, we published the results on investigations of 13-membered azo- and azoxythiacrown ethers in ion selective membrane electrodes towards alkali and alkaline earth, hard and transition metal cations [5]. It should be noticed that these compounds showed high Ag^+ selectivity. The inverted selectivity pattern for Cu^{2+} versus Pb^{2+} ion and, to some extent, for Ag^+ versus Hg^{2+} , was observed depending whether a harder $-\text{N}(\text{O})=\text{N}-$ or a softer $-\text{N}=\text{N}-$ electron donor is present in the macrocycle. It was also shown [6] that membranes based on silver-azothiacrown ether and copper-azoxy-

thiacrown ether complexes can be considered as potentially useful for anion sensing.

Continuing investigations into the binding of hard and soft transition metal ions by compounds containing sulfur atoms, this paper describes the research undertaken on the use of 16-membered sulfur containing crown ethers. The details of synthesis of 16-membered azo-**A** and azoxythiaanalogs **B** were published earlier [7].

The aim of this paper is the evaluation of properties of azothiacrown **A** and azoxythiacrown ether **B** as cation carriers in ion-selective membranes and determination of complex formation constants in the polymeric membrane phase. Structures of azo- and azoxycrown ethers and their thiaanalogs are presented in Figure 1.

Experimental

High molecular weight polyvinyl chloride (PVC), potassium tetrakis[3,4-bis-(trifluoromethyl)-phenyl] borate (KTFPB), 2-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl)sebacate (DOS) 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.

Selectivity measurements

In general, the polymeric membranes evaluated for ion response contained 1 wt% ionophore (**A** or **B**), 30–

* Author for correspondence. E-mail: biernat@chem.pg.gda.pl

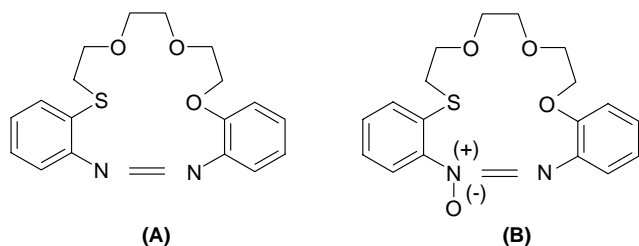


Figure 1. Structures of azo- and azoxythiacrown ethers (compounds **A** and **B**).

33 wt% PVC, 66–67 wt% *o*-NPOE or DOS and 30 mol% KTFPB (relative to the ionophore). 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 mold 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.

All measurements were performed with the use of the above membranes at ambient temperature (22 ± 1 °C) using a galvanic cell of the following type:

Ag/AgCl_(s) | 3M KCl | 1M CH₃COOLi || sample | ion-selective membrane | internal electrolyte | AgCl_(s) | Ag.

Unless otherwise stated, the 0.01 M NaCl solution was used as the internal filling solution for assembled electrodes.

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

Potentiometric selectivity coefficients were determined by the separate solution method (SSM) [9]. Before measurements, electrodes were conditioned overnight in a 0.01 M NaCl solution. Initially, the selectivity sequence was examined on the basis of preliminary measurements in 0.01 M solutions of tested cations. Then, in order to obtain unbiased values of selectivity coefficients, the calibration of the electrodes was performed for various cations, starting from most discriminated ones. Selectivity coefficients were calculated according to a procedure described by Bakker et al. [9]:

$$\log K_{I,J}^{\text{pot}} = \frac{(E_J^0 - E_I^0)z_I F}{2.303 \cdot RT}, \quad (1)$$

where E_I^0 and E_J^0 are the EMF values obtained by extrapolating the individual potentials to 1 M activity for the ions *I* and *J*. *R*, *T* and *F* are the gas constant, the absolute temperature, and the Faraday constant, respectively; z_I – charge of the ion *I*. Activity coefficients were calculated according to Debye–Hückel approximation [10].

Complex formation constants measurements

Experiments were carried out according to the sandwich membrane method described in [11]. The PVC/plastizer (1:2) membranes containing 20 mmol/kg of ionophore and 5 mmol/kg of KTFPB (total membrane mass 140 mg) were cast. Additionally, membranes without ionophore, but with other constituents the same, were prepared. A 7 mm i.d. discs were cut from both types of membranes and these disks were conditioned overnight in 0.01 M solution of the appropriate salt (NaCl, CaCl₂, KCl, CuCl₂, Pb(NO₃)₂, Cd(NO₃)₂ or AgNO₃).

The sandwich membranes were made, after drying of individual membranes, by attaching the membrane with ionophore to the membrane without ionophore. Such a segmented membrane was then mounted into a Philips electrode body (membrane with ionophore faced the sample solution) and immediately immersed into an appropriate salt solution (identical to the conditioning of the membrane). The potential was recorded as the mean of the last minute of a 10 min measurement period in the test solution. In a separate measurement, the potential of an electrode with the membrane containing no ionophore was measured in the same solution.

The formation constant was calculated according to Equation (2) [11, 12]:

$$\log \beta_{ML} = \frac{E_M \cdot z_I F}{2.303 \cdot RT} - n \log \left(L_T - \frac{n}{z_I} R_T \right), \quad (2)$$

where *n* is the complex stoichiometry, L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of the lipophilic ionic site additives, and *R*, *T* and *F* are the gas constant, the absolute temperature, and the Faraday constant, z_I – charge of the tested ion. The membrane potential E_M is determined by subtracting the cell potential for the membrane without ionophore from that for the sandwich membrane [11, 12].

Results and discussion

Complex stability constants

It is well established that potentiometric selectivity of polymeric membranes is related to the differences in the lipophilicity of the ions, the membrane composition and the stability constants of ion-ionophore complexes [13]. As the last factor is typically the most important one, several methods suitable for the determination of stability constants in the membrane phase were proposed. Among them, the sandwich membrane method seems to be the most appropriate due to its simplicity and reliability. Using this method, complex formation constants for various cations and both thiacrown ethers **A** and **B** were determined in this work. The obtained results are presented in Table 1.

Table 1. Complex formation constants, $\log \beta_{ML}$, of azothiacrown ether **A** and azoxythiacrown ether **B** with various cations, measured in DOS or *o*-NPOE plasticized poly(vinyl chloride) membranes

PI Cation	$\log \beta_{ML}^a$			
	<i>o</i> -NPOE		DOS	
	A	B	A	B
Ag ⁺	11.6	9.2	11.3	8.6
Na ⁺	5.2	3.9	<2.5	<2.5
K ⁺	5.4	4.0	3.2	<3.0
Ca ²⁺	5.4	4.0	<2.5	<3.0
Cd ²⁺	6.1	4.9	3.2	<2.5
Cu ²⁺	10.8	5.7	4.9	3.4
Pb ²⁺	10.4	7.2	5.7	3.9

It was found that both ionophores (**A** and **B**) form the strongest complexes with Ag⁺ ion, independently whether measurements were carried for membranes plasticized with *o*-NPOE or DOS. The complex stability constants, $\log \beta_{ML}$, measured for other cations, are significantly lower, compared to silver. While the values of $\log \beta_{ML}$ for Pb²⁺ and Cu²⁺ are similar for ionophore **A**, in the case of ionophore **B** stronger interaction with Pb²⁺ than Cu²⁺ can be seen. However, the relative changes in $\log \beta_{PbL}$ and $\log \beta_{CuL}$ for 16-membered azo- (**A**) and azoxythia- (**B**) crown ethers are not sufficient to reverse the potentiometric selectivity (see next section), as was observed when 13-membered azo- and azoxythiacrown ethers were used as ionophores. Both these 13-membered crowns discriminate alkali and alkaline metal cations and also show high affinity towards Ag⁺ and Hg²⁺. Membranes doped with azocrown ether are more selective towards Cu²⁺ than Pb²⁺ ($\log K^{pot}_{Cu, Pb} = -2.4$), whereas azoxythiacrown ether shows higher selectivity towards Pb²⁺ than Cu²⁺ [5].

The complex stability constants determined for azothiacrown ether **A** are higher than analogous constants for azoxythiacrown ether **B** for examined cations. This indicates stronger complexing properties of compound **A**, which may originate from the nature of this compound. The presence of a sulfur atom in the macroring increases complexing properties of thiacycrown ethers towards heavy metal cations, but the presence of the 'hard' oxygen atom of the azoxy group of thiacycrown ether causes lowers the effects of complexation.

The formation constants are larger in NPOE than in DOS containing membranes (see Table 1). The main reasons affecting the binding constants seem to be the dielectric constants as well as the binding properties of the plasticizers. The dielectric constant of NPOE, with about $\epsilon = 24$ [14], is larger than that of DOS [15] ($\epsilon \approx 4$). The DOS plasticizer has two ester groups that are in principle capable of binding to cation species. In effect, it will solvate the extracted cations in ionophore – free membranes or membrane segments more strongly than NPOE – based membranes, which leads to smaller binding constants. A similar influence of plasticizer was reported earlier by Bakker et al. [16].

Potentiometric response to cations and membrane selectivity

Taking into account lipophilicity of Ag⁺ ion and its relatively strong complexation by examined carriers (compared to other cations), the preparation of electrodes highly selective towards silver ion can be envisioned. Thus, a series of electrodes with PVC membranes plasticized with DOS or *o*-NPOE and doped with ionophore **A** or **B** was prepared. In preliminary experiments the sequence of cations for more detailed selectivity studies have been investigated. The solutions of nitrate salts of Cu²⁺, Pb²⁺, Cd²⁺, Ca²⁺, Mg²⁺, TMA⁺, K⁺, Na⁺ and Li⁺ ions were examined. After that, the calibrations of electrodes were performed starting from most discriminated cations in order to obtain unbiased selectivity coefficients (for values of selectivity coefficients, $\log K^{pot}_{Ag, M}$, see Table 2). As was expected, the membranes plasticized with both DOS and *o*-NPOE and doped with azothiacrown ether **A** or azoxythiacompound **B** show the highest selectivity for silver over all other cations. The strongest interference was noted from highly lipophilic cations such as TMA⁺ and K⁺. However, even in these cases the selectivity coefficients values, $\log K^{pot}_{Ag, M}$, are -5 . For other investigated cations, the selectivity coefficients, $\log K^{pot}_{Ag, M}$, were typically -8 .

The calibration curves toward Ag⁺ for electrodes based on DOS and *o*-NPOE as plasticizers and doped with azo-**A** or azoxythiaether **B**, obtained during the very first contact with silver ions, exhibited the near-Nernstian slope at the range of concentrations 10^{-5} – 10^{-3} M. At low concentrations of silver ion, a significantly super-Nernstian response was observed, which can be ascribed to a discrepancy between silver ion activities in the bulk of the membrane and at the membrane-sample solution phase boundary [17]. To overcome this problem, electrodes conditioned overnight before the measurement in 2×10^{-3} M AgNO₃ solution were prepared. As expected, the initial super-Nernstian EMF change at low Ag⁺ concentrations was replaced with near-Nernstian response over wide linear silver concentration range, with lower detection limit, LDL = 10^{-7} and upper detection limit, UDL = 10^{-3} .

Table 2. Selectivity coefficients, $\log K_{Ag,M}^{pot}$, of poly(vinyl chloride) membranes plasticized with *o*-NPOE or DOS, containing azothiacrown ether **A** or azoxythiacrown ether **B** as ionophores

PI Cation	$\log K_{Ag,M}^{pot}$			
	<i>o</i> -NPOE		DOS	
	A	B	A	B
Na ⁺	-9.3	-8.2	-9.6	-6.0
TMA ⁺	-7.3	-4.9	-8.5	-4.6
Li ⁺	-11.3	-10.2	-10.3	-6.4
K ⁺	-7.6	-6.6	-8.3	-5.2
Mg ²⁺	-12.0	-10.2	-12.4	-8.7
Ca ²⁺	-11.8	-10.2	-12.3	-8.5
Cd ²⁺	-11.4	-10.0	-12.2	-8.8
Cu ²⁺	-11.2	-9.7	-11.7	-7.1
Pb ²⁺	-9.4	-8.4	-10.3	-7.3

The Ag⁺ calibration curves for these electrodes are shown in Figure 2. It should be pointed out that such low values of LDL can be obtained even at high background concentration of interfering ions owing to the high silver selectivity observed for ionophores **A** and **B**. For high concentrations of silver cation ($\log a > -3$), cationic response is replaced with anionic due to a coextraction process of primary cations and interfering anions from the sample to the ion-selective membrane phase. Such behavior, observed typically for very strong cation-carrier complexes, was already described for 13-membered azo- and azoxycrown ethers. Electrodes doped with the last compounds do not differentiate strongly discriminated ions. Electrode, doped with azocrown ether as an ionophore and soaked

in Ag⁺ solution exhibit cationic response only in low concentration of the examined cations; for high concentrations cationic response is replaced with the anionic one. Electrodes doped with 13-membered azoxythiacrown ether soaked in solution of Hg²⁺ [6] behave in a similar manner.

Conclusions

The properties of 16-membered azothia- and azoxythiacrown ethers have been characterized potentiometrically in polymeric ion-selective membranes. It was shown, using the sandwich membrane method, that both compounds form very strong complexes with silver ions

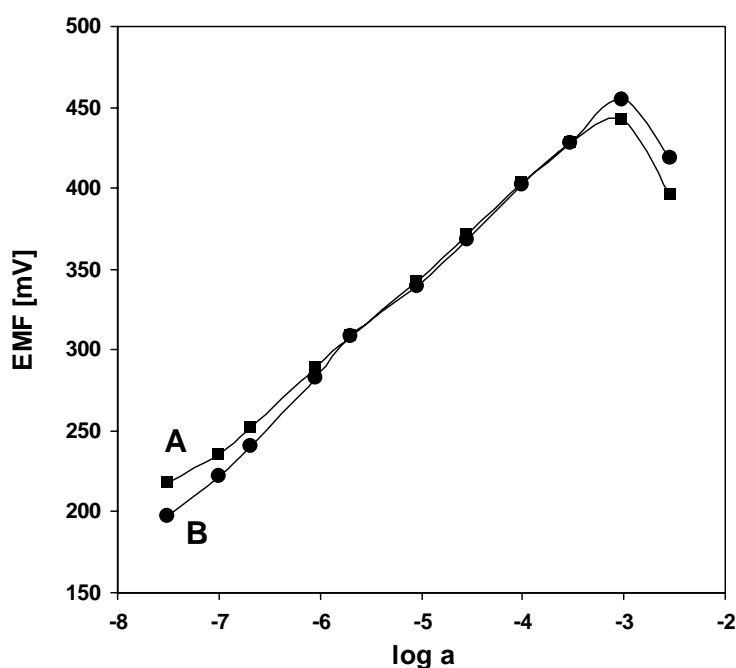


Figure 2. Potentiometric response of ion-selective electrodes based on azothiacrown ether **A** (black squares) and **B** (black circles) towards silver cation. Membrane's composition: 1 wt% of ionophore **A** or **B**, PVC/*o*-NPOE (1:2), 30% mol KTFPB (relative to the ionophore). Conditioning and innerfiling solution: 2×10^{-3} M AgNO₃.

in PVC membranes plasticized with *o*-NPOE or DOS. The complex formation constants measured for other cations tested were found to be lower for several orders of magnitude. The selectivity measured for tested electrodes confirm strong silver complexation properties observed for the investigated thiacrown ethers. Calculated selectivity coefficients for silver are higher for at least 4 orders of magnitude, compared to strongest interfering cations: TMA⁺ and K⁺. Electrodes prepared with membranes containing investigated ionophores and pre-conditioned in Ag⁺-containing solution show a linear, near-Nernstian response over a wide silver concentration range: 10⁻⁷–10⁻³ M. High silver selectivity and wide range of linear response allow to envision a practical application of electrodes based on investigated 16-membered azothia- and azoxythiacrown ethers.

References

1. E. Luboch, J.F. Biernat, E. Muszalska, and R. Bilewicz: *Supramol. Chem.* **5**, 201 (1995).
2. E. Luboch, J.F. Biernat, Yu.A. Simonov, A.A. Dvorkin, and V.K. Bel'skii: *Tetrahedron* **54** 4977 (1998).
3. J.F. Biernat, E. Luboch, A. Skwierawska, R. Bilewicz, and E. Muszalska: *Biocybernet. Biomed. Eng.* **16**, 125 (1996).
4. 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*, Vol. 1, Pergamon, United Kingdom (1996), p. 71; H.K. Frensdorff: *J. Am. Chem. Soc.* **93**, 600 (1971).
5. K. Wygladacz, E. Malinowska, J. Szczygelska-Tao, and J.F. Biernat: *J. Incl. Phenom.* **39**, 303 (2001)
6. K. Wygladacz, E. Malinowska, J. Szczygelska-Tao, and J.F. Biernat: *J. Incl. Phenom.* **39**, 307 (2001)
7. J. Szczygelska-Tao, V.Ch. Kravtsov, and J.F. Biernat: *Polish J. Chem.* **75**, 991 (2001).
8. Z. Brzozka: *Pomiary, Automatyka, Kontrola (Warsaw)* **9**, 197 (1988).
9. E. Bakker, E. Pretsch, and P. Bühlmann: *Anal. Chem.* **72**, 1127 (2000).
10. P.C. Meier: *Anal. Chim. Acta* **136**, 363 (1982).
11. Y. Qiu, Y. Mi, and E. Bakker: *Anal. Chim. Acta.* **421**, 207 (2000).
12. Y. Mi and E. Bakker, *Anal. Chem.* **71**, 5279 (1999).
13. E. Bakker, P. Bühlman, and E. Pretsch: *Chem. Rev.* **97**, 3083 (1997).
14. O. Dinten, Diss. ETH Zurich, 8591 (1988).
15. J.K. Sears and J.R. Darby, *The Technology of Plasticizers*, Wiley, New York.
16. E. Bakker, A. Xu, and E. Pretsch: *Anal. Chim. Acta* **295**, 253 (1994).
17. E. Bakker: *Anal. Chem.* **69**, 1061 (1997).