



Azothia- and Azoxythiacrown Ethers as Ion Carriers. Part II. Anionic Response of Membrane Electrodes

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(Received: 2 May 2000; in final form: 1 September 2000)

Key words: azothiacrown, azoxythiacrown, anion carrier, membrane electrodes, selectivity

Abstract

Ion-selective electrodes with plasticized poly(vinyl chloride) membranes containing 13-membered azothia- and azoxythiacrown ether complexes with silver, mercury or copper ions have been investigated. The potentiometric response towards various anions was studied. For membranes based on azothiacrown ether (**B**) complexes the following selectivity patterns were found: $I^- > SCN^-$, $Br^- > Cl^- \gg ClO_4^- > \text{salicylate}$, NO_3^- (complex **B** with silver), $I^- > ClO_4^- > SCN^-$, $Br^- > \text{salicylate} > Cl^-$, NO_3^- (complex **B** with mercury) and $SCN^- > I^- > Br^- > ClO_4^- > Cl^- > \text{salicylate} > NO_3^-$ (complex **B** with copper). For azoxythiacrown ether (**A**) only membranes containing its complex with mercury exhibited pronounced anion response and the selectivity pattern was similar to that observed for complex **B** with mercury. The origin of the anion response has been discussed.

Introduction

Carriers that bind primary cations too strongly cannot be used to develop cation-selective membrane electrodes, since such membranes exhibit anion sensitivity. Thus, very strong cation-carrier complexes have been employed as ionophores for anions [1]. Their selectivity patterns significantly differ from the so-called Hofmeister selectivity sequence (i.e., when selectivity is controlled by the lipophilicity of anions [2]) observed for anion-selective electrodes based on anion-exchangers [1]. It was shown that metallophthalocyanines [3], metalloporphyrins incorporating different metal cations (e.g., Mn(III) [4, 5], Sn(IV) [6, 7], Co(III) [8, 9], In(III) [8, 10], Tl(III) [10], and Ga(III) [10]), and Schiff base complexes [11, 12] exhibit unique anion ionophore properties due to the selective interaction of anions with the metal center. Thus, the nature of the metal center is expected to play an important role in the selectivity pattern observed.

Ion-selective electrodes that employed cation complexes with neutral carrier as anion sensing material have also been reported. Specifically, Ag^+ [13–15], Hg^{2+} [16, 17], and Au^{3+} [18], have been used as metal centers of these complexes. Florido et al. suggested that for triisobutylphosphine sulfide complexes with Ag^+ and Hg^{2+} the response mechanism of neutral carrier-metal complex-based ion-selective electrodes toward anions could be related either to the formation of a thin film of insoluble halide salts of a given

cation at the membrane interface or could originate from the selective association of anions with the incorporated cation-carrier complex within the membrane [13, 14, 16]. Bakker showed that the principle of anion sensing is similar to precipitate-based ion-selective electrodes [15]. The free silver ion activity at the electrode surface is ruled by sample anion activity *via* a dissolution equilibrium. However, there are certain differences in the working mechanism of these two systems. While an upper limit of anion detection does not exist for silver halogenide precipitate-based membranes, an extremely high selectivity of the carrier-based membrane is needed for successful anion measurements. Otherwise other sample cations may compete and displace silver ions from the membrane. This competing influence of sample cations is reflected by an upper anion detection limit of the electrode.

In this study, the anion-selective properties of poly(vinyl chloride) membrane electrodes based on complexes of a 13-membered azoxythiacrown ether with Hg^{2+} and an azothiacrown ether with Ag^+ , Hg^{2+} and Cu^{2+} are described.

Experimental

The salts, 2-(*N*-morpholino)ethanesulfonic acid (MES), 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) in highest available purity (puriss.

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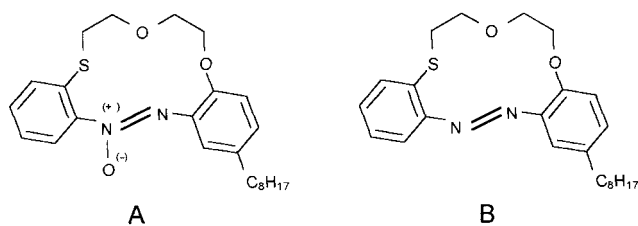


Figure 1. Structures of the azoxy- and azothiacrown ethers (**A** and **B**).

p.a.) were purchased from Fluka (Ronkonkoma, NY). 13-Membered azoxythia- (**A**) and azothiacrown (**B**) ethers were obtained as described [19]. The thiacycrown ether structures are shown in Figure 1.

All aqueous solutions were prepared using distilled-deionized water.

Membrane preparation

In general, the polymeric membranes contained 1 wt% ionophore (**A** or **B**), 30–33 wt% PVC, 66–67 wt% *o*-NPOE and lipophilic anionic additives (0 or 20 mol% of KTpCIPB for **A** and 0 or 40 mol% for **B**). The membrane components, total 200 mg, were dissolved in 2 mL 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.

Potentiometric measurements

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

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

The bridge electrolyte consisted of 1 M lithium acetate. Unless otherwise stated, 0.01 M AgNO₃, 0.01 M CuCl₂ or 0.01 M Hg(NO₃)₂ solution was used as the internal filling solution for the assembled electrodes. Electrodes were conditioned in the solution of the same composition as the internal filling solution for at least 24 hours before measurement.

The EMF values were measured using a custom made 16-channel electrode monitor. Details of this equipment were described previously [20].

To obtain calibration curves standard solutions of different anions were added in successive aliquots to a beaker containing 50.00 mL of 0.05 M MES-NaOH, pH 5.5 buffer solution. Activity coefficients were calculated according to the Debye-Hückel approximation [21].

Results and discussion

As was shown recently [22], membrane electrodes based on azoxythiacrown ether (**A**) and azothiacrown ether (**B**) exhibited high affinity towards Hg²⁺, Ag⁺, Pb²⁺ (Hg²⁺ >

Ag⁺ > Pb²⁺) and Hg²⁺, Ag⁺, Cu²⁺ (Ag⁺ >> Hg²⁺ > Cu²⁺), respectively. It was found that electrodes with membranes containing azoxythiacrown ether (**A**) showed fast and reversible response for Ag⁺ and Pb²⁺ ions with nearly theoretical slopes for a wide range of their concentrations, even after conditioning of the electrodes in AgNO₃ or Pb(NO₃)₂ solutions. In contrast, electrodes based on membranes containing azoxythiacrown ether (**A**) after the equilibration with Hg(NO₃)₂ solution, as well as azothiacrown ether (**B**) after the conditioning in AgNO₃, Hg(NO₃)₂ or Cu(NO₃)₂ solution, exhibited either cationic response over a narrow concentration range of nitrate salts (Hg²⁺ for carrier **A** and Ag⁺ for carrier **B**) or no cationic response (Hg²⁺ and Cu²⁺ in the case of carrier **B**) followed by anionic response for higher than 10⁻³ M solutions. This type of electrode response can be attributed to the formation of too strong cation-carrier complexes in the membrane phase during the conditioning process and co-extraction of anions from the sample solution into the membrane phase or to kinetic limitations.

The electrodes listed above have been evaluated for their response toward anions. Electrodes were calibrated using sodium salts of several anions in MES-NaOH buffer solution, pH 5.5.

Membranes based on complexes of azoxy- (**A**) or azothiacrown ether (**B**) with silver

It was found that electrodes based on azoxythiacrown ether **A** (after equilibration with AgNO₃ solution) showed cationic response toward the changes of sodium ion activity without any pronounced influence of the nature of the anion present in the sample solution (see Figure 2). In contrast, electrodes based on the Ag⁺-azothiacrown ether (**B**) complex behaved as anion selective electrodes (in the absence of Ag⁺ in the sample).

Because sodium salts have been used for the investigation of the anion response of the studied electrodes, the selectivity for silver over sodium ion observed for the azoxy- (**A**) and azo- (**B**) derivatives can be responsible for the difference in the electrodes' behavior [15]. The selectivity for silver over sodium found for carrier **A** ($\log K_{\text{Ag,Na}}^{\text{pot}} = -2.7$; [20]) seems to be insufficient to prevent an ion-exchange reaction of sodium with silver ion at the membrane/sample interface and to reflect any anion interaction. The selectivity coefficient determined for **B** ($\log K_{\text{Ag,Na}}^{\text{pot}} = -11.5$; [22]) indicates very high selectivity towards silver and strong discrimination of sodium and proves itself to be sufficiently low to see a selective response of electrodes toward several anions.

Figure 3 illustrates the response of electrodes based on the Ag⁺ – azothiacrown ether (**B**) system to the various anions. For anions that do not form insoluble silver salts, even such lipophilic anions as perchlorate and salicylate, almost no response was observed for membranes without and with anionic additives. Electrodes showed significant response to sample thiocyanate and halide anions. Indeed, the selectivity pattern obtained for these electrodes (I⁻ > SCN⁻, Br⁻ > Cl⁻) can be related to the solubility product values (K_{sp}) of the silver salts formed with the corresponding anions. Elec-

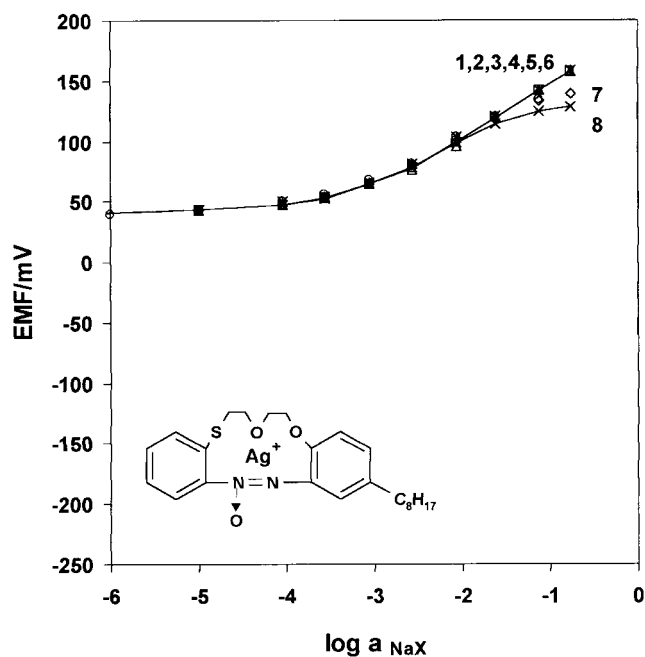


Figure 2. Potentiometric response of ion-selective electrodes based on azoxythiacrown ether **A** conditioned in AgNO_3 solution before measurements. The electrodes were exposed to sodium: (1) sulfate, (2) nitrate, (3) chloride, (4) bromide, (5) thiocyanate (6), iodide (7), salicylate and (8) perchlorate solutions.

trodes based on the Ag^+ -**B** complex preferred anions that form less soluble silver salts.

It has been shown that the detection limit of electrodes based on neutral carriers can be effectively decreased by adding to the sample solution a ligand that is able to form complexes with the primary ion [23, 24]. By analogy, it can be expected that by increasing the anion (X^-) concentration in the sample it is possible to decrease the silver ion activity at the sample-membrane phase boundary according to $K_{\text{sp}} = a_{\text{Ag}^+} \cdot a_{\text{X}^-}$ and observe decreasing EMF. Experimental points presented in Figure 3 were replotted in Figure 4 for changes in silver ion activities by considering the expression of the product solubility and the appropriate values of K_{sp} [25]. Also the response of the electrode to silver ion was inserted. Indeed, the measured data points appear to fit nicely to the theoretically predicted straight line as long as sodium ion does not interfere.

To prove that the non linear response for anions observed at high concentration is caused by the interference originating from the presence of cations, a simple experiment was designed. The calibration curves for bromide ion were carried out using sodium, potassium and cesium salt solutions. The results presented in Figure 5 reflect exactly the selectivity pattern $\text{Cs}^+ > \text{K}^+ > \text{Na}^+$ obtained for azothiacrown ether (**B**) (see Figure 2 in [22]).

As shown by Bakker, the range of cation interference can be used to determine the selectivity of the silver electrode over other sample cations and to calculate the upper limit of detection for a given halogenide [15]. The upper detection limits (UDL) can be calculated for anions from Equation (9) in [15]. Assuming 0.1 M sodium background activity, a UDL of $\log a = +2.9$ for NaCl , $+0.3$ for NaBr ,

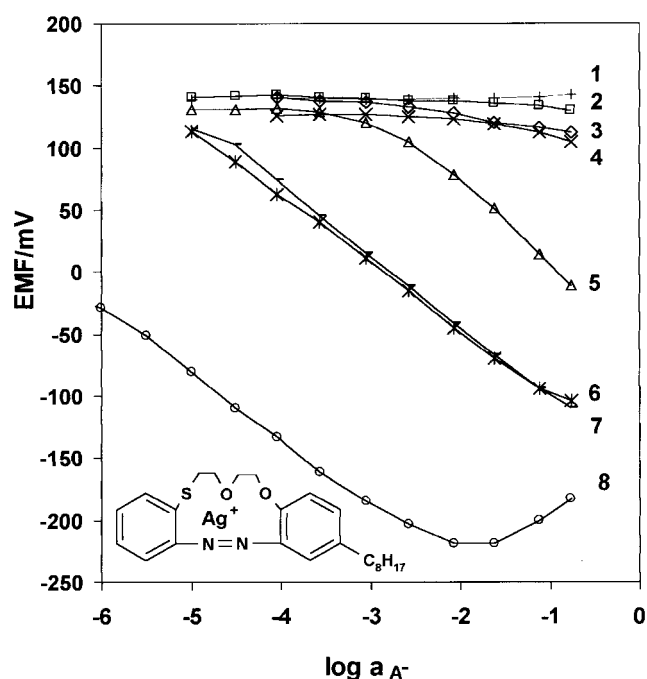


Figure 3. Selectivity pattern of an electrode based on the Ag^+ -azoxythiacrown ether (**B**) complex. The electrode was exposed to sodium: (1) sulfate, (2) nitrate, (3) salicylate, (4) perchlorate, (5) chloride, (6) bromide, (7) thiocyanate and (8) iodide; 0.05 M MES-NaOH, pH 5.5 buffer.

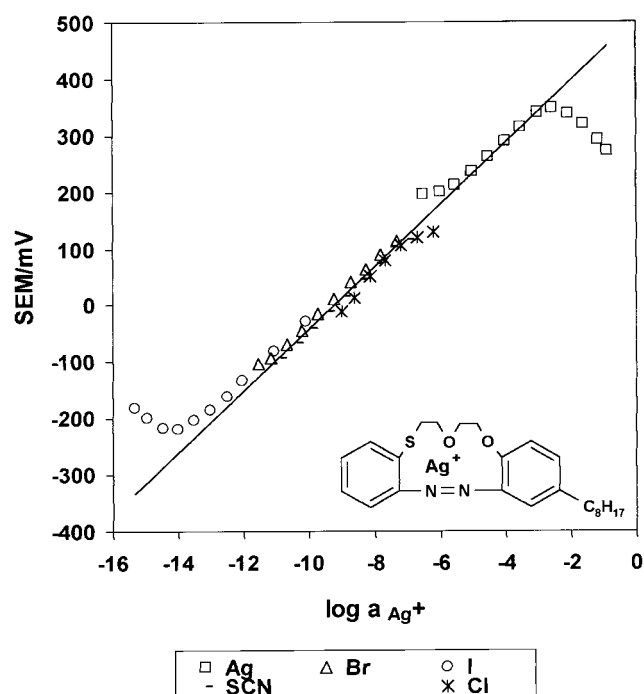


Figure 4. Visualization of the anion buffering effect of the Ag^+ -azoxythiacrown ether (**B**) complex based electrodes by replotting the data from Figure 3 as a function of free silver activity as calculated via appropriate solubility product expressions. Symbols: experimental data and the line: theoretically predicted by dissolution equilibrium.

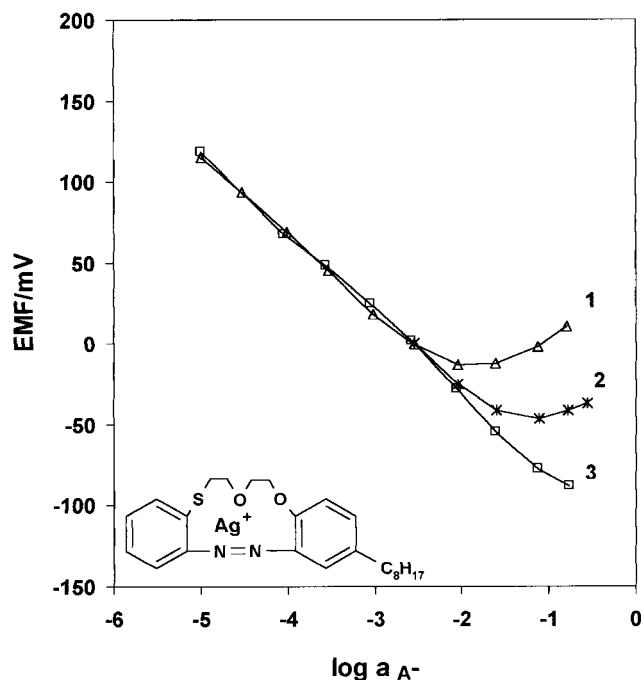


Figure 5. The influence of a cation on the response toward bromide observed for electrodes with membranes containing the Ag^+ -azothiacycrown ethers (**B**) complex; (1) Cs^+ , (2) K^+ and (3) Na^+ .

+0.6 for NaSCN and -3.5 for NaI can be expected for **B** as ionophore. Indeed, the linear response toward changes in chloride, bromide and thiocyanate anion concentration was observed up to 0.1 M solutions. Electrodes responded with nearly theoretical slopes (-53 to -55 mV dec^{-1}). For iodide ion the UDL, due to sodium interference, appeared at $\log a \approx -2.5$ that is by ca. 1 log unit higher than the predicted one.

A comparison of results presented here and reported earlier for electrodes with membranes containing silver complexes with neutral carriers (e.g., triisobutylphosphine sulfide [13], *N*-thiocarbamoylimine-dithioether derivative [14], methylene-bis-*N,N*-diisobutyldithiocarbamate and bis-thioether functionalized derivatized calix[4]arene [15]) leads to the conclusion that electrodes based on the azothiacycrown ether (**B**) silver complex seem to suffer from sodium interference the least, assuming that experimental points that deviate from typical anionic response were ignored in figures shown in [13, 14].

Membranes based on complexes of azoxy- (A) or azothiacycrown ether (B) with mercury

The response of electrodes based on Hg^{2+} -azothiacycrown ether (**B**) and Hg^{2+} -azoxythiacycrown ether (**A**) to the various anions are illustrated in Figures 6 and 7, respectively. The decrease of EMF upon the addition of anion solutions is also observed in these cases. In contrast to membranes with the silver complex, significant response was also observed for perchlorate, salicylate and nitrate ions. The selectivity pattern obtained for electrodes containing the azothiacycrown ether complex (**B**) with mercury ($\text{I}^- > \text{ClO}_4^- > \text{SCN}^-, \text{Br}^- > \text{Sal}^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$) differs from the Hofmeister

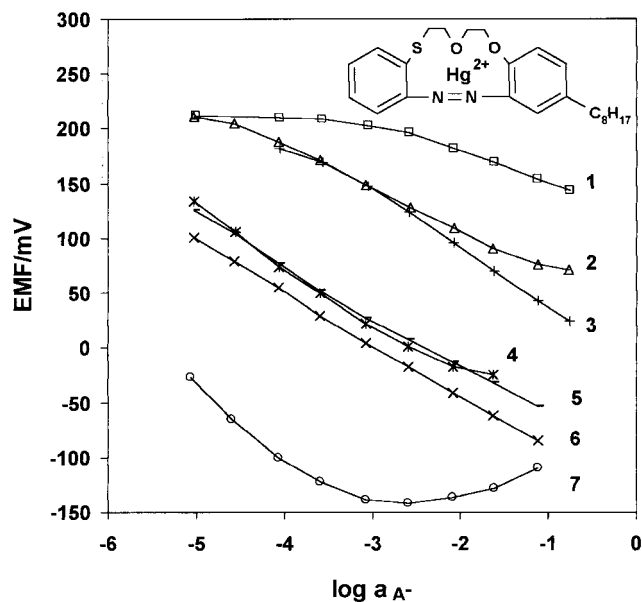


Figure 6. Selectivity pattern of an electrode based on the Hg^{2+} -azothiacycrown ether (**B**) complex. The electrode was exposed to sodium: (1) nitrate, (2) chloride, (3) salicylate, (4) bromide, (5) thiocyanate, (6) perchlorate and (7) iodide; 0.05 M MES- NaOH , pH 5.5 buffer.

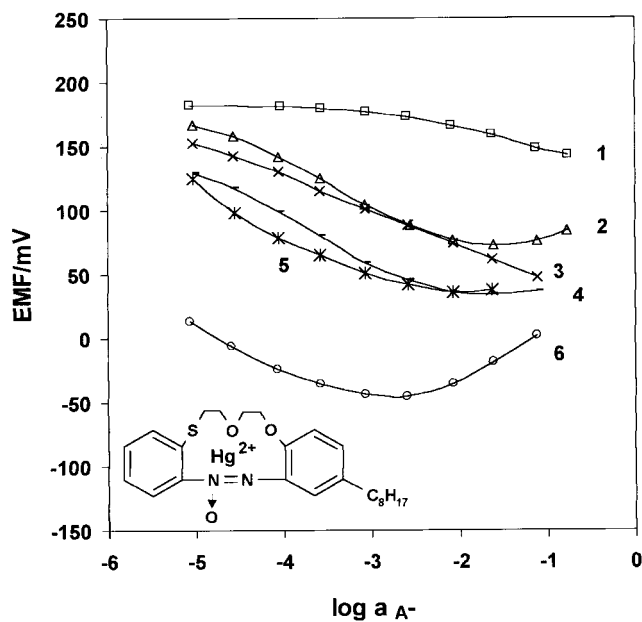


Figure 7. Selectivity pattern of an electrode based on the Hg^{2+} -azoxythiacycrown ether (**A**) complex. The electrode was exposed to sodium: (1) nitrate, (2) chloride, (3) bromide, (4) thiocyanate, (5) perchlorate and (6) iodide; 0.05 M MES- NaOH , pH 5.5 buffer.

sequence related to the lipophilicity of anions and reflects the affinity of iodide, thiocyanate, bromide and chloride toward Hg^{2+} [25]. A similar selectivity sequence was exhibited by electrodes based on azoxythiacycrown ether (**A**) with mercury.

For anion-selective electrodes based on charged metal-ligand complexes and working according to the charged carrier mechanism it is known that an addition of anionic lipophilic additives (e.g., KTpCIPB) into the membrane improves its selectivity with reference to lipophilic anions [8,26,27]. When membranes containing carrier **A** (or **B**) are

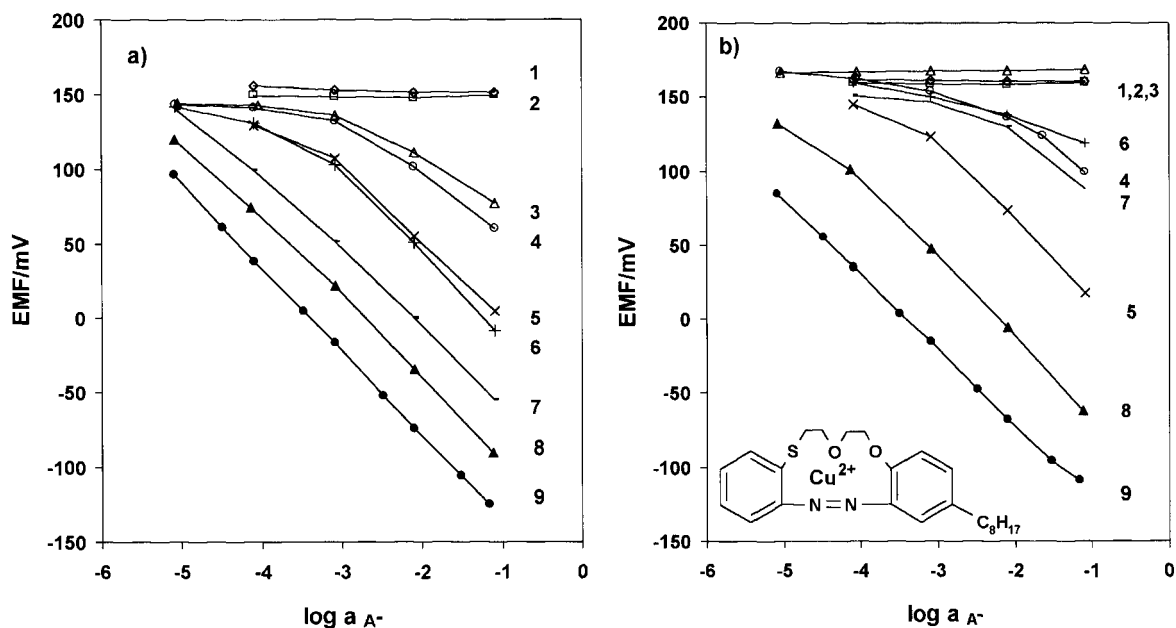


Figure 8. Selectivity pattern of an electrode based on the copper-azothiacycrown ether (**B**) complex. The electrode was exposed to sodium: (1) phosphate, (2) sulfate, (3) nitrate, (4) chloride, (5) bromide, (6) salicylate, (7) perchlorate, (8) iodide and (9) thiocyanate; 0.05 M MES-NaOH, pH 5.5 buffer; (a) 0 mol% of KTpCIPB and (b) 40 mol% of KTpCIPB.

in contact with $\text{Hg}(\text{NO}_3)_2$ solution, the formation of a stable charged mercury complex (B_nHg^{2+}) occurs. However, KTpCIPB added to a membrane containing mercury complexes with azoxy- (**A**) or azothiacycrown ether (**B**) has not affected the selectivity of electrodes compared to membranes without anionic sites.

Electrodes based on mercury complexes with **A** or **B** responded to changes in anion concentration with sub-Nernstian slopes (-38 to -42 mV dec^{-1} for **A** and -48 to -52 mV dec^{-1} for **B**). While for lipophilic anions (e.g., perchlorate, salicylate and nitrate) a linear response was observed over the whole range of anion activity, for halide anions a flattening of the calibration curve appeared at a high anion concentration range. For iodide even cationic response was observed when the concentration was higher than 10^{-3} M. In these cases, the upper detection limit has appeared at a lower anion concentration (especially for Hg^{2+} - azoxythiacycrown ether (**A**)) than observed for Ag^+ - azothiacycrown ether (**B**)-based electrodes. Again such behavior can be explained by the interference from cations present in the sample solution. Indeed, the greater discrimination of sodium in the case of azothiacycrown ether (**B**) ($\log K_{\text{Hg,Na}}^{\text{pot}} = -11.8$) than for azoxythiacycrown ether (**A**) ($\log K_{\text{Hg,Na}}^{\text{pot}} = -8.4$) [22] explains why anion response is less pronounced for membranes with ionophore **A** than for membranes with **B**.

A comparison of results presented above and reported earlier for electrodes with membranes containing mercury complexes with neutral carriers (e.g., triisobutylphosphine sulfide [16] and thioamide derivatives of calix[4]arene [17]) revealed that this type of complex induces a similar selectivity pattern toward halide and thiocyanate anions. However, in contrast to results shown here and in [17], no significant response for the hydrophobic perchlorate anion was

observed in the case of the triisobutylphosphine sulfide complex with mercury [16].

Membranes based on complexes of azothiacycrown ether (**B**) with copper

As mentioned earlier [20], the response for Cu^{2+} ion, initially observed for electrodes with membranes containing azothiacycrown ether (**B**), disappeared gradually when electrodes were conditioned in Cu^{2+} solutions. These electrodes have been examined for anion response. Surprisingly, they exhibited anion sensitivity with the selectivity pattern ($\text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$) that can be correlated with the K_{sp} 's of the corresponding Cu^+ salts rather than with the stability constants of complexes formed by Cu^{2+} with these anions (except for iodide for which the red-ox reaction with Cu^{2+} might be expected) [25, 28]. This may suggest that membranes somehow accumulate Cu^+ ion slowly in time, and Cu^+ as a soft Lewis acid forms a strong complex with the ionophore. However, the origin of the behavior of membranes incorporating ionophore **B** that have stayed in contact with copper ion solutions cannot be explained based only on potentiometric measurements and further investigations are needed.

The selectivity pattern of an electrode based on the copper-azothiacycrown ether (**B**) complex is presented in Figure 8a for membranes without anionic sites and for membranes containing also KTpCIPB in Figure 8b. It can be easily seen that the addition of lipophilic anionic sites into the membrane phase eliminated the response of electrodes toward lipophilic anions such as perchlorate and salicylate without any significant changes in electrode selectivity for other anions.

As can be seen from Figures 8a and b, the copper-azothiacycrown ether (**B**) complex based electrodes exhibited

a linear response even for the most favorable SCN^- anion over the whole examined range of anion concentration. For highly preferred anions the slopes of the calibration curves were nearly theoretical (-53 to -56 mV dec^{-1}). The electrodes responded to changes in anion activity with a response time (t_{95}) shorter than 30 seconds. The EMF recovery to the base line (EMF measured for MES-NaOH buffer solution) depended on the nature of the anion. The recovery time (t_{95}) was found to be shorter than 5 minutes for anions interacting with a charged copper-carrier complex due to their lipophilicity (e.g., perchlorate and salicylate) and longer than 20 minutes for anions exhibiting affinity for copper.

To summarize results on the anion response of the examined electrodes it can be said that silver- and copper-azothiacrown ether (**B**) complex-based membranes can be considered as potentially useful for anion sensing. However, as also pointed out by Bakker [15], the amount of silver or copper released, respectively, can vary with time and does not self-adjust very quickly to the sample anion activity. Indeed, the response time (t_{95}) of electrodes was found to be faster than 1 minute, while the recovery time depended on the examined anion and for the anions showing high affinity toward a metal center present in the complex (e.g., iodide) exceeded 20 minutes. For this reason a very careful optimization of the composition of the internal solution, the membrane composition, the conditioning and the washing solutions should be done when a practical application of a neutral carrier-metal ion complex based as an anion ionophore is considered.

Acknowledgments

KW and EM gratefully acknowledge the State Committee for Scientific Research (grant No. PBZ-19-15) for financial support of this work. JST and JFB gratefully acknowledge the Technical University of Gdansk (Grant No. BW 083) for partial financial support of this study.

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