Nitrite-selective ISE based on uranyl salophen derivatives

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Abstract

Anion selectivities of membranes based on uranyl salophen derivatives with substituents at the 4-position are presented. Derivative **2** (with 4-nitro substituent) has been applied to design a nitrite-selective ion-selective electrode (ISE) that shows linear response in the range 1–3 of pNO_2^- with a slope of 56.2 mV decade⁻¹. The highest selectivity over other anions and optimum performance of the electrodes are obtained for membranes containing tridodecylmethylammonium chloride (TDMAC) at 10 mol% versus ionophore as an additive.

Keywords: Anion selectivity; Uranyl salophenes; Nitrite ion-selective electrodes

1. Introduction

The selectivity pattern of most anion-sensitive membranes is governed by the Hofmeister series. However, if the membrane contains in addition to the anion-exchange sites receptor molecules that are able to bind specific anions, the membrane may become selective towards those anions. The binding energy of the complex that is formed by the association of the anion and the receptor effectively reduces the transfer energy that is required to extract the anion from the aqueous phase to the membrane. Neutral receptors containing H-bond donors [1–3], Lewis-acidic metal centres [4–6] or electrophilic carbon atoms [7] can be applied for this purpose.

The uranyl cation is a Lewis acid that is able to bind polar molecules [8,9]. Because of this property, the uranyl cation was incorporated in several organic host structures to serve as the electrophilic binding centre for guest molecules. The salophen moiety was used as a ligand to design functionalized UO_2 -salenes [10–12]. The UO_2^{2+} cation favours a pentagonal bipyramidal coordination with the two oxygen atoms in the apical positions. Consequently in UO_2 -salenes there is one Lewis-acidic binding site available in an equatorial position for anion complexation.

Substituents in the salophen moiety influence the complexation properties of the uranyl cation. To investigate the magnitude of this influence, several uranyl salophen deriva-

tives were studied. Anion selectivities and responses of membranes based on derivatives with substituents at the 4-position were determined. The optimum of the membrane composition for nitrite sensing in ion-selective electrodes (ISEs) was evaluated.

2. Experimental

2.1. Chemicals

All sodium and potassium salts employed were of analytical grade and were purchased from POCH Gliwice, Poland. The standard stock solutions (0.1 M) of sodium salts of anions 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 or sodium hydroxide solutions.

2.2. Ionophores and membrane materials

The synthesis of ionophores **1–6** has been described previously [11–13]. High-molecular-weight poly(vinyl-chloride) (PVC), *o*-nitro-phenyl octyl ether (*o*-NPOE), bis(1-butylpentyl adipate) (BBPA), tridodecylmethyl ammonium chloride (TDMAC), tetradecylammonium bromide (TDAB) and tetrabutylammonium chloride (TBAC) were obtained from Fluka. Freshly distilled tetrahydrofuran (THF) p.a. (POCH Gliwice) was used as a solvent for the membrane components.

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2.3. Membrane and electrode preparation

The membranes contained 1 wt.% ionophore, 66 wt.% plasticizer, and 33 wt.% poly(vinyl chloride) (PVC). Some membranes contained lipophilic salts as additives (0–50 mol% versus ionophore). The membrane components (100 mg in total) were dissolved in 1 ml of THF. This solution was placed in a glass ring of 24 mm i.d. resting on a glass plate. After solvent evaporation overnight, the resulting membrane was peeled off 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, The Netherlands) for electromotive force (e.m.f.) measurements. As internal filling solution a 0.1 M solution of KCl adjusted to pH = 4.5 by HNO₃ was used. The electrodes were conditioned overnight in a dilute solution of internal electrolyte. For each membrane composition two electrodes were prepared.

2.4. E.m.f. measurements

All measurements were carried out at 20°C with cells of the following type:

Ag; AgCl; KCl(0.1 M)|0.1 M KCl|sample solution||sensor membrane||internal filling solution; AgCl; Ag.

The e.m.f. values were measured using a custom-made 16-channel electrode monitor. Details of this equipment have been described previously [14]. Potentiometric selectivity coefficients ($\log K(\text{NO}_3^-, X)$) were determined by the fixed interference method (FIM) [15] by increasing the activity of primary ion in the solution in steps of $0.5 \log a(\text{NO}_3^-)$ for several anions and by the separate solution method (SSM) using 0.1 M solutions of sodium salts of anions at a constant pH 4.5. The activities of anions in aqueous solutions were calculated according to the Debye–Hückel approximation [15]. The performance of the electrodes was examined by measuring the e.m.f. values of the primary ion solutions (concentration range 10^{-7} – 10^{-1} M) stirred with a magnetic stirrer.

3. Results and discussion

The structures of the investigated uranyl salophen ionophores with 4-substituents are displayed in Fig. 1.

The selectivities of PVC/BBPA ISEs with ionophores 1 to 6 are presented in Figs. 2 and 3. These Figures also show the selectivity patterns of membranes without ionophore ('blank' membrane) according to the Hofmeister series of ion-exchanger-TDMAC. The most important result of these ISE studies is the high selectivity of nitrite over all other anions (except perchlorates). This effect is the most pronounced for 2 and 5. Ionophore 6 has a 1,2-diaminocyclohexyl unit instead of the 1,2-diaminobenzene moiety in the salophen ligands 1–5. An advantage of the cyclohexyl over benzene derivative is the higher solubility in the membrane matrix. Comparing the selectivity patterns for membranes

Fig. 1. Structures of ionophores 1–6.

Fig. 2. Selectivity coefficients, $\log K(\text{NO}_3^-, X)$ for PVC membranes containing ionophores 1–3 and blank (without ionophore) membrane. Membrane: BBPA as a plasticizer. SSM method: 0.1 M solutions of anions, pH = 4.5. Internal electrolyte: KCl 0.1 M, pH = 4.5.

Fig. 3. Selectivity coefficients, $\log K(\text{NO}_3^-, X)$ for PVC membranes containing ionophores 4–6 and blank (without ionophore) membrane. Membrane: BBPA as a plasticizer. SSM method: 0.1 M solutions of anions, pH = 4.5. Internal electrolyte: KCl 0.1 M, pH = 4.5.

based on 1 and 6 in Figs. 2 and 3, we conclude that the sequence of selectivity coefficients is not altered and only larger differences between these values were found.

The highest selectivity for nitrite of ionophore 2 can be explained by the presence of an electron-withdrawing substituent in this compound (other ligands contain electron-donating groups or a hydrogen atom in the 4-positions). Electron-withdrawing substituents increase the Lewis acidity of uranium atom, improving the complexation of the nitrite anion which is a relatively hard Lewis base. The association constants of ionophore 2 for some anions were determined by conductometry in organic homogeneous phase [11–13]. The sequence of K_a values is $\text{H}_2\text{PO}_4^{2-} > \text{Cl}^- \sim \text{NO}_2^- > \text{SO}_4^{2-} \gg \text{NO}_3^-$ and differs significantly from the selectivity pattern found by membrane ISE measurements. This fact shows that the response of a membrane is also determined by the partition of anions between water and the organic phase (membrane). The observed selectivities are the result of two factors determined by the association constants and the partition coefficients.

The membranes contain only 1 wt.% of ionophore and 10 mol% of TDMAC. This low amount of lipophilic ammonium salts was chosen to preserve sufficient membrane polarity and not cause the tendency to follow the Hofmeister series. The observed slopes are only slightly sub-Nernstian (Fig. 4). For 2 and 5 slopes are found between 56 and 58 mV decade⁻¹ NO_2^- in the presence of 0.1 M interfering NO_3^- . Membranes based on ionophore 1 show sub-Nernstian responses of 53 mV decade⁻¹ with a significantly smaller linear range. The responses of the electrodes containing the best ionophore 2 have almost Nernstian slopes in the presence of 0.1 M Br^- or SO_4^{2-} in the activity range of the nitrite from -3.1 to -1.1 (Fig. 5). The slopes of the nitrite response decreased to 41.9 mV/p NO_2^- in the presence of a more interfering anion such as perchlorate and a decrease of the linear range was also observed. The response curves and the selectivity coefficients were reproducible during a period of six weeks with permanent treatment of the membranes by tap water.

Fig. 4. NO_2^- responses of electrodes based on ionophore: (a) 1; (b) 2; (c) 5 and (d) without ionophore and BBPA as a plasticizer (internal electrolyte: KCl 0.1 M, pH=4.5) in the presence of interfering anions NO_3^- (0.1 M, pH=4.5).

Fig. 5. NO_2^- responses of electrodes based on ionophore 2 and BBPA as a plasticizer (internal electrolyte: KCl 0.1 M, pH=4.5) in the presence of interfering anions (0.1 M, pH=4.5): (a) SO_4^{2-} ; (b) Br^- ; (c) NO_3^- ; (d) ClO_4^- .

Table 1

Comparison of selectivity coefficients $\log K(\text{NO}_2^-, Y)$, of electrodes based on membranes containing ionophore 2, TDMAC as an additive (10 mol% vs. ionophore) and BBPA as a plasticizer, determined by SSM (0.1 M solutions of anions, pH=4.5) and FIM methods

Y =	SO_4^{2-}	Br^-	NO_3^-	ClO_4^-
SSM	-2.75	-2.55	-2.45	-1.45
FIM	-2.80	-2.50	-2.40	-1.80

For membranes with ionophore 2, the selectivity coefficients determined by the SSM and FIM are nearly the same (Table 1). Logarithmic values of selectivity coefficients for the more interfering anion ClO_4^- evaluated by the FIM method are lower than with the SSM method. This might be due to fact that the observed slopes of the NO_2^- responses in solutions of these anions deviated from the Nernstian slope.

The influence of the polarity of the plasticizer on the anion selectivity of the membrane was investigated. 'Blank' membranes (without ionophore) based on BBPA as a plasticizer show nearly no nitrite response (Fig. 4). More polar 'blank' membranes based on *o*-NPOE as plasticizer give nitrite responses in a narrow linear range with a detection limit of about 10^{-6} M. However, the slope of this response is below 30 mV decade⁻¹. There are no differences between the selectivity patterns of 'blank' membranes based on the investigated plasticizers. The membranes containing ionophores (2 and 5) and a less polar plasticizer (BBPA) show better selectivity for NO_2^- over ClO_4^- and Br^- compared to the membranes plasticized with the more polar *o*-NPOE (Fig. 6).

The response for NO_2^- anions of membranes containing ionophore 2 and different ammonium salts as additives was examined (Fig. 7). The lipophilic salts differ in number and in size of the alkyl substituents. Membranes containing more lipophilic salts (TDMAC and TDAB) show responses with near-Nernstian slopes, in contrast to the membranes with less lipophilic salts (TBAC) or without additives, where slopes of nitrite response decreased to 29 and 21 mV/p NO_2^- .

Fig. 6. Selectivity coefficients, $\log K(\text{NO}_3^-, \text{X})$ for PVC membranes containing ionophores 2, 5 and blank (without ionophore) membrane. Membrane: *o*-NPOE as a plasticizer. SSM method: 0.1 M solutions of anions, pH = 4.5. Internal electrolyte: KCl 0.1 M, pH = 4.5.

Fig. 7. NO_2^- responses of electrodes based on ionophore 2 and BBPA as a plasticizer with different additives in membranes: (a) TDAB; (b) TDMAC; (c) TBAC; (d) without additive; (e) without ionophore (internal electrolyte: KCl 0.1 M, pH = 4.5) in the presence of interfering anions NO_3^- .

For the optimal membrane composition for nitrite sensing the selectivity of membranes with different amounts of TDMAC (0–50 mol % versus ionophore) was evaluated. The best selectivity for nitrite over perchlorate anions and the highest slope of nitrite response was found with a membrane containing 10 mol% of TDMAC (Fig. 8 and Table 2).

4. Conclusions

Anion selectivities of plasticized PVC membranes based on uranyl salophen derivatives with substituents at the 4-position were evaluated. Ligand 2, containing an electron-withdrawing substituent that increases the Lewis acidity of the uranyl cation (UO_2^{2+}) demonstrated the highest nitrite selectivity. The optimized membrane containing ionophore 2 and 10 mol% TDMAC was applied to design a nitrite-selective electrode. In contrast, the membrane with TDMAC but without ionophore did not show nitrite selectivity.

$\log K(\text{NO}_2^-, \text{ClO}_4^-)$

Fig. 8. Selectivity coefficients, $\log K(\text{NO}_2^-, \text{ClO}_4^-)$ for PVC membranes containing ionophore 2, BBPA as a plasticizer and different amounts of TDMAC as additive. SSM method: 0.1 M solutions of anions, pH = 4.5. Internal electrolyte: KCl 0.1 M, pH = 4.5.

Table 2

Slopes of electrodes based on membranes containing ionophore 2, BBPA as a plasticizer and different amounts of TDMAC as an additive (mol% vs. ionophore)

% TDMAC in membrane	0	5	7.5	10	15	25	50
Slope [mV/p NO_2^-]	20.7	41.5	51.6	56.2	55.7	43.0	42.5

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Wojciech Wróblewski obtained a Ph.D. (1995) from the Warsaw University of Technology (WUT), where he is an assistant professor in the Department of Analytical Chemistry. He works on ion recognition and membrane chemical sensors (both electrochemical and optical).

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David N. Reinhoudt obtained his Ph.D. (1969) from Delft University of Technology. In 1975 he was appointed as a part-time professor at University of Twente and his appointment as a full professor followed in 1978. The major part of his research deals supramolecular chemistry and its application in membrane transport, in the fields of electronic or optical sensor systems, catalysis and molecular (NLO) materials.