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DETERMINATION OF THIOCYANATE USING AN IRONPORPHYRIN-BASED SENSOR

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SUMMARY

In the present paper, the potentiometric response characteristics of a metalloporphyrin-based electrode in plasticized polyvinyl chloride (PVC) membranes are presented for a set of monovalent anions. As membrane ionophore, 5,10,15,20-tetrakis-(3,4-dimethoxyphenyl)-porphyrin-Fe(III) (FeMeOPP) was used. To establish the optimum composition of the membrane, different ionic additives (mol.% relative to ionophore) were used. Electrodes formulated with membranes containing 1 wt.% ionophore, 66 wt.% o-NPOE, 33 wt.% PVC (plasticizer: PVC = 2:1) and the lipophilic cationic derivative TDMACl (20mol%) are shown to exhibit high selectivity for thiocyanate with a near-Nernstian slope in the working concentration range of 1.0×10^{-1}–5.0×10^{-6} M, with a good stability in time.

Keywords: metalloporphyrins; thiocyanate; anion-selective electrode; near-Nernstian slope; neutral carrier.

INTRODUCTION

Among a lot of other applications, metalloporphyrins are used as ionophores in solvent / polymeric membrane electrodes. They can induce potentiometric anion selectivity patterns different from the classical Hofmeister pattern. Porphyrins are interesting anion carriers because of their ability to have a Lewis acidic metal as the coordinating site. The binding affinity of this central metal could be controlled by the surrounding porphyrin ring as well as the fifth or sixth ligand attached to the metal. In these cases, electrode selectivity towards anions is not governed by anion lipophilicity as in the case of dissociated ion-exchanger, but by specific chemical interactions between the metalloporphyrin from the membrane and the anions in the sample solution [1-5]. It has been shown that the nature of the ionophore-anion interaction is influenced by the charge of the central metal ion from the porphyrinstructure. The operative mechanism (neutral carrier versus charged carrier) must be known, because the optimization of membrane permselectivity is highly dependent on the incorporation of additional membrane additives [6].

Thiocyanate is present as a normal constituent in mammalian tissues and body fluids and it is well known that SCN- has important effect on the environment. Thiocyanate is present in human body as a metabolic degradation product of sulfur containing compounds in tobacco. Since SCN- is a detoxication product of cyanide, and its content is higher in the body fluids of smokers the concentration of SCN- in saliva can be used as identification of non-smokers and smokers. Researchers in Norway [7] examined thyroid function at birth in term infants after maternal smoking during pregnancy and correlated thyroid function parameters with growth parameters and with the cord serum thiocyanate concentration. It is known that chronically elevated levels of blood thiocyanate can inhibit the uptake of iodine by the thyroid gland [8]. Another source of thiocyanate is industrial pollution from the toxic cyanide, which in mining solutions can undergo several types of reactions with forms of sulfur including thiosulfates, or sulfide ions, to produce thiocyanates (SCN-). Heming and Blumhagen [9] report that thiocyanates cause "sudden death syndrome" in trout, partly as a response to stress, and because they accumulate.

In this paper, the potentiometric response of several electrodes based on tetradimethoxyphenylporphyrin-iron(III) chloride (1) as ionophore is examined. Because the metallic cation has a trivalent charge and acts either as neutral or charged carrier, membranes formulated with different amounts of additives were made and their potentiometric responses were compared. It results that the electrode based on compound 1 as ionophore is thiocyanate-selective and acts as a neutral carrier.

MATERIALS AND METHODS

The porphyrine, 5,10,15,20-tetrakis-(3,4-dimethoxyphenyl)-porphyrin-Fe(III) (FeMeOPP) was synthesized and purified. PVC of high molecular weight, *o*-nitrophenyloctilether (o-NPOE) and dioctylphtalate (DOP) and bis(2-ethylhexyl)sebacate (DOS) were obtained from Merck and Aldrich. Tridodeocylmethylammonium chloride (TDMACl), sodium tetraphenylborate (NaTPB) and tetrahydrofuran (THF) of highest purity were available from Merck and Fluka and were used without further purification, except THF which was distilled prior to use. The sample solutions for all potentiometric measurements consisted of sodium salts of the given anions in 0.05 M MES, adjusted to pH 5.5 with NaOH.

ISE membrane formulation and EMF measurements

The composition of the PVC membranes were: 1 wt.%FeMeOPP, 66 wt.% plasticizer, 33 wt.% PVC (plasticizer: PVC = 2:1). . Tridodeocylmethylammonium chloride (TDMACl) and sodium tetraphenylborate (NaTPB) were used as additives in the membranes (20 %mol. relative to the ionophore).

Potentiometric measurements were performed with the following galvanic cell: Hg/Hg_2Cl_2/bridge electrolyte/sample/ion-selective membrane/Cu(Hg)/internal cable.

The bridge electrolyte consisted of 0.1 M KNO_3. Prior to EMF measurements, the electrodes were conditioned for 24 h in a 0.01 M NaCl solution. All experiments were performed at ambient temperature (22 ± 2°C). Potentials were measured using a Hanna Instruments HI223 pH/mV-meter. Potentiometric selectivity coefficients were determined according to the separate solution method [10].

RESULTS AND DISCUSSION

The potentiometric response characteristics of the liquid / polymeric membrane electrodes based on ionophore FeMeOPP were determined using solutions from 1.0×10^{-6} to 1.0×10^{-1} M of the following anions: ClO^-_4, SCN^-, I^-, Salicylate$^-$, F^-, Cl^-, NO_2^-, NO_3^- in 0.05 M of 4-morpholino-ethanesulfonicacid (MES), adjusted to pH 5.5 with NaOH.

Due to the fact that iron ion has the charge 3+, both of additives: cationic and anionic were used for the construction of membranes. The sensors were tested in solutions of SCN^-. No slope was observed for the sensors having anionic NaTFB added, so that we can conclude that the ionophore FeMeOPP acts as a neutral carrier, the cationic additive TDMACl being used for the improvement of the potentiometric answer. This is the reason why three membranes, all of them having the cationic additive added (20% mol. TDMACl relative to the ionophore) were tested using different plasticizers. The composition of the membranes is given below and the potentiometric answer of the sensors in all tested solutions is presented in figures 1, 2 and 3:

Sensor 1 -1% ionophore, 66% o-NPOE, 33% PVC (figure 1);

Sensor 2 -1% ionophore, 66% DOP, 33% PVC (figure 2);

Sensor 3 -1% ionophore, 66% DOS, 33% PVC (figure 3).

(All the membranes contain 20 mol% of TDMACl as lipophilic cationic additive relative to the ionophore).

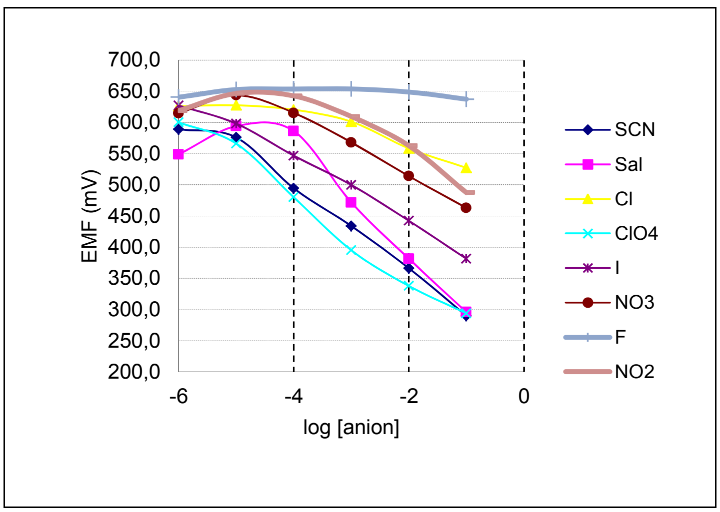

Figure 1. Potentiometric anion response and selectivity in 0,05 M MES buffer (pH5,5) of the electrodes with PVC/o-NPOE (1:2) membranes containing 1% wt FeMeOPP and 20 mol% (relative to ionophore) of TDMACl.

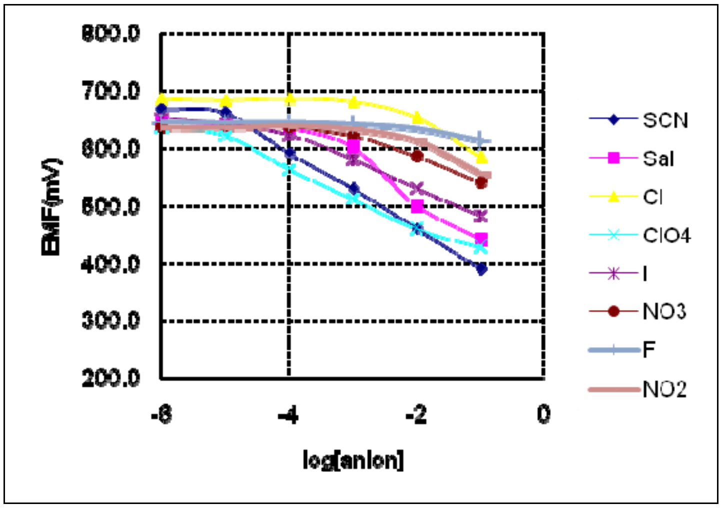

Figure 2. Potentiometric anion response and selectivity in 0,05 M MES buffer (pH5,5) of the electrodes with PVC/DOP (1:2) membranes containing 1% wt FeMeOPP and 20 mol% (relative to ionophore) of TDMACl.

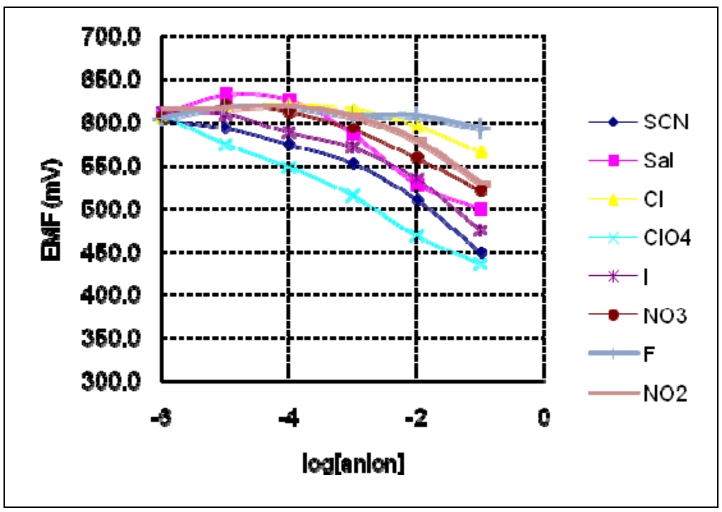

Figure 3. Potentiometric anion response and selectivity in 0,05 M MES buffer (pH5,5) of the electrodes with PVC/DOS (1:2) membranes containing 1% wt FeMeOPP and 20 mol% (relative to ionophore) of TDMACl.

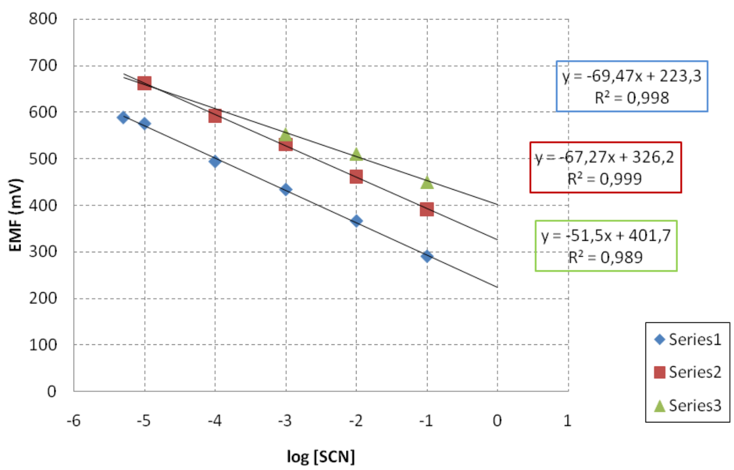

Figure 4. Potentiometric responses to thiocyanate of electrodes with membranes containing FeMeOPP and different plasticizers.

Analyzing the values of the slopes presented in figure 4 it results that near-Nernstian values were obtained for the sensors plasticized with o-NPOE and DOP. The slope is sub-Nernstian for the sensor plasticized with DOS with a narrow linear range. The best linear range has the sensor no 1, from 1x10-1 to 5x10-6 M.

Because thiocyanate is the interest anion, the selectivity coefficients log KSCN,Y- were calculated and are presented in table 1:

Table 1

Selectivity coefficients toward nitrite for membrane electrodes containing different plasticizers

Plasticizer	$\log K^{pot}_{SCN,Y}$							
	NO_2^-	ClO_4^-	SCN^-	NO_3^-	Sal^-	I^-	F^-	Cl^-
o-NPOE	-3,33	-0,06	0	-2,92	-0,10	-1,54	-5,87	-4,00
DOP	-2,77	-0,63	0	-2,53	-0,85	-1,53	-3,74	-3,28
DOS	-1,34	+0,22	0	-1,22	-0,85	-0,44	-2,42	-1,97

From the point of view of selectivity coefficients, good results were obtained also for sensors plasticized with o-NPOE and DOP. So, we can conclude that the sensor having the optimum composition of the membrane is sensor 1, plasticized with *o*-NPOE and having cationic additive added.

CONCLUSION

1. 5,10,15,20-tetrakis-(3,4-dimethoxyphenyl)-porphyrin-Fe(III) (FeMeOPP) was used as ionophore in polymeric membranes ion-selective sensors.
2. Both types if additives were used to establish the working mechanism of the sensor.
3. It results that the ionophore acts as a neutral carrier.
4. Different types of plasticizers were also used in the membranes.
5. The best potentiometric results: linear range, selectivity coefficients and slope were obtained for the sensor with the composition 1% ionophore, 66% o-NPOE, 33% PVC and 20 %mol. relative to the ionophore.
6. The sensor is thiocyanate-selective.

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