Thiocyanate-selective electrode based on rhodium porphyrin derivates

D. VLASCICI[a], O. SPIRIDON BIZEREA[a], E. FĂGĂDAR-COSMA[b*]

[a]*West University of Timisoara, Faculty of Chemistry – Biology – Geography, Inorganic Chemistry Department, Pestalozzi Street, No. 16, 300115 - Timisoara, Romania*
[b]*Institute of Chemistry –Timişoara of Romanian Academy, M. Viteazul Ave, No. 24, 300223-Timişoara, Romania*

The potentiometric response properties of an anion-selective electrode based on meso–tetraphenylporphyrin–rhodium(III) chloride as a novel ionophore incorporated into plasticized polyvinyl chloride (PVC) membranes were investigated. The effects of lipophilic cationic and anionic additives on the response characteristics were investigated. The testing of the electrode shows that the sensitivity, selectivity, detection limit and working range are strongly dependent of the type and concentration of the used additives. Membrane electrodes with added lipophilic cationic sites exhibit reversible and near-Nernstian response toward thiocyanate ions in the concentration range of 10^{-5}–10^{-1} M, with a good stability in time. The electrodes were successfully applied to the potentiometric determination of thiocyanate in human biological samples (urine and saliva).

1. Introduction

In the last years, a number of ion-selective electrodes that can recognize specific anions by chemical methods have been developed. The potentiometric response of these electrodes is very different from that of the conventional electrodes.

The electrodes based on anion-exchangers such as quaternary ammonium salts have selectivity patterns always correlated with anion lipophilicity and the result is the classical Hofmeister [1] series based on anion free energy of hydration:

$$ClO_4^- > SCN^- > Salicylate^- > I^- > NO_3^- > Br^- > NO_2^- > Cl^- > F^-$$

Therefore, highly hydrated anions are difficult to monitor due to significant interference with more lipophilic anion species that may be present in the sample. This is the reason why a number of compounds that have strong, but reversible interactions with target anions, are used as ionophores with non-Hofmeister selectivity for anions. Among them, metalloporphyrins offer many interesting possibilities. Various valence metallo-porphyrins are inducing a unique anion selectivity (often significantly deviated from the classical Hofmeister sequence) when incorporated into plasticized PVC membranes [2-5]. The working mechanism of such membranes, based on metalloporphyrins as ionophores, is governed by the charge of the central metal ion within the porphyrin structure. It has been shown that electrode response and selectivity are enhanced by the addition of tetraphenylborate (TPB) derivatives, when the metallo-porphyrins are acting as charged carriers, while tetraalkylammonium species are required as additives for membrane doped with ionophores that act as neutral carriers [6].

In this paper, the potentiometric response of several electrodes based on tetraphenylporphyrin–rhodium(III) chloride (**1**) as ionophore is examined. Because the metallic cation has a trivalent charge and act 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. We used this electrode to determine thiocyanate in biological samples (saliva and urine), where the levels of thiocyanate indicate the amount of nicotine intoxication.

2. Experimental

Reagents

The ionophore rhodium(III) tetraphenylporphyrin chloride (RhTPPCl) **1** was synthesized and purified according to literature data [7] and characterized by UV-VIS, IR, ^{1}H-RMN spectra and elemental analysis [8]. PVC of high molecular weight and dioctylphtalate (DOP) were obtained from Merck and Aldrich. Trioctylmethylammonium chloride (TOMACl), 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 before use.

All aqueous solutions were prepared with salts of the highest available purity. The sample solutions for all potentiometric measurements consisted of sodium or potassium salts of the given anions in 0.05 M 4–morpholino–ethanesulfonic acid (MES), adjusted to pH 5.5 with NaOH.

Ion-selective electrode membrane formulation and EMF measurements

The composition of the PVC membranes was: 1 wt.% Rh-porphyrin **1**, 66 wt.% DOP, 33 wt.% PVC (plasticizer: PVC = 2:1). Various amounts of cationic (TOMACl) and anionic (NaTPB) additives (mol% relative to ionophore) were also used in the membrane.

First, the ionophore and the additive were dissolved in the solvent mediator. Then the PVC and a sufficient amount of THF were added and mixed to obtain a transparent solution. This mixture was transferred onto a glass plate of 20 cm^2, and the THF was allowed to evaporate at room temperature leaving a though flexible membrane trapped in a PVC matrix. The cast membranes were approximately 150 μm thick.

Potentiometric measurements were performed with the following galvanic cell:

Hg/Hg$_2$Cl$_2$/bridge electrolyte/sample/ion-selective membrane/Ag(Hg)/internal cable

The bridge electrolyte consisted of 0.1 M KNO$_3$. Prior to electromotive force (EMF) measurements, the electrodes were conditioned for 24 h in a 10 mM NaCl/0.01 mM NaSCN solution. All experiments were performed at ambient temperature (22 ± 2°C). Potentials were measured using a Hanna Instruments HI8817 pH/mV-meter. Potentiometric selectivity coefficients were determined according to the separate solution method [9] by using the experimental EMF values obtained for 0.1 M solutions of the test anions and a theoretical slope of -59.2 mV /pSCN for the primary anion. Activity coefficients were assumed to be constant for all analyzed anions, and no correction was made for the slight changes in the liquid junction potential of the reference electrode.

HCl and NaOH solutions having different concentrations were used to study the pH dependence of thiocyanate-selective electrode. The pH of the test solutions was measured using a glass electrode. The effect of the thiocyanate solution pH on the measured potential was followed by using solutions of NaSCN from 10^{-1} to 10^{-5} M in MES buffer having different values of pH: 4.5; 5.5; 6.5.

3. Results and discussion

The present work investigates, for the first time, the ability of rhodium(III) porphyrins to serve as anionic ionophores in polymeric membranes. In order to be considered an useful sensor for quantitative analysis of the ions, a membrane ion-selective electrode must exhibit certain characteristics, like: the slope, the selectivity, the limit of detection, the response time, lifetime and working pH range, which are presented below.

The potentiometric response characteristics of the liquid/polymeric membrane electrodes based on compound **1,** were determined using solutions in the concentration range of 10^{-5} to 10^{-1} M, of the following anions: ClO_4^-, SCN^-, NO_3^-, NO_2^-, I^-, Br^-, Cl^-, F^-, Salicylate$^-$ in 0.05 M of MES, adjusted to pH 5.5 with NaOH.

It is well known that the potentiometric response characteristics (slope, selectivity and linear dynamic range) of an ion-selective electrode depends not only on the nature of the ionophore, but also significantly on the membrane composition and the nature of the used additives. To establish the working mechanism of the membranes based on metalloporphyrin **1**, respectively to determine the type of the additive who needs to be added for the optimum potentiometric answer, a lot of membranes were prepared with and without additives in the membrane. The compositions and the corresponding potentiometric response properties of the various examined membrane formulations are presented in Table 1.

Table 1. Composition of the membranes and characteristics of the potentiometric response for primary anion.

Membrane	Ionophore	Ionic additives[a] (mol%)	Matrix	Primary anion	Slope (mV per decade)
A	RhTPPCl	-	PVC	SCN$^-$	-34,9
B	RhTPPCl	TOMACl 10%	PVC	SCN$^-$	-43,0
C	RhTPPCl	TOMACl 20%	PVC	SCN$^-$	-59,8
D	RhTPPCl	TOMACl 80%	PVC	SCN$^-$	-59,8
E	RhTPPCl	NaTPB 10%	PVC	SCN$^-$	-21,3
F	RhTPPCl	NaTPB 20%	PVC	SCN$^-$	-12,3

[a] Values relative to ionophore

The potentiometric responses of the membranes from A to F, having the compositions above mentioned, for thiocyanate are presented in Fig. 1.
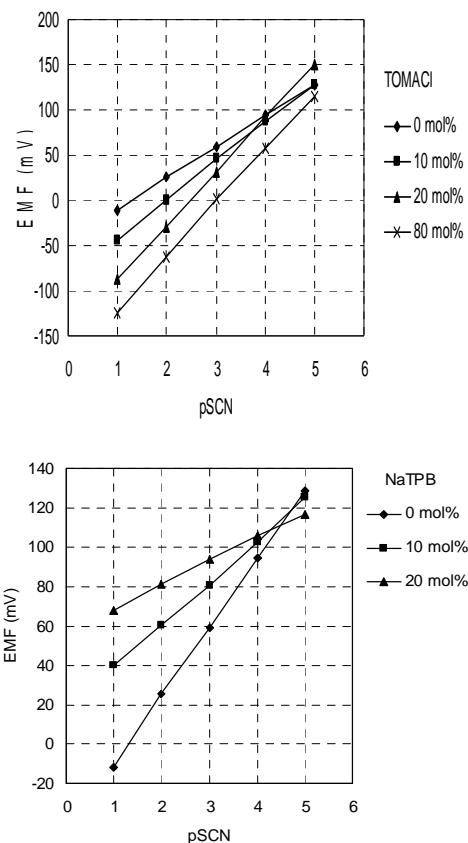

Fig. 1. The potentiometric responses of membranes A-F for thiocyanate.

One of the most important characteristics of any ion-selective electrode is the relative response for the primary ion over other ions that may be present in solution, and is expressed in terms of potentiometric selectivity coefficients. We have compared the potentiometric selectivity of the membranes A-F based electrodes. The results are presented in Fig. 2.

As it can be seen from Figs. 1, 2 and Table 1, with the incorporation of TPB$^-$ sites in RhTPPCl based ion-selective electrodes, the resulting selectivity patterns exhibited are similar to the Hofmeister series, the electrodes showing more tendency for the highly lipophilic anions, and the tendency increases at higher concentrations of this additive. The slopes were sub-Nernstian for thiocyanate ion but the linear range of the calibration plots was not affected.

Upon the addition of TOMA$^+$ as cationic sites, the selectivity pattern shifts, and the potentiometric response of the membrane is greatly improved, the electrodes behaving Nernstian, with a linear range of about 10^{-5} to 10^{-1} M thiocyanate concentration. However, when the ratio additive/ionophore was considerably increased, perchlorate became the primary anion.

Such changes in the selectivity pattern due to the addition of ionic additives, indicate that compound **1** functions as a neutral carrier in PVC films while the incorporation of trioctylmethylammonium chloride (TOMACl) as a cationic additive in the membranes results in an enhancement of the anionic response toward thiocyanate.

The highest preference for thiocyanate over perchlorate occurs for membranes containing 20 mol% TOMACl relative to the metalloporphyrin **1**. The potentiometric response of the electrode having the optimal membrane composition (membrane C) for various anions is presented in Fig. 3.
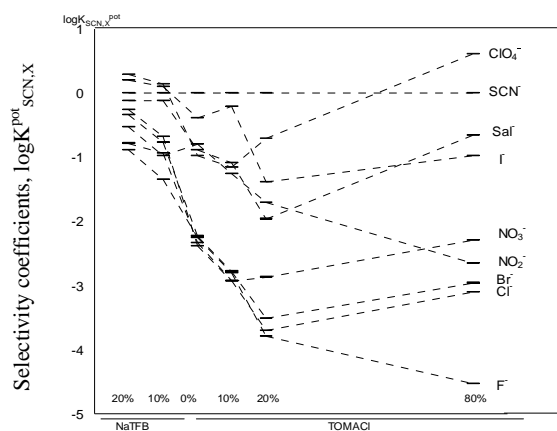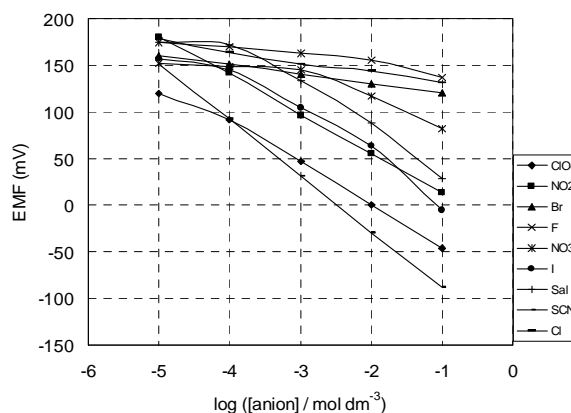

Fig. 3. Potentiometric anion responses of the electrodes prepared with a membrane having the optimal composition.

The average time for the thiocyanate-selective electrode to reach 95% of the final potential value after successive immersion of the electrode in a series of thiocyanate ion solutions, each having a 10-fold difference in concentration, was measured. Fig. 4 presents the potential plotted versus time, as the concentration of thiocyanate was changed from 10^{-4} to 10^{-3} M. The obtained response time was about 70 s. For lower concentrations of the solution the response time was the same, but it became longer for concentrated solutions.
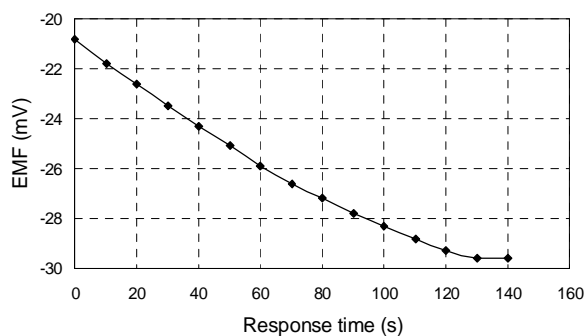

Fig. 4. The response time of thiocyanate-selective electrode with respect to the change of the thiocyanate concentration from 10^{-4} to 10^{-3} M.

The dynamic response of the electrode after a month of intensive use is presented in Fig. 5. It was obtained by measuring the response time of the electrode from low to high concentrations and vice versa. As it can be seen, after a month of intensive use, the response time and reversibility remain excellent.
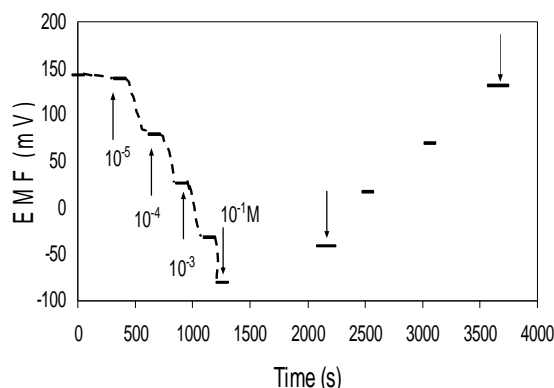

Fig. 2. Selectivity coefficients, log $K_{SCN,X}^{pot}$, for electrodes prepared with PVC/DOP (1:2) membranes containing Rh–porphyrin 1 and ionic additives in different concentrations (mol% relative to the ionophore).

Fig. 5. Dynamic potentiometric response to thiocyanate and recovery time for a 1 month old electrode.

Fig. 6. Evolution of slopes in time.

Fig. 7. The pH dependence of RhTPP-based electrode.
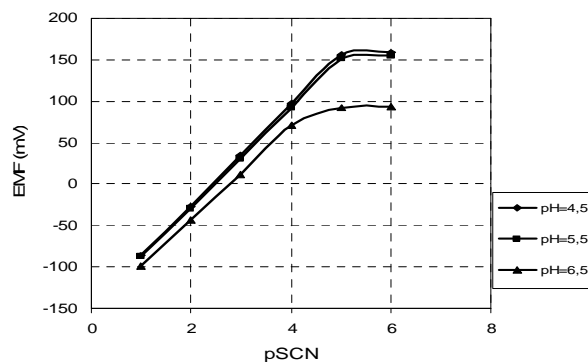
Fig. 8. The effect of sample pH on the potentiometric response to thiocyanate.
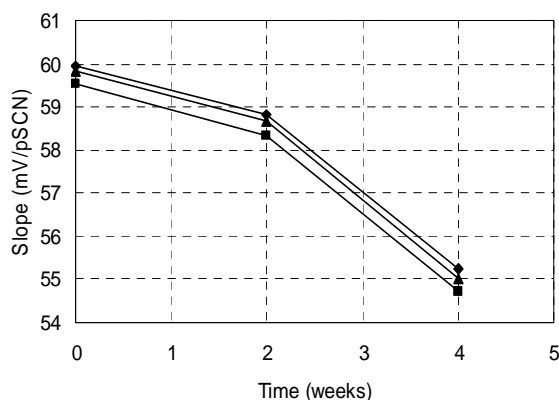
The evolutions of the thiocyanate-selective electrode slopes in time, measured for three electrodes having the optimum composition of the membrane, is presented in Fig. 6. There was a little decrease of the slope in time, but it still remains, after a month of intensive use, in the analytical useful range of 50-60 mV/pSCN (respectively 55.1 ± 0.5 mV per decade).

A distinctive feature of metalloporphyrin-based electrodes is their pH dependence of the potential, which limits sometimes their practical application. The pH dependence of Rh−porphyrin **1** based electrodes, having the optimal composition of the membrane, is presented in Figs. 7 and 8.

From Fig. 8 it can be seen that the detection limit of the electrode depends on the pH sample. Literature data [10] provide that there are two different mechanisms which govern the pH dependence of the metalloporphyrin-based electrodes. At high pH values, the HO^- and SCN^- anions are in a strong competing ligation with the central Rh(III) ion of the porphyrin. Since the pH value is higher, the hydroxyl concentration grows and the potentiometric answer of the electrode can deviate from linearity.
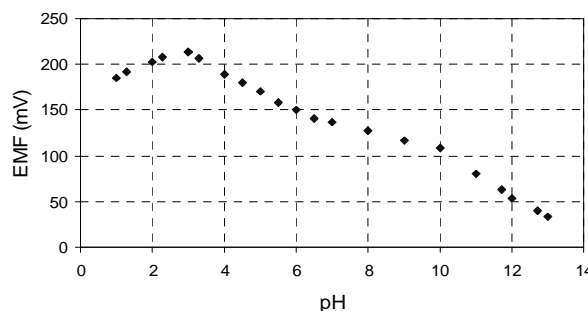
In acid media, where the hydroxyl concentration is low, the electrode responds probably to H^+ ions because the membranes contain neutral carriers of amine nature. Such a nature is intrinsic to free tetraphenylporphyrin which can be present in the membrane as an impurity in the initial ionophore, or may appear in the membrane surface layer as a result of partial demetallation of the metalloporphyrin complex **1** during the membrane contact with the low pH test solution.

Analytical application

In human biological samples (saliva and urine), elevated levels of thiocyanate are correlated with excessive nicotine intoxication [11]. The analytical control of thiocyanate in these samples can be potentiometrically made by using an ion-selective electrode. The high degree of thiocyanate selectivity exhibited by the electrodes based on Rh(III) porphyrin **1** makes them potentially useful for this purpose.

For the potentiometric determination of thiocyanate in urine and saliva, measurements were carried out by standard addition method and direct potentiometry on two types of samples: one from a cigarette smoker and the other from a non-smoker. The samples were diluted by a factor of 10 with MES buffer at pH 5.5. The results were compared with a colorimetric method used as the reference method, and are presented in Table 2.

As it can be seen from Table 2, there is a good agreement between the potentiometric and colorimetric procedures.

Table 2. Results of the analysis of biological fluids.

Sample	Method	Non-smoker		Smoker	
		SCN⁻ (mol/L) ± S^a	RSD (%)	SCN⁻ (mol/L) ± S^a	RSD (%)
Urine	Direct potentiometry	$(3.0 \pm 0.2) \times 10^{-4}$	6.7	$(8.9 \pm 0.3) \times 10^{-4}$	3.4
	Potentiometry (standard addition method)	$(3.1 \pm 0.2) \times 10^{-4}$	6.5	$(9.0 \pm 0.2) \times 10^{-4}$	2.2
	Spectrophotometry	$(3.3 \pm 0.2) \times 10^{-4}$	6.1	$(9.2 \pm 0.3) \times 10^{-4}$	3.3
Saliva	Direct potentiometry	$(5.1 \pm 0.3) \times 10^{-4}$	5.9	$(1.6 \pm 0.2) \times 10^{-3}$	12.5
	Potentiometry (standard addition method)	$(5.2 \pm 0.2) \times 10^{-4}$	3.9	$(1.6 \pm 0.1) \times 10^{-3}$	6.3
	Spectrophotometry	$(5.3 \pm 0.2) \times 10^{-4}$	3.8	$(1.7 \pm 0.2) \times 10^{-3}$	11.8

[a] Average of determinations on three samples of the same origin

4. Conclusions

The results of the present study show that electrodes having compound **1** as ionophore in *o*-nitrophenyloctylether plasticized PVC membranes, realized with an internal electric solid contact, exhibit a relatively high selectivity for thiocyanate over many anions. The ionophore act as neutral carrier in the membrane, therefore a lipophilic cationic derivative is required as a membrane additive to optimize potentiometric selectivity for thiocyanate over other anions. Anionic additives change the sensitivity of the electrode response and decrease the selectivity for thiocyanate with respect to the more lipophilic anions such as perchlorate.

The best composition of the membrane was found to be the one with 20 mol% TOMACl as additive. The electrodes having the optimal composition of the membrane exhibit fast and reversible responses to thiocyanate and a near-Nernstian value of the slope. The electrodes were successfully used to determine thiocyanate in biological fluids.

References

[1] E. D. Steinle, U. Schaller, M. E. Meyerhoff, Anal. Sci. **14**, 79 (1998).
[2] E. Malinowska, J. Niedziolka, M. E. Meyerhoff, Anal. Chim. Acta **432**, 67 (2001).
[3] N. A. Chaniotakis, A. M. Chasser, M. E. Meyerhoff, J. T. Groves, Anal. Chem. **60**, 185 (1988).
[4] E. Malinowska, M. E. Meyerhoff, Anal. Chim. Acta **300**, 33 (1995).
[5] E. Malinowska, J. Niedziolka, E. Rozniecka, M. E. Meyerhoff, J. Electroanal. Chem. **514**, 109 (2001).
[6] E. Bakker, E. Malinowska, R. D. Schiller, M. E. Meyerhoff, Talanta **41**, 881 (1994).
[7] K. S. Tse, B-M. Wu, T. C. W. Mak, K. S. Chan, J. Organomet. Chem. **568**, 257 (1998).
[8] D. Vlascici, E. Făgădar-Cosma, O. Spiridon-Bizerea, A. Pascariu, A. Chiriac, Rev. Chim.- Bucharest **56**(3), 224 (2005).
[9] Y. Umezawa, K. Umezawa, P. Buhlmann, N. Hamada, H. Aoki, J. Nakanishi, M. Sato, K. P. Xiao, Y. Nishimura, Pure Appl. Chem. **74**(6), 923 (2002).
[10] V. V. Egorov, E. M. Rakhman'ko, A. A. Rat'ko, J. Anal. Chem. **57**(1), 46 (2002).
[11] J. H. Khorasani, M. K. Amini, H. Motaghi, S. Tangestaninejad, M. Moghadam, Sensors Actuators B, **87**, 448 (2002).

_____

* Corresponding author: efagadar@yahoo.com