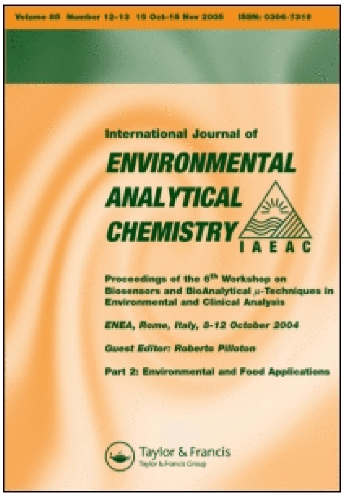

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Thiocyanate-selective membrane electrode based on cobalt(III) Schiff base as a charge carrier

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To cite this Article Shokrollahi, Ardeshir , Ghaedi, Mehrorang , Ghaedi, Hamed and Kianfar, Ali Hossein(2008) 'Thiocyanate-selective membrane electrode based on cobalt(III) Schiff base as a charge carrier', International Journal of Environmental Analytical Chemistry, 88: 12, 841 — 856

To link to this Article: DOI: 10.1080/03067310802123981

URL: http://dx.doi.org/10.1080/03067310802123981

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 12, 15 October 2008, 841–856

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Thiocyanate-selective membrane electrode based on cobalt(III) Schiff base as a charge carrier

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(*Received 17 October 2007; final version received 19 March 2008*)

A highly selective polyvinylchloride (PVC) membrane electrode based on Schiff base complex i.e. [Cobalt (Salpen) (PBu_3)] ClO4 · H2O (Salpen = bis(salycil aldehyde)propylene diamine) is reported as new carrier for thiocyanate selective electrode by incorporating the membrane ingredients on the surface of graphite electrodes. The proposed electrode possesses a very wide Nernestian linear range to thiocyanate from 1.0×10^{-6} to 1.0×10^{-1} M with slope of -59.05 ± 0.91 mV per decade of thiocyanate concentration, very low detection limit (8.0×10^{-7} M) and good thiocyanate selectivity over the wide variety of other anions. Fast and stable response, good reproducibility, long-term stability, applicability over a wide pH range (2.8–9.8) are advantages of the reported electrode. The sensor has a response time of <5 s and can be used for at least 14 weeks without any considerable change in respective potential response. The proposed electrode was used for the determination of thiocyanate in saliva, wastewater and human urine with satisfactory results and good agreement with colorimetric as reference method.

Keywords: thiocyanate-selective electrode; potentiometric titration; [cobalt (Salpen) (PBu_3)] $ClO_4 \cdot H_2O$, coated-graphite electrode

1. Introduction

The thiocyanate ion is usually present in low concentrations in human serum, saliva and urine as a result of the digestion of some vegetables of the brassica genus containing glucosinolates (cabbage, turnip, kale) [1] or by intake of thiocyanate-containing foods such as milk and cheese [2]. Higher concentrations of this ion, which is a metabolic product of cyanide, arise from tobacco smoke [1,2]. In this respect, the level of thiocyanate content is a good probe for distinguishing smokers from non-smokers. It has been found that there is a correlation among the blood cyanide, the plasma thiocyanate and the salivary thiocyanate [3]. Therefore, the development of an accurate, simple and rapid method for the determination of thiocyanate in various complicated matrixes in medicine and in life sciences is necessary [4].

Ion-selective electrodes (ISEs) have grown substantially over recent years and were widely used for the direct and rapid analytical detection of inorganic and organic ions due to their potentiometric response characteristics such as relatively fast response, wide linear response range, low detection limit, reasonable selectivity and low cost [5,6].

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802123981
http://www.informaworld.com

A simple, cheaper and convenient method with fast response is required for the analysis of large numbers of environmental and other samples. Analysis by ion-selective sensor provides such procedures [6,7]. Ion-selective electrodes based on solvent polymeric membranes with incorporation of ion carriers are shown to be very useful tools for chemical, clinical and environmental analyses as well as in process monitoring [8,9].

Several reported thiocyanate selective electrodes have been based mainly on lipophilic cationic salts, quaternary ammoniums, organometallic compounds, Vitamin B_{12} derivatives, metallo-porphyrins and Schiff base complexes [11–26].

Unfortunately, most of these electrodes have one, two or, in some cases, all of the following problems: (a) narrow linear ranges; (b) high detection limit; (c) long response time; (d) instability; and/or, (e) serious interfering effect from anions such as ClO_4^-, NO_3^-, Br^-, and Cl^-.

In order to overcome some of these limitations, a thiocyanate selective electrode is developed in this work, based on plasticized PVC membranes, containing [Cobalt (Salpen) (PBu_3)] ClO4 · H2O (Salpen = *bis*(salycilaldehyde)propylene diamine) with high tendency toward thiocyanate as the membrane active ingredients coated on the surface of graphite disk electrode. The influence of effective parameters such as selectivity for a variety of ions and the effect of membrane matrix, ionophore concentration, additives, and pH on the potentiometric response properties of the proposed electrode were investigated.

2. Experimental

2.1 *Reagents*

Reagent grade dibutylphthalate (DBP), sodium tetraphenyl borate (NaTPB), dioctylphthalate (DOP), 4-nitrophenylocthyl ether (NPOE), dimethyl sebacate (DMS), tetrahydrofuran (THF), high relative molecular weight polyvinylchloride (PVC) and methyltrioctyl ammonium chloride (MTOAC) were procured from Aldrich and were used as received, while THF was distilled before use. Sodium and potassium salts of anions (all from Merck) were of the highest purity available and used without any further purification. The complexes presented in scheme 1 were synthesised following the schemes in the literature [27].

All aqueous solutions were prepared with deionised distilled water. The pH adjustments were made with dilute nitric acid or potassium hydroxide solutions as required.

2.2 *Preparation of electrodes*

The coated-graphite electrodes were prepared according to previously published methods [28,29]. Graphite rods (3 mm diameter and 10 mm long) were prepared from spectroscopic grade graphite. A shielded copper wire was glued to one end of the graphite rod with silver loaded epoxy resin and the rod was inserted into the end of a PVC tube. The working surface of the electrode was polished with a polishing cloth. The electrode was rinsed with water and methanol and allowed to dry. A mixture of PVC, plasticizer and the membrane additive (MTOAC) was dissolved in about 4 mL of THF. To this mixture was added the electroactive material L1 with a total mass of 100 mg, and the solution was mixed well. The polished graphite electrodes were then coated by repeated dipping (several times, a few minutes between dips), into the membrane solution. A membrane was formed on the graphite surface which was allowed to set overnight. The electrodes were rinsed with water and conditioned for 18 h in 0.05 M potassium thiocyanate solution for L1. The coating solutions are stable for several weeks if kept in refrigerator and can be used for the construction of new membranes.

2.3 *Potential measurement*

The response characteristics of the prepared coated graphite electrodes were determined by recording potential across the membrane as a function of thiocyanate concentration at a constant temperature of 25°C. All the potential and pH measurements were carried out with a pH/Ion meter model 691 (Metrohm). The potential build up across the membrane electrode was measured using the galvanic cell of the following type: $Hg/Hg_2Cl_2/KCl$ (sat′d) || test solution | PVC membrane | Graphite electrode. The performance of each electrode was investigated by measuring its potential in potassium thiocyanate solutions prepared in the concentration range 1.0×10^{-7} to 1.0×10^{-1} M by serial dilution of the 0.5 M stock thiocyanate solution at constant pH. The solutions were stirred and potential readings recorded when they reached steady state values. The data were plotted as observed potential versus the logarithm of the thiocyanate ion concentration.

2.4 *Procedure for the determination of thiocyanate in water and urine samples*

Urine, saliva and wastewater samples containing different thiocyanate concentrations were prepared by adding known amounts of thiocyanate to blank urine, saliva and wastewater. 5 ml of samples was added and the pH was adjusted to 5.2 by the addition of HNO_3 or KOH and the solution was diluted to 50 ml with distilled water. The thiocyanate-selective and reference electrodes were immersed and the thiocyanate concentration was determined by potentiometry using the standard addition technique.

2.5 *Spectrophotometric titration*

Standard stock solutions of complex (0.002 M) and the thiocyanate ions (0.02 M) were prepared by dissolving appropriate and exactly weighed (with an accuracy of 0.0001 g) pure solid compounds in pre-calibrated 25.0 ml volumetric flasks and diluted to the mark with methanol. Working solutions were prepared by appropriate dilution of the stock solutions. According to the spectra reported in Figure 1, titration of the complex solution (0.002 M, 2.1 ml) was carried out by the addition of microlitre amounts of a standard solution of the thiocyanate ion in acetonitrile (0.02 M) using a pre-calibrated micropipette, followed by absorbance intensity reading at 25.0°C at the related λ_{max}. Since the volume of titrant added during titration was negligible (at the most 0.05 ml) as compared with the initial volume of the ligand (2.1 ml), no volume correction was carried out.

3. Results and discussion

The potentiometric response of L1-L4 PVC-based membranes conditioned for thiocyanate as principal anion under similar conditions has been examined and the corresponding results are presented in Figure 2. The square planar structure and square pyramidal M(II) and M(III) complexes (where M(II) = Cu and M(III) = Co(III)) as

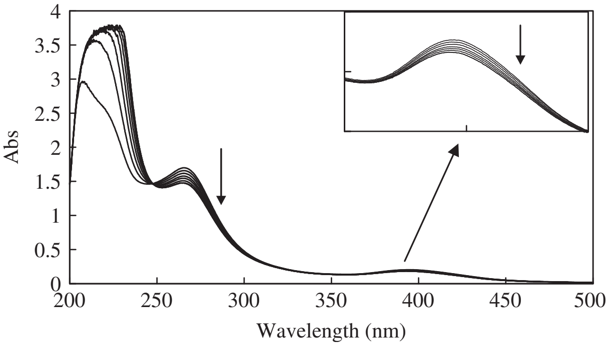

Figure 1. UV–Vis spectra of 0.002 M Co-salpen complex after increasing addition of thiocyanate to methanol solutions.

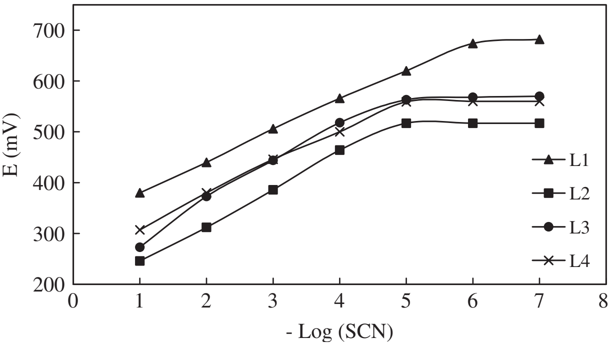

Figure 2. Potentiometric response characteristics of PVC membranes with various carriers.

carriers has been incorporated in the PVC membrane to prepare electrodes with significant potentiometric selectivity toward thiocyanate. Such complexes, in the presence of polar solvent molecules or anions, prefer to increase their coordination number to 5 or 6, by direct interaction of solvent or anions to central metals. As it can be seen from Figure 2, among them, L1 ionophore has Nernstian response, wide linear range and lower detection limit, while the potentiometric response characteristics of the electrodes based on L2, L3, and L4 are poor (Figure 3 shows the structure of the ionophores used). These difference in potentiometric response characteristics indicate the influence of the chemical environment of the ionophore (especially a certain substituent) on the characteristic performances of the electrode. The results also demonstrate that the substituents on the Schiff base structure indeed have a significant effect on the thiocyanate response. It appears that the hydrophobic character of the substituents around the coordination sites improved the response toward SCN^-. In this regard, among the different membranes studied, those based on Co-Salpen generally show the best potentiometric response for thiocyanate. It seems that, the propyl group substituents in L1 will provide a more hydrophobic environment around the coordination sites and a resulting marked increase in its response to thiocyanate [30].

The electronic and steric hindered effects of these complexes are responsible for such differences in the electrodes response. The L1–L3 group has a five-coordinated structure

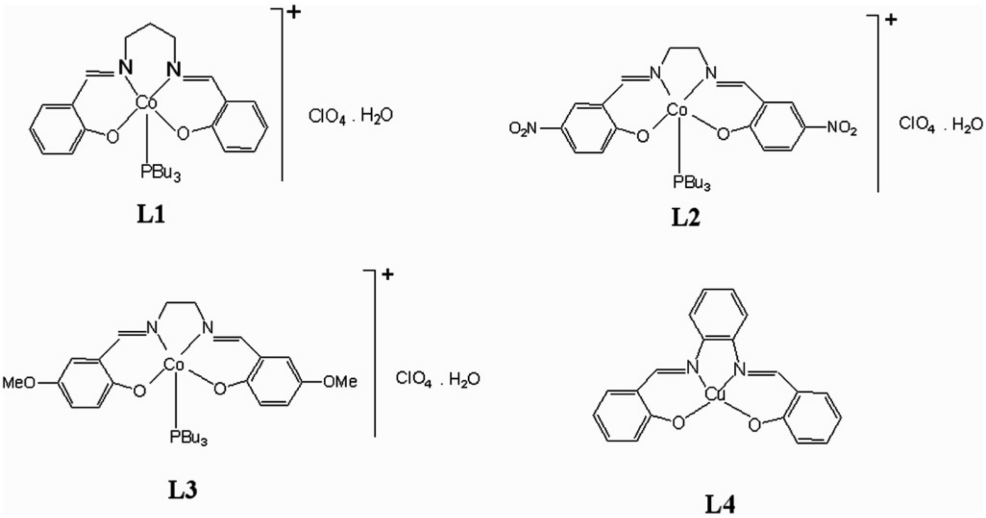

Figure 3. Structure of ionophores used.

and can interact with the other ligands like anions, phosphins, phosphates and amines [31–36] or water to occupy the six positions of such complexes with a week interaction. The interaction of other anions with such complexes is related to the water mole fraction in solution and decreases with increasing water mole fraction [32,34]. Such five-coordinated complexes in the presence of H_2O molecule formed a six-coordinate complex, according to Equation (1).

$$[\mathrm{Co(Chel)(PBu_3)}]^+ + \mathrm{H_2O} \leftrightarrow [\mathrm{Co(Chel)(PBu_3)(OH_2)}]^+ \tag{1}$$

In the presence of SCN^-, six positions could be occupied in a competition reaction according to Equations (2) and (3) (a competition between H_2O and thiocyanate ion for interaction with five-coordinate complexes).

$$[\mathrm{Co(Chel)(PBu_3)}]^+ + \mathrm{H_2O} \leftrightarrow [\mathrm{Co(Chel)(PBu_3)(OH_2)}]^+ \tag{2}$$

$$\updownarrow \mathrm{NCS} - [\mathrm{Co(Chel)(PBu_3)(NCS)}] \tag{3}$$

It seems that in the complexes used, the interaction of L1 with thiocyanate in comparison to the other complexes is stronger [32,34,36].

When cobalt complexes have been incorporated in the membrane as ionophores, anions such as iodide and thiocyanate could be bound to them selectively. Preliminary experiments were performed to determine whether the corresponding ionophore (L1) cobalt complex could serve as useful chelating agent for complexing trace amounts of thiocyanate in methanol. To assess this possibility, 0.002 M Co-Salpen complex in methanol was used for quantitative complexation by adding various amounts of thiocyanate and other common inorganic and organic ions after 30 s shaking time.

The spectrum of Co-Salpen in methanol shows an absorption band at 264 and 393 nm. As it can be seen in Figure 1, a decrease in the peak at about 264 and 393 nm is observed upon addition of increasing quantities of thiocyanate ion to Co-Salpen solution, which could be attributed to the complexation between the ligand L1 and SCN^- ion. Since the changes in the spectrum of the cobalt ionophore (as previously reported for other anions with cobalt complexes) is only observed at high concentrations of thiocyanate with respect to ionophore, it is not possible to obtain the mole ratio of the L1-SCN complex.

On the other hand, the Co(III) ion is a hard acid and it is expected to prefer thiocyanate by linkage through nitrogen atom via reaction 3. The higher lipophilicity of thiocyanate with respect to cyanide favours the conditions for migration of thiocyanate to the membrane. The complexes studied here are five-coordinate and have a highly trans effect for PR_3 [34,36], which provide the proper conditions for occupying the six positions by ligands like NCS^-, ClO_4^- and CN^- in an equilibrium reaction. It seems that weak ligands like NCS^- can react with the complexes with high trans effect better than the CN^- strong ligand.

This indicates a preferred interaction between Co(III) metal-ion centre of the ionophore and SCN^- anions in comparison with the interactions with other anions. This finding is consistent with previously reported membrane electrodes based on different Co(III) lipophilic complexes (e.g., Co(III) complexes of porphyrins and phthalocyanines that exhibited enhanced potentiometric responses toward SCN^- [31–38].

Due to the interaction of the ionophore with thiocyanate and the relatively strong response of MTOAC to thiocyanate as an ion-exchanger, the slope of the sensor will be close to the Nernstian values. The ion carrier L1 was used as a potential carrier to prepare the plasticized PVC-based membrane electrode for a large number of anions. The potential responses of the electrodes are shown in Figure 4. As can be seen, the membrane sensors displayed a remarkable response for thiocyanate over other anions. As well as the critical nature of the ionophore used in the membrane preparation, the amount of ionophore, the nature of solvent plasticizer, the plasticizer/PVC ratio and, especially, the nature of the additive used, significantly influence the sensitivity and selectivity of an ion-selective electrode [13–16]. The presence of lipophilic positively charged additives improves the potentiometric behaviour of certain selective electrodes by reducing the ohmic resistance [23,39] and improving the response behaviour and selectivity [40,41]. In the presence of additive, especially when the extraction capability of the ionophore is poor, the sensitivity of the membrane electrode response is improved [42].

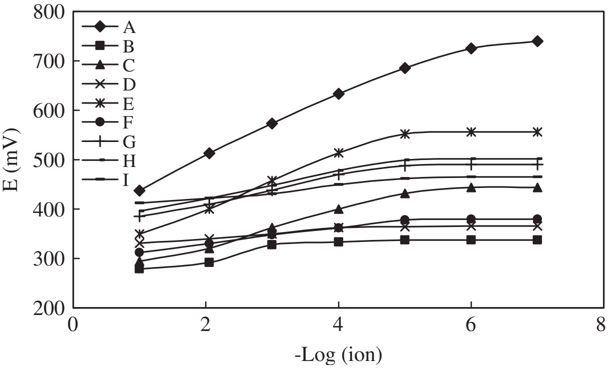

Figure 4. Potential responses of ion-selective electrode based on Co-salpen complex for various anions.
Notes: A, SCN^-; B, Imidazol; C, I^-; D, $C_2O_4^-$; E, ClO_4^-; F, NO_2^-; G, Cl^-; H, Br^-; I, CrO_4^{2-}.

Moreover, the additives may catalyze the exchange kinetics to the sample–membrane interface. The influence of the type and concentration of the membrane additives were also investigated by incorporating MTOAC or NaTPB into the membranes [26].

The potentiometric response of the membranes based on carriers was greatly improved in the presence of the lipophilic cationic additive, MTOAC, compared to the membranes with no additive at all, but no response was observed when the anionic additive was incorporated into the membranes. The effect of MTOAC concentration in the membranes was investigated at several additive/carrier mole ratios. The electrode with MTOAC/carrier mole ratios of ca. >1 showed Nernstian response in a wide range of thiocyanate concentration. The response of the blank membrane containing additive but no carrier had low linear range. On the basis of the above discussions, it seems that the ionophore act as charge carrier in the membranes. Membrane electrodes generally contain 60–70% wt. of a plasticizer, so the dielectric constant, ε, is similar to that of the pure liquid plasticizer. The characteristic performance of electrodes with different composition of membrane ingredients such as different plasticizers and additive are presented in Table 1. Among the different used plasticizers (NPOE, DBP, DMS, DOP), DOP is a more effective solvent mediator in preparing the thiocyanate selective membrane electrode. It should be noted that the nature of the plasticizers influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex. The binding of the coordinating anion such as thiocyanate with the metal centres of the complexes is expected to be stronger as the polarity of the solvents decreases. The less polar membrane solvent is more suitable for the anti-Hofmeister behaviour of a given anion ionophore. The amount of ionophore was also found to affect the response of the membrane electrode (Table 1). The sensitivity of the electrode response increased with the increase in the ionophore content up to 2 mg.

Table 1. Response performance of the thiocyanate ion-selective electrodes.

No.	Plasticizer*	PVC	Ionophore	MTOAC	LR[a]	S[b]	RT (S)[c]
1	–	32.4	2.0	0.6	10^{-4}–0.05	28.3	
2	65.0 (DOP)	32.4	2.0	0.6	10^{-6}–0.1	56.06	<15
3	65.0(DMS)	32.4	2.0	0.6	10^{-5}–0.1	54.02	<10
4	65.0 (DBP)	32.4	2.0	0.6	5×10^{-4}–0.1	52.23	<18
5	65.0(NPOE)	32.4	2.0	0.6	5×10^{-4}–0.1	54.45	<30
6	66.0 (DOP)	33.4.	–	0.6	10^{-5}–0.01	51.33	<15
7	65.8 (DOP)	32.9	1.0	0.3	10^{-5}–0.05	46.71	<10
8	64.1 (DOP)	32.0	3.0	0.9	5×10^{-6}–0.1	41.11	<10
9	63.2 (DOP)	31.6	4.0	1.2	10^{-6}–0.05	40.05	<10
10	65.3 (DOP)	32.7	2.0	–	5×10^{-5}–0.05	38.7	–
11	64.8 (DOP)	32.2	2.0	1.0	10^{-5}–0.1	52.43	<10
12	64.3 (DOP)	31.7	2.0	2.0	10^{-6}–0.1	58.63	<5
13	63.8 (DOP)	31.2	2.0	3.0	10^{-5}–0.1	54.05	<5
14	54.3 (DOP)	41.7	2.0	2.0	10^{-5}–0.1	50.09	<5
15	59.3 (DOP)	36.7	2.0	2.0	10^{-5}–0.1	51.91	<5
16	62.3 (DOP)	33.7	2.0	2.0	5×10^{-5}–0.1	54.91	<5
17	65.3 (DOP)	30.7	2.0	2.0	10^{-6}–0.1	59.05	<5
18	65.3 (DOP)	30.7	2.0	(NaTPB)	10^{-2}–0.1	16.2	

Notes: Various membrane compositions, conditioned 18 h in 0.05 M KSCN;
*All membrane compositions are presented in percentage; [a]linear range (M); [b]slope (mV per decade concentration); [c]response time.

However, further addition of the ionophore will result in the response of the electrode diminishing, probably due to some inhomogenities and possible saturation of the membrane [43].

The optimised membrane compositions and their potentiometric response characteristics are given in Table 2. The membrane electrode prepared could be used for at least 14 weeks without any considerable divergence in potentials. The potentiometric response of the thiocyanate electrode was found to be sensitive to pH changes. Thus, the pH dependency of the potential of the proposed electrode for 1.0×10^{-3} and 1.0×10^{-4} M thiocyanate was determined over the pH range of 1.5 to 11.5. The results given in Figure 5 show that the potential response remains constant over the pH range of 2.8 to 9.8. The significant change in potential response at pH values <2.8 can be due to simultaneous response of the electrode to the oppositely charged H_3O^+ and SCN^- ions. The contribution of H_3O^+ to potential response counteracts that of SCN^- ions. The observed potential drift at high pH values could be due to the response of the sensor to OH^- and SCN^- ions. The response time of the electrode was determined by measuring the time required to achieve a 90% of the steady state potential. The static response time thus obtained was 5 s over the entire concentration range (Figure 6).

Table 2. Response characteristics of the proposed thiocyanate selective electrode.

Properties	Values/range
Optimised membrane composition	PVC: plasticizer: ionophore: MTOAC (30.7 : 65.3 : 2 : 2)
Electrode type	Coated-graphite electrode
pH range	2.8–9.8
Conditioning time	At least 18 h in 0.05 M KSCN
Linear range (SCN^-, M)	1.0×10^{-6}–1×10^{-1}
Slope (mV/decade)	-59.05 ± 0.91
Detection limit (M)	8×10^{-7}
S.D of measurement	±0.61 at 1×10^{-3} M & ±0.32 at 1×10^{-2} M
S.D of slope (mV decade $^{-1}$)	±0.91
Response time (s)	5
Life time of the electrode	At least 14 weeks

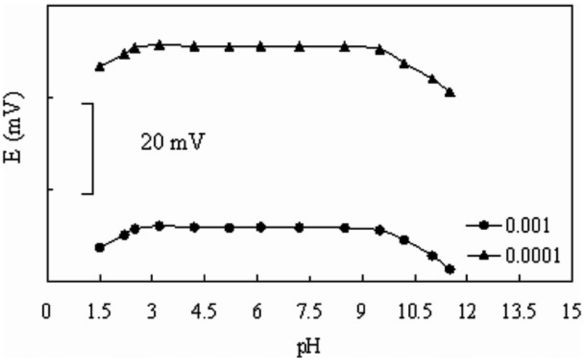

Figure 5. Effect of pH of the test solution on the potential response of the SCN^--selective electrode.

The potentiometric response of the electrodes was examined in the concentration range 1.0×10^{-7} to 1.0×10^{-1} M. As it is obvious from the calibration plot presented in Figure 7, the response of the proposed electrode is linear over the concentration range of 1.0×10^{-6}–1.0×10^{-1} M, with a detection limit of ca. 8×10^{-7} and sensitivity of 59.05 ± 0.91 mV/decade of thiocyanate concentration.

3.1 *Selectivity of the electrodes*

The potentiometric selectivity coefficient ($K^{\mathrm{Pot}}_{\mathrm{SCN^-,B}}$) is one of the most important characteristics of an ion-selective electrode [44–51]. In the present work it has been determined by the matched potential method (MPM) and separation solution method [44,52,53].

According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion ($A = 1.0 \times 10^{-5}$ M thiocyanate ions) and the interfering ion ($B = 10^{-2}$ M) that gives the same potential change in a reference solution (1.0×10^{-6} M of thiocyanate ions). In the first change in potential upon changing the primary ion activity is measured.

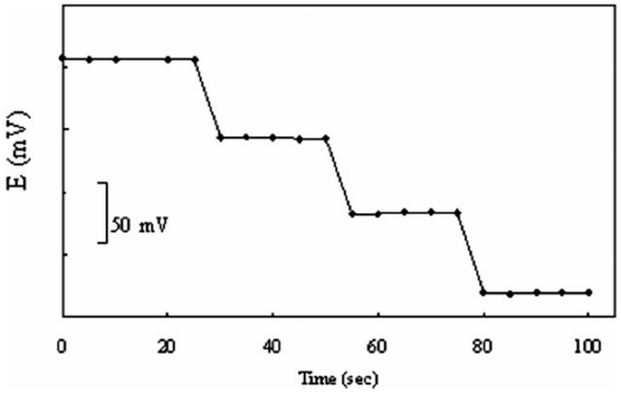

Figure 6. Dynamic response of CGE for step changes in concentration of SCN$^-$ (10^{-4} to 10^{-1} M).

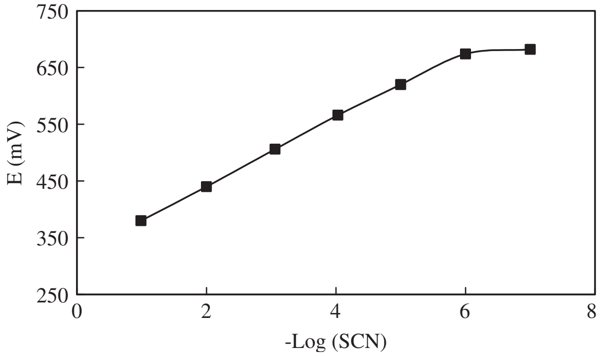

Figure 7. Potential response of the proposed electrode.

Then, the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient K is determined as:

$$K_{\mathrm{Pot}AB=\Delta A/aB}$$

where $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity and a'_A is the activity of A, in the presence of the interfering ion, a_B.

The resulting potentiometric selectivity coefficients are given in Table 3. The obtained selectivity coefficients revealed that these anions did not disturb the function of the proposed thiocyanate membrane sensor. The typical selectivity pattern for a series of anions shown by these electrodes was as follows: $SCN^- > ClO_4^- > I^- > ClO_3^- > NO_2^- > NO_3^- > C_2O_4^{2-} > CN^- \approx CrO_4^{2-} \approx N_3^- > IO_3^- \approx CH_3COO^- \approx Br^- > Cl^- > F^- >$ Imidazole.

It is interesting to note that the observed selectivity pattern for the proposed sensors significantly differs from the so-called Hofmeister selectivity sequence (i.e. selectivity based solely on the lipophilicity of anions) [54]. As can be seen from Table 3, the proposed sensor in terms of selectivity coefficient against the most interfering ions tested is superior to most of the thiocyanate sensors previously reported. The effect of additive amount on the selectivity by incorporating various amounts of additive to MTOAC/carrier weight ratios of ca. 1.0 and 2.0 was examined and the respective results are presented in Table 4.

Table 3. Selectivity coefficients of the coated-graphite electrodes based on Co(III)–salpen complex.

	Log K_{SCN}^{Pot}			Log K_{SCN}^{Pot}	
Interfering ion	SSM[a]	MPM[b]	Interfering ion	SSM	MPM
ClO_4^-	−0.89	−0.81	CH_3COO^-	−3.70	−3.67
Cl^-	−3.90	−3.82	$C_2O_4^{2-}$	−2.98	−2.92
Br^-	−3.65	−3.59	ClO_3^-	−1.98	−1.90
F^-	−4.00	−3.96	NO_3^-	−2.7	−2.66
I^-	−1.21	−1.16	CrO_4^{2-}	−3.37	−3.23
N_3^-	−3.47	−3.39	IO_3^-	−3.62	−3.56
CN^-	−3.40	−3.36	Imidazol	−4.28	−4.20
NO_2^-	−2.33	−2.30			

Notes: [a]Separation solution method; [b]Match potential method.

Table 4. Effect of additive ratio on selectivity coefficient of the coated-graphite electrodes based on Co(III)–salpen complex based on SSM method.

	MTOAC% (w/w)			MTOAC% (w/w)	
Interfering ion	1%	2%	Interfering ion	1%	2%
ClO_4^-	−2.01	−0.89	CH_3COO^-	−3.37	−3.70
Cl^-	−3.20	−3.90	$C_2O_4^{2-}$	−2.91	−2.98
Br^-	−3.05	−3.65	ClO_3^-	−2.40	−1.98
F^-	−3.40	−4.00	NO_3^-	−2.70	−2.7
I^-	−1.91	−1.21	CrO_4^{2-}	−2.90	−3.37
N_3^-	−1.62	−3.47	Imidazol	−3.81	−3.62
NO_2^-	−2.50	−3.40			

As can be seen, at lower weight ratios higher selectivity, even in the presence of lipophilic ions, could be obtained.

We were interested to compare the potentiometric selectivity of the membranes containing various amounts of MTOACl. Typical results of the logarithmic selectivity coefficients, log $K^{\mathrm{j}}_{\mathrm{SCN}}$, obtained from the electrode responses of various membranes based on the same ionophore L1 with different amounts of additives are given in Table 3. The membranes containing large amounts of MTOACl, clearly show more tendency for the highly lipophilic anions, and this tendency increases at higher concentrations of this additive. In fact, the electrode containing MTOACl/ionophore mole ratio >1 is more selective to $\mathrm{ClO_4^-}$ than thiocyanate. This is consistent with the reports on the use of quaternary ammonium salts for the development of thiocyanate-selective electrodes. These electrodes respond better to thiocyanate with respect to several other anions, while their preferred anion is perchlorate [55,56]. Since the response of the classical ion-exchangers is based on the lipophilicity of anions, these electrodes are essentially nonselective. For the charged carrier-based ion-selective electrodes, the charge sign of the ionic sites that give the highest potentiometric selectivity depends on the charge of the ionophore, charge of the primary and interfering ions, and on the stoichiometry of their complexes with the ionophore [33]. ISEs with electrically neutral carriers only function if sites with the charge opposite to the primary ion are present [40,52].

Such remarkable selectivity of the proposed thiocyanate ion-selective electrode over other anions reflects the high affinity of the cobalt coordination sites of the Co(III) complexes and ligands toward the thiocyanate ions. As can be seen, the electrode based on carrier do not show tendency toward the highly lipophilic anions such as $\mathrm{N_3^-}$, $\mathrm{Br^-}$, $\mathrm{NO_3^-}$ and $\mathrm{NO_2^-}$. The mechanism of thiocyanate response shown by these ionophores could be related to the rapid complex formation and exchange of ions at the membrane interface (ion exchange processes) where the substitution of the counter ion of the complexes by the analyte takes place.

3.2 *Effect of organic solvent*

The performance of the electrode was also tested in partially non-aqueous media using 10, 20, 25, 35, 45 and 75% methanol–water mixtures (v/v). As can be seen from Table 5, the membrane works satisfactorily up to a maximum 25% (v/v) of methanol content. It appears that 25% (v/v) methanol in water do not affect the properties of the membrane significantly to bring about the change in potential, slope and working

Table 5. Effect of organic solvent on response of thiocyanate selective electrode.

Methanol %	Slope (mV decade^{-1})	Linear range (M)
0	59.05	1×10^{-6} to 1×10^{-1}
10	59.0	1×10^{-6} to 1×10^{-1}
20	58.91	1×10^{-6} to 1×10^{-1}
25	58.83	1×10^{-6} to 1×10^{-1}
35	54.33	5×10^{-5} to 1×10^{-1}
45	50.0	1×10^{-4} to 1×10^{-1}
75	40.1	5×10^{-4} to 1×10^{-1}

Table 6. Determination of thiocyanate in wastewater samples and human urine and saliva.

Sample	Proposed method (SCN−, mmol/L)	Colorimetric method
Saliva of non-smoker	0.62 ± 0.08	0.72 ± 0.05
Saliva of smoker	1.82 ± 0.05	1.69 ± 0.06
Urine of non-smoker	0.3 ± 0.03	0.24 ± 0.05
Urine of smoker	0.75 ± 0.05	0.67 ± 0.05
Wastewater (laboratory)	1.08 ± 0.12	0.93 ± 0.06

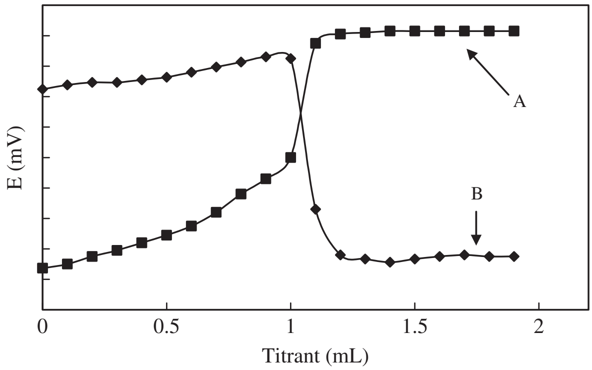

Figure 8. Potentiometric titration curve of 50.0 ml 1.0×10^{-2} M SCN^- with 5.0×10^{-1}M of Ag^+, using the proposed SCN^--selective sensor as an indicator electrode.
Notes: *A* = titration curve of SCN^- with Ag^+; *B* = titration curve of Ag^+ with SCN.

concentration range. Above 25% (v/v) methanol content, a decrease in slope and working concentration range occurred and the membranes were destroyed due to the leaching of the ionophore and plasticizer from the PVC matrix. Hence, the electrode assembly can only be used in non-aqueous medium when its content is below 25%.

3.3 *Determination of thiocyanate in real samples*

To assess the applicability of the membrane electrode to real samples, an attempt was made to determine SCN^- in smoker and non-smoker urine and saliva and wastewater. Quantification of urinary or salivary thiocyanate provides a reliable prediction of cyanide exposure such as tobacco smoking and as a suitable index for distinguishing smokers from non-smokers, because there is a significant difference in the salivary thiocyanate level between these groups [7,20]. Measurements were carried out on different samples, taken from a cigarette smoker and a non-smoker by the standard addition method. The samples were diluted by a factor of 10 with deionisation water and pH was adjusted by addition amount of HNO_3 and KOH at pH 5.2. A colorimetric procedure for the assay of thiocyanate was used as the reference method [57,58].

The results are presented in Table 6. Moreover, an attempt was made to determine SCN^- in a laboratory wastewater sample. The sample was collected by a routine technique, acidified with HNO_3 and then pH adjusted to about 5.2. The sample was

Table 7. Comparison of some characteristics of the proposed electrode with previous thiocyanate ISEs.

Ionophore*	^{a}S	^{b}LR (*M*)	^{c}LD (*M*)	Interfering ion	pH	Ref.
ZPCH	-58.1 ± 0.5	1.0×10^{-6} to 1.0×10^{-1}	7.5×10^{-7}	Salycilate$^-$, I^-, ClO_4^-	2.0–7.0	[14]
BDBSHZ	-56.5 ± 1.1	1.0×10^{-6} to 1.0×10^{-1}	7.0×10^{-7}	–	3.5–8.5	[15]
BBGM	−57.6	1.0×10^{-7} to 9.0×10^{-1}	7.0×10^{-7}	ClO_4^-	At pH 4.6	[16]
CECMATH	−57.6	1.0×10^{-6} to 1.0×10^{-1}	–	IO_4^-	3.8–9.2	[17]
BPHSPD	−57.3	1.0×10^{-6} to 7.0×10^{-1}	–	I^-, Salycilate	4.0–6.5	[18]
MBPHTBZ	−57.5	4.0×10^{-7} to 1.0×10^{-2}		ClO_4^-, Br^-, NO_3^-, I^-, SO_4^{2-}	–	[19]
DBHACTN	-58.4 ± 0.3	3.3×10^{-6} to 0.10	3.0×10^{-6}	ClO_4^-, I^-, CN^-	4.0–8.0	[20]
OOAEAEA	−57.20	1×10^{-5} to 1×10^{-1}	3.8×10^{-6}	Salicylate iodide	at pH 5.6	[21]
ZTBTHHB	-59.4 ± 1.2	6.3×10^{-7} to 1.0×10^{-2}	3.16×10^{-7}	–	3.5–9.0	[22]
IP	−55.6 to −58.3	9×10^{-6} to 10^{-2}	5×10^{-7}	IO_4^-	2.0–8.0	[23]
TTPPMC	No reported	4×10^{-6} to 4×10^{-3}	-3×10^{-4}	Salicylate$^-$	2.0–4.0	[24]
NPH	−58.1	5×10^{-7} to 10^{-1}	5×10^{-7}	I, ClO_4	3–10	[25]
$Hg(MBO)_2$	−60.6	10^{-6} to 10^{-1}	6×10^{-7}	–	3–11	[26]
CSPBC	59.05	10^{-6}–10^{-1}	8×10^{-7}	ClO_4^-, I	2.8–9.8	This work

Notes: ^{a} = Slope (mV decade^{-1}), ^{b} = Liner range (M), ^{c} = Limit of detection (M).

*Abbreviations: ZPCH (Zinc-phthalocyanine complex); BDBSHZ (Butane-2,3-dione *bis*(salicylhydrazonato) zinc(II)); BBGM (*N*,*N′*-*bis*-(benzalde hyde)-glycine metallic complexes); CECMATH (Crown ether-cetyltrimethyl ammonium-thiocyanate); *BPHSPD* (*N*,*N*_-*bis*-(4-phenylazosalicylidene) *o*-phenylene diamine); MBPHTBZ (2,2_[Methylenebis (4,1phenylenenitrilomethylidyne)] bisphenol Zn(II) complex; *DBHACTN* (*1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane*– Ni(II)); OOAEAEA (octyl-[2-(2-octylamino-ethylamino)-ethyl]-amine); ZTBTHHB (Zinc-tris(*N*-*tert*-butyl-2-thioimidazolyl)hydroborate complex); IP (Imidepyridine derivatives); MPH (Mn(II) porphyrin); TTPPMC (5,10,15,20-tetrakis(2,4,6-triphenylphenyl) porphyrinato)manganew(III) chloride; NPH (nickel phthalocyanines); $Hg(MBO)_2$ *bis*(2-mercaptobenzoxazolato) mercury(II); CSPBC (Cobalt (Salpn) (PBu3)]ClO4 · H2O).

analysed in five replicates using the electrode and the results were compared with those obtained by a standard colorimetric method [57,58]. The results, shown in Table 6, indicate that the amount of SCN^- evaluated with the help of the sensor is in good agreement with those obtained by the standard colorimetric method and thereby reflect the utility of the proposed sensor. Since there is little or no protein found in urine, satisfactory results can be achieved without prior treatment of the samples [59]. The proposed electrode was also successfully used as an indicator electrode in conjunction with an Ag/AgCl reference electrode in the potentiometric titration of SCN^- solutions with Ag^+ as a suitable titrant. The results of the titration for 50 ml of 0.01 M SCN^- with 0.5 M Ag^+ showed that the amount of SCN^- ions in solution could be accurately determined with the electrode (Figure 8). A very good inflection point in the titration plot shows the perfect stoichiometry.

4. Conclusion

Some lipophilic organometallic compounds were reported as anion ionophores exhibiting specific anion-selective behaviour which deviated from the so-called Hofmeister anion response pattern. Their anion selectivity's were mainly controlled by the geometric configuration of the carriers and specific interactions between the central metals in organometallic complexes and anions rather than by the lipophilicity of anions or simple electrostatic interactions with anions.

Based on the results discussed in this paper, the complex [Cobalt (Salpen) (PBu_3)] $ClO_4 \cdot H_2O$ is considered to be a charge carrier for constructing a PVC-based membrane electrode to determine concentrations of thiocyanate ion. The proposed electrode has good operating characteristics such as sensitivity, stability, life-time, response time and a wide concentration range. The proposed sensor can be used successfully for thiocyanate ion determination both by direct potentiometry and potentiometric titration. It can also be used in determination of thiocyanate ions in wastewater and urine and saliva samples.

Considering the results of this paper and those presented in Table 7, one can see that the proposed electrodes are superior to those previously reported in the literature in terms of selectivity [14,19,20], slope [15,23,26], linear range [20,21], detection limit [20,21] and applicable pH [14–17,21].

Acknowledgement

The authors express their appreciation to the Graduate School and Research Council of the Yasouj University for financial support of this work.

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