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Highly selective thiocyanate membrane electrode based on butane-2,3-dione bis(salicylhydrazonato)zinc(II) complex

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Abstract

A highly selective poly(vinyl chloride) (PVC) membrane electrode based on butane -2,3-dione bis(salicylhydrazonato) zinc(II) [Zn (BDSH)] complex as carrier for thiocyanate-selective electrode is reported. The influence of membrane composition, pH and possible interfering anions were investigated on the response properties of the electrode. The sensor responds to thiocyanate in linear range from 1.0×10^{-6} to 1.0×10^{-1} M with a slope -56.5 ± 1.1 mV decade^{-1}, over a wide pH range of 3.5–8.5. The limit of detection of the electrode was 7.0×10^{-7} M SCN^-. Selectivity coefficients determined with fixed interference method (FIM) indicate a good discriminating ability towards SCN^- ion in comparison to other anions. The proposed sensor has a fast response time of about 5–15 s and can be used for at least 3 months without any considerable divergence in potential. It was applied as indicator electrode in titration of thiocyanate with Ag^+ and in potentiometric determination of thiocyanate in saliva and urine samples.

Keywords: Thiocyanate-selective electrode; Potentiometry; PVC membrane

1. Introduction

The thiocyanate ion is present in humans as a result of the digestion of some vegetables and as a metabolic product of compounds in tobacco smokes containing cyanide [1,2]. In this respect, the concentration level of thiocyanate is considered to be a good probe to distinguish between smokers and non-smokers. Thiocyanate is also known to block iodine uptake by the thyroid gland. Determination of thiocyanate in serum has been advocated to monitor therapy with sodium nitroprusside. The concentration level of thiocyanate is also considered to be important to assure the quality of vegetables: in fact nutritional effects of glucosinolates, processing effect on oilseed rape and on cruciferous vegetables rich in indol-3-ylmethylglucosinolatws could be revealed by its presence [3].

A large number of methods have been developed for the determination of this ion in several matrices. Spectrophotometric techniques based on the formation of a red complex with Fe(III), molecular fluorescence based on the modified Köning method [4], generation of carbonyl sulfide by the SCN^- ion and its detection by gas-phase molecular absorption spectrometry [5] has been developed. Other methods such as polarography [6], ion chromatography [7] and potentiometry based on ion-selective electrodes (ISEs) [8,9], have been reported for the determination of thiocyanate concentration in various samples. Among these methods, carrier based ISEs, because of their unique advantages such as simplicity, speed of analysis, fast response time; low cost, wide linear range, reasonable selectivity and non-destructiveness have emerged as one of the most promising tools for this purpose. These advantages of ISEs have inevitably led to the development of potentiometric sensors for many inorganic and organic species.

It has been well documented that the selective complexation of anions by synthetic ionophores can be used to design

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anion selective electrodes. Solid-state thiocyanate-selective electrodes are commercially available but show a large interference from I^- and S^{2-} [10]. Most of these electrodes are based on vitamin B12 derivatives [11,12], metalloporphyrines [13–15], organomercury compounds [16], Schiff base complexes of metal ions [17], phthalocyanines [18–20], organometallic complexes [21–23], and zinc Schiff base [24]. In all these cases, ligation of the primary anion to the central metal ion is responsible for the observed selectivity.

For a truly anion-selective electrode, a strong interaction between the ionophore and the anion is required in order to complex anion in a selective fashion. Potentiometric response of the membranes doped with these complexes is believed to be based on the coordination of analyte anion as axial ligand to the metal center of the carrier molecule [25,26]. Most of the thiocyanate potentiometric sensors have serious interfering affect of other anions such as I^-, $ClO_3{}^-$, Cl^-, Br^- and $IO_4{}^-$.

The purpose of the present work has been the development of a thiocyanate-selective electrode based on poly(vinyl chloride) (PVC) membrane of a new zinc Schiff's base. This sensor is potentially useful for detection of thiocyanate in biological samples (e.g., urine), where evaluated levels of thiocyanate correlate with excessive cigarette smoking. The proposed sensor displays a low detection limit and high selectivity and sensitivity to thiocyanate determination in real samples.

2. Experimental

2.1. Reagents

PVC of high relative molecular weight, trioctylmethyl ammonium chloride (TOMAC), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) were used as received from Aldrich. Potassium or sodium salts of all anions, tetrahydrofuran (THF) and all other chemicals were of highest purity available from Merck, and were used without further purification, except THF, which was distilled before use. The ionophore of butane-2,3-dione bis(salicylhydrazonato) zinc(II) [Zn (BDSH)] (Fig. 1) was synthesized and used after purification. All of the solutions were prepared using doubly distilled deionized water. The pH adjustments were made with dilute nitric acid and sodium hydroxide solutions as required. Wastewater samples were filtered through a filter paper. A stock solution of thiocyanate was prepared by dissolving the appropriate amount of potassium thiocyanate in 100 mL of water. Working solutions were prepared by successive dilutions with water. All of the working solutions were buffered at pH 5.0, using phosphate buffer solution. Carrier, [Zn (BDSH)] was prepared according to the following procedures.

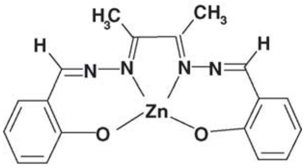

Fig. 1. Structural representation of butane-2,3-dione bis(salicylhydrazonato)zinc(II) [Zn (BDSH)] the compound of used as ionophore for SCN^--ISE.

2.1.1. Synthesis of butane-2,3-butane dihydrazone

2,3-Butane dihydrazone was prepared by the method of Bush and Bailar [27]. To a boiling solution of 11.63 g of aqueous hydrazine (0.24 mol) in 100 mL of methanol was added 75 mL of biacetyl (0.12 mol, 10.33 g) over a period of 120 min. Refluxing was continued for an additional 60 min. Two hundred milliliters of water was then added and the methanol was removed by distillation when the resulting aqueous solution was cooled in an ice-bath, with crystals formed. These were filtered, washed with a little water, recrystallized from 100 mL of hot methanol and dried in vacuum, m.p. 158–159 °C (reported 158 °C); yield ∼54%. Anal. calcd. for $C_4H_{10}N_4$: C, 42.09; H, 8.83; N, 49.08. Found: C, 42.16; H, 8.71; N, 49.14. IR (KBr, cm^{-1}): 3330, 3180 ($\upsilon_{N–H}$); 1580 ($\upsilon_{C=N}$), 1615 (υ_{NH_2}).

2.1.2. Synthesis of butane-2,3-dione bis(salicylhydrazone)

Salicylaldehyde (4.88 g, 0.02 mol) was mixed with 100 mL of distilled ethanol in a 250 mL round bottom flask, which was stirred using a magnetic stirrer. 2,3-Butanedihydrazone (1.14 g, 0.01 mol) dissolved in 50 mL of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for 4 h to get a yellow solid precipitate of ligand, which was cooled, filtered, washed with petroleum ether and dried. The Schiff-base ligand was then recrystallised from hot ethanol (yield ∼86%). Anal. calcd. for $C_{18}H_{18}N_4O_2$: C, 67.07; H, 5.63; N, 17.38. Found: C, 66.86; H, 5.56; N, 17.51%. IR (KBr, cm^{-1}): 3450 ($\upsilon_{O–H}$), 1610, 1580 ($\upsilon_{C=N}$).

2.1.3. Synthesis of butane-2,3-dione bis(salicylhydrazonato)zinc(II) [Zn(BDSH)]

Zinc(II) acetate dehydrate (1.55 g, 7.1 mmol) was dissolved in 50 mL of ethanol. To this solution was added a warm ethanol solution (50 mL) containing BDSH (2.29 g, 7.1 mmol). The mixture was stirred for 4 h at room temperature and refluxed for another 4 h. Removal of the solvent gave a solid upon cooling. Crystallization of the solid from chloroform produced analytically pure complex. Anal. calcd. for $C_{18}H_{16}N_4O_2Zn$: C, 56.04; H, 4.18; N, 14.53; Zn, 16.95%. Found: C, 55.83; H, 4.01; N, 14.67; Zn, 16.78%. IR (KBr, cm^{-1}): 1606 ($\upsilon_{C=C}$); 2890, 2760 ($\upsilon_{C–H}$), 1615 ($\upsilon_{C=N}$); 387, 1101, 769 (ring vibration).

2.2. Electrode preparation

The membrane ion-selective electrodes were prepared according to a previously reported method [28]. A mixture of PVC, plasticizer (DOP or DBP), and the membrane additive (TOMAC), total mass 200 mg was dissolved in approximately 10 mL freshly distilled THF. To this mixture was added the electroactive material [Zn (BDSH)], and solution was mixed well. The resulting mixture was poured into a small flat bottom dish of 2 cm diameter, covered with a filter paper and the solvent was allowed to evaporate at room temperature. The resulting membrane (ca. 0.2 mm thick) was then sectioned with a cork borer and mounted across the opening of a PVC tube of about 7 mm i.d. and 1.5 cm length using a glue of PVC in THF. The PVC tube with the membrane was then filled with an internal solution of in 1.0×10^{-5} M KSCN. The filled electrode was conditioned by soaking in 1.0×10^{-5} M KSCN. The first conditioning time was approximately 24 h and then 30–40 min for successive uses. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. Potential measurement and calibration

The potential build up across the membrane electrode was measured using the galvanic cell of the following type:

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{KCl(3\,M)internalsolution}(1.0 \times 10^{-5}\,\mathrm{MKSCN})$$

$$|\,\mathrm{PVCmembrane}\,|\,\mathrm{testsolution}\,||\,\mathrm{SCE}$$

All potentials were measured at 25 ± 1 °C using a digital pH/mV, model 691 Metrohm. A saturated calomel electrode (SCE, Metrohm) with a fiber junction was used as the external reference electrode. Activities were calculated according to the Debye–Hückle procedure [29], for the calibration curve, concentration instead of activity was used. The pH of the sample solution was monitored simultaneously with a conventional glass pH electrode (Metrohm).

Before starting the measurements, the electrode was preconditioned in stirred water until a steady potential was obtained. The performance of the electrode was investigated by measuring its potential in potassium thiocyanate solutions prepared in the concentration range from 1.0×10^{-7} to 1.0×10^{-1} M by serial dilution at constant pH. All solutions were freshly prepared by dilution from the stock standard solution, 1.0×10^{-1} M, with doubly distilled water. The solutions were stirred and potential readings recorded when they became stable. The data were plotted as observed potential versus the logarithm of the SCN^- concentration. Potentiometric titration of 15 mL 1.0×10^{-3} M SCN^- solution was carried out with 0.01 M Ag^+ solution using the thiocyanate-selective electrode as the indicator electrode in conjunction with a fiber function SCE electrode.

3. Results and discussion

The plasticized PVC-based membrane electrode containing the [Zn (BDSH)] carrier generated stable potential responses in solutions containing thiocyanate. Therefore, we studied in detail the performance of the membrane electrode based on this carrier for thiocyanate in aqueous solutions.

In preliminary experiment, membranes with and without carrier were constructed. The membrane with no carrier displayed insignificant selectivity toward thiocyanate and their response was not reliable, whereas, in the presence of the proposed carrier, the optimized membrane demonstrated Nernstian response and remarkable selectivity for thiocyanate over several common inorganic and organic anions. The preferential response toward SCN^- is believed to be associated with the coordination of thiocyanate with central metal ion of the carrier.

3.1. The influence of membrane composition

It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives employed [30,31]. Thus, the influence of the membrane composition, nature, and amount of plasticizer, and lipophilic additives on the potential response of the membrane was investigated. Several membranes were prepared with different compositions. The best response was observed with the membrane composed of the following ingredients: 32% PVC, 60% DOP, 6% ionophore, 2% TOMAC.

The potentiometric response of the membranes was greatly improved in the presence of lipophilic cationic additives. It is known that, lipophilic salts not only reduce the membrane resistance, but also enhance the response behavior and selectivity, and reduce interference from sample [32,33]. Previous studies have shown that there is an optimal concentration of lipophilic ionic additives in the membranes that gives the best electrode performance. The effect of TOMAC concentration in the membranes was investigated at several carrier/additive mole ratios. Better response characteristics, i.e. Nernstian response and improved selectivity, were usually observed with an ionophore/TOMAC weight ratio of approximately 3.0, which corresponds to a mole ratio of approximately 3.0. The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier-based ion-selective electrodes [34,35]. The response of the blank membranes containing additives but no carrier at all was far from Nernstian.

The influence of the two type plasticizer DOP and DBP on the characteristics of the thiocyanate ion-selective electrode was investigated. According to a previous report [36], the electrode containing DOP generally showed better potentiometric responses, i.e. sensitivity and linear dynamic range. It seems that DOP, as a low polarity compound provides more appropriate conditions for incorporation of the highly lipophilic thiocyanate ion into the membrane.

Several membrane compositions were investigated by varying the proportions of PVC, DOP, and membrane active material, [Zn (BDSH)]. Irrespective of ionophore concentration the slope was relatively larger when DOP/PVC weight ratio was approximately 2.0. It has been shown that the plasticizer/PVC ratios of ca. 2 produced maximum sensitivity [36].

It was also observed that the potentiometric response of the electrode toward thiocyanate ion depended on the concentration of the ionophore incorporated within the membrane. Increasing the amount of butane-2,3-dione bis(salicylhydrazonato)zinc(II) up to 6% resulted in membranes for which slopes were larger and the linear range wider. Further addition of the ionophores concentrations worsened the electrode response, most probably due to saturation of the membrane or due to some non-uniformity of the membrane.

3.2. Response characteristics of the electrode

The potentiometric response of the prepared thiocyanate-selective electrode was investigated against the thiocyanate ion concentration. For this purpose, appropriate aliquots of a stock solution of thiocyanate were introduced to the cell, and the corresponding potentials were determined. The potential readings were plotted against—log of the thiocyanate concentration. The characteristic properties of the optimized membrane are summarized in Table 1.

Over the concentration range from 1.0×10^{-6} to 1.0×10^{-1} M of thiocyanate in the calibration solution, the electrode potential response was linear with the concentration of thiocyanate. The calibration curve slope was—56.5 ± 1.1 mV/p [SCN^-] and the detection limit, calculated as recommended by the IUPAC, was 7.0×10^{-7} M. In practice, slopes of between 55 and 59 mV decade^{-1} are referred to as Nernstian for analytical purposes [37,38]. This range was found to be in a compatible with other thiocyanate electrodes. The calibration plot is shown in Fig. 2, which shows the linear range to be from 1.0×10^{-6} to 1.0×10^{-1} M; the Nernstian slope is -56.5 ± 1.1 mV decade^{-1} of SCN^- concentration.

Table 1
Characteristics of optimized SCN^--ISE

Linear range (M)1	1.0×10^{-6} to 1.0×10^{-1} M
Slope (mV decade^{-1})	−56.5
pH range	3.5–8.5
Standard deviation of slope (mV decade^{-1})	±1.1
Precision	At concentrations of 1.0×10^{-2} M, 1.0×10^{-3} M and 1.0×10^{-4} M SCN^- standard deviations were of ±0.3, ±0.4 mV and ±0.7, respectively.
Detection limit (M)	7.0×10^{-7}
Life time (months)	>3
Response time (s)	5–15

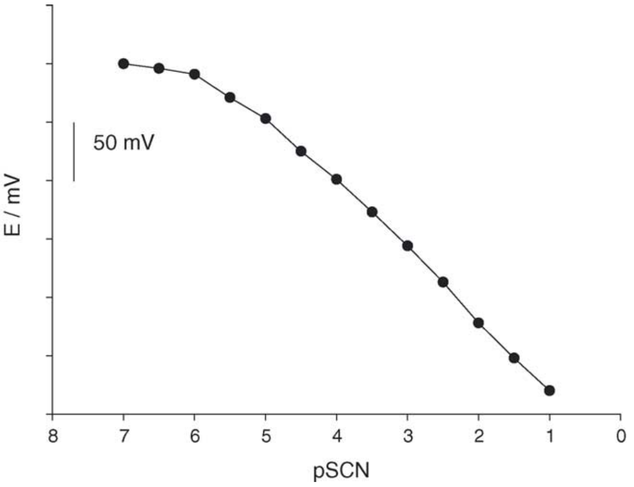

Fig. 2. Potentiometric response of the SCN^--ISE to thiocyanate using optimised membrane electrode.

The influence of the concentration of internal solution (range of 1.0×10^{-3} to 1.0×10^{-1} M) on the potential response of the thiocyanate-selective electrode was studied and the results showed the concentration of the internal solution does not cause any significant difference in the potential response of the electrodes, except for an expected change in the intercept of the resulting Nernstian plots.

The optimum equilibration time for the membrane electrode in the presence of 1.0×10^{-5} M KSCN was 24 h, after which it would generate stable potentials in contact with thiocyanate solution. The potentiometric response of the membrane electrode to different concentrations of SCN^- was examined using the optimized membrane composition and conditions described above.

The effect of the pH of the test solution on the response of the membrane electrode was examined at three SCN^- concentrations (1.0×10^{-2} to 1.0×10^{-4} M). pH was adjusted with dilute nitric acid and sodium hydroxide as required. As illustrated in Fig. 3 the potentials remain constant

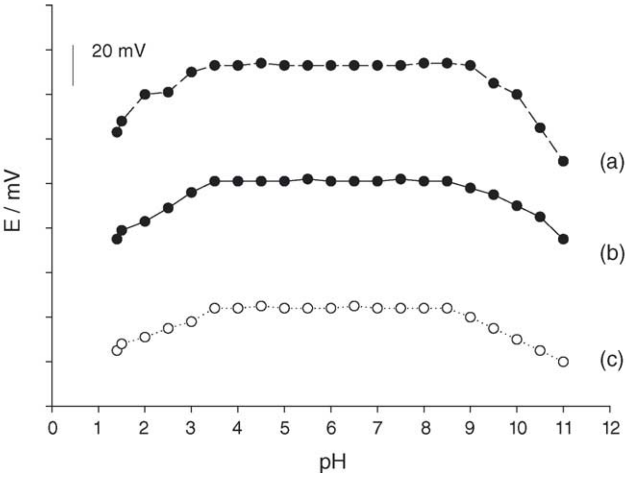

Fig. 3. The influence of pH on the potential response of the optimized SCN^--ISE: (a) 1.0×10^{-4} M, (b) 1.0×10^{-3} M and (c) 1.0×10^{-2} M.

within a pH range of approximately 3.5–8.5. Variation of the potential at $pH < 3.5$ could be related to protonation (due to the nitrogen and oxygen sites protonation) of [Zn (BDSH)] in the membrane phase, which results in a loss of its ability to interact with SCN^- ions. At higher pH (>8.5), the potential drop (negative slope) may be because of interference of hydroxide ion. In high pH media, hydroxyl ion will compete with thiocyanate ion for the cation site in the membrane.

The stability and reproducibility of the electrode was also tested. The standard deviation of 20 replicate measurements at three thiocyanate concentration of 1.0×10^{-2}, 1.0×10^{-3} and 1.0×10^{-4} M was ±0.3, ±0.4 and ±0.7 mV, respectively.

The response time of the electrode was measured after successive immersion of the electrode in a series of SCN^- solutions, in each of which the SCN^- concentration increased tenfold, from 1.0×10^{-6} to 1.0×10^{-1} M. The static response time thus obtained was 5 s for 1.0×10^{-1} M SCN^- concentrations. At lower concentrations, however, the response time was longer and reached 15 s for a SCN^- concentration of 1.0×10^{-5} M. The actual potential versus time traces is shown in Fig. 4. The potentials remained constant for approximately 5 min, after which a very slow change within the resolution of the meter was recorded. The sensing behavior of the membrane electrode did not depend on whether the potentials were recorded from low to high concentrations or vice versa.

The electrode was tested over a period of 3 months to investigate stability. During this period, the electrode was in daily use and was stored in 1.0×10^{-4} M SCN^- solution when not in use. No significant change in the performance of electrode (slope, linear range) was observed during this period. Storage of the electrode in solution for extended periods, however, especially in stirred solution, resulted in a slight gradual decrease in the slope, as is usual for many plasticized PVC membranes, probably as a result of leaching of the ionophore from the membrane.

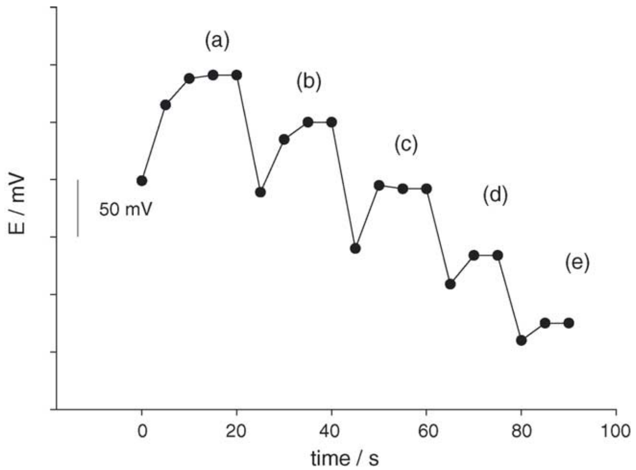

Fig. 4. Response time of the optimized SCN^--ISE for step changes in concentration of SCN^-: (a) from 1.0×10^{-6} to 1.0×10^{-5} M, (b) from 1.0×10^{-5} to 1.0×10^{-4} M, (c) from 1.0×10^{-4} to 1.0×10^{-3} M, (d) from 1.0×10^{-3} to 1.0×10^{-2} M and (e) from 1.0×10^{-2} to 1.0×10^{-1} M.

Table 2

Selectivity of coefficients, determined by use of the fixed interference method, for the thiocyanate-selective electrode

Interfering ion	$\log K^{pot}_{SCN^-,A^-}$	Interfering ion	$\log K^{pot}_{SCN^-,A^-}$
ClO_4^-	−2.8	CO_3^{2-}	−4.0
Cl^-	−4.1	MnO_4^-	−3.4
Br^-	−3.3	NO_3^-	−3.0
I^-	−3.8	SO_4^{2-}	−4.1
NO_2^-	−3.1	$S_2O_3^{2-}$	−4.2
CN^-	−3.5	PO_4^{3-}	−4.2
OAc^-	−4.2	$C_2O_4^{2-}$	−4.0
Sal[a]	−3.2	HPO_4^{2-}	−4.0
$Cr_2O_7^{2-}$	−3.4	CrO_4^{2-}	−3.4
F^-	−4.1	ClO_3^-	−3.2

[a] Salicylate.

The most important characteristics of any ion-sensitive sensor are its response to the primary ion in the presence of other ions in solution, which is expressed in terms of the potentiometric selectivity coefficient. Potentiometric selectivity coefficients ($K^{pot}_{SCN^-,A^-}$) describing the preference of the membrane for an interfering ion A^- relative to SCN^- were determined by the fixed interference method (FIM) [39]. The selectivity coefficient for various anions was evaluated by the mixed solution method with a fixed concentration of interference, and varying amounts of SCN^- concentrations. Table 2 lists the potentiometric selectivity coefficient data of the sensor for several anions relative to SCN^-. The selectivity coefficients clearly indicate that the electrode is selective to thiocyanate over a number of other inorganic and organic anions. As it is evident from the data in Table 2, the electrode based on [Zn (BDSH)] has relatively high selectivity toward SCN^- relative to anions such as perchlorate, salicylate, oxalate, and several common anions. It is interesting to note that the observed selectivity pattern for the SCN^--ISE significantly differs from the so-called Hofmeister selectivity sequence. The interfering effect of the ions is in the following order:

$$\begin{aligned} & ClO_4^- > NO_3^- > NO_2^- > IO_3^- \\ & = \text{Sal} > Br^- > CrO_4^{2-} \\ & = Cr_2O_7^{2-} = MnO_4^- > CN^- > I^- > CO_3^{2-} \\ & = C_2O_4^{2-} = HPO_4^{2-} > F^- > Cl^- = SO_4^{2-} > S_2O_3^{2-} \\ & = PO_4^{3-} = OAc^- \end{aligned}$$

The sequence is characterized by the Hofmeister series:

$$\begin{aligned} & R^- > ClO_4^- > SCN^- > I^- > NO_3^- > Cl^- > HCO_3^- \\ & > SO_4^{2-} > HPO_4^{2-} \end{aligned}$$

The reason that the selectivity coefficients of this electrode do not comply with the Hofmeister series, and show an anti-Hofmeister behavior, is thought to be due to the possible interaction of the anions with Zn [40]. According to hard–soft

Table 3
Comparison of the potentiometric parameters of the proposed thiocyanate-selective electrode with the other thiocyanate-selective electrodes

A^-	The proposed SCN^--ISE	Reference [36][a]	Reference [41]	Reference [42]	Reference [43][b]	Reference [44]
Nernstian slope (mV $decade^{-1}$)	-56.5 ± 1.1	Ionophores (I, II, respectively), -60.6 ± 0.8, -57.5 ± 1.2	-58.9 ± 0.5	-57.8	Ionophores (I, II, III, respectively), -56.8, -58.3, -55.6	-58.1
Linear range (M)	1.0×10^{-6} to 1.0×10^{-1}	Ionophores (I, II, respectively), 1.0×10^{-6} to 1.0×10^{-1}	1.0×10^{-6} to 1.0×10^{-1}	1.0×10^{-7} to 1.0×10^{-1}	Ionophores (I, II, III, respectively), 1.0×10^{-5} to 1.0×10^{-2}, 9.0×10^{-6} to 1.0×10^{-2}, 1.0×10^{-5} to 1.0×10^{-2}	5.0×10^{-5} to 1.0×10^{-2}
Limit of detection (M)	7.0×10^{-7}	6.0×10^{-7}	5.0×10^{-7}	4.8×10^{-8}	5.0×10^{-6}	4.0×10^{-5}
Response time (s)	5–15	5	5–20	15–120	<10	5
Interfering ions	–	I^-	–	–	IO_4^-	NO_3^-, NO_2^-, I^-, Cl^-, ClO_4^-, Br^-

[a] Ionophores of I, II, were bis(2-mercaptobenzoxazolato) mercury(II) and bis(2-pyridinethiolato) mercury(II), respectively.

[b] Ionophores I, II, III, were di-, tetra-, and hexa-imidepyridine derivatives, respectively.

acid and base (HSAB) theorem, interaction of NCS^- with complex is via nitrogen.

Table 3 lists the linear range, detection limit, slope, response time and selectivity coefficients of some of other thiocyanate-selective electrodes against proposed thiocyanate-selective electrode for comparative purposes [36,41–44]. As can be seen from the table, the selectivity coefficients obtained for the proposed electrode are superior to those reported for other SCN^--selective electrodes listed in Table 3.

3.3. Analytical applications

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. 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 phosphate buffer of pH 5. The results are compared with the standard colorimetric method [45]. The results are presented in Table 4. Also, an attempt was made to determine SCN^- in an industrial wastewater sample. The sample was collected by a routine technique, treated by acidification with HNO_3 and then adjusted pH about 5. Sample was analyzed in five replicate using the electrode, and the result was compared with those obtained by a standard colorimetric method [45]. The results given in Table 4, show that the amount of SCN^- evaluated with the help of the sensors are in good agreement with those obtained by the standard colorimetric method, thereby reflecting the utility of the proposed sensors.

Table 4
Determination of thiocyanate in different samples

Sample	Spectrophotometric method (SCN^-, mM)[a]	ISE (SCN^-, mM)[a]
Urine of smoker	0.75 ± 0.03	0.74 ± 0.04
Urine of non-smoker	0.29 ± 0.02	0.30 ± 0.03
Saliva of non-smoker	0.67 ± 0.05	0.68 ± 0.04
Saliva of smoker	1.79 ± 0.06	1.77 ± 0.08
Wastewater	0.81 ± 0.04	0.79 ± 0.04

[a] Mean value ± standard deviation (five determinations).

The proposed electrode was also successfully used as an indicator electrode in conjunction with SCE in the potentiometric titration of SCN^- solution with Ag^+ a suitable titrant. Results of the titration for 15 mL of 0.001 M SCN^- with 0.01 M Ag^+ was showed, the amount of SCN^- ion in solution can be accurately determined with the electrode. A very good inflection point, showing prefect stochiometry, is observed in the titration plot.

4. Conclusions

On the basis of these results discussed in this paper, complex of butane-2,3-dione bis(salicylhydrazonato)zinc(II) [Zn (BDSH)] can be regarded as a carrier for construction of a PVC-based membrane ISE for thiocyanate ion. The thiocyanate ion-selective electrode was used for the analytical applications. The proposed electrode has been shown to have good operating characteristics (sensitivity, stability, response time, detection limit, and a wide linear range). It is easy to prepare and use. This electrode can be used for determination of thiocyanate ion in biological samples.

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