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Novel selective thiocyanate PVC membrane electrode based on new Schiff base complex of 2.2-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis-benzenethiolato cadmium(II)

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An ion selective electrode for thiocyanate based on a complex as ionophore is described. The influence of membrane composition, pH and interference anions were investigated. The sensor responds to thiocyanate in the linear range from 1×10^{-6}–1×10^{-1} M with a slope -58.9 ± 0.5 mV decade^{-1}. The limit of detection is 5×10^{-7} M SCN^-. Selectivity coefficients determined with the 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 5–20 s and can be used for at least 2 months without any considerable divergence in potential. It was applied as indicator electrode in the titration of thiocyanate with Ag^+ and in the potentiometric determination of thiocyanate in saliva and urine samples.

Introduction

It has been well documented that the selective complexation of anions by synthetic ionophores can be used to design anion selective electrodes. Solid-state thiocyanate-selective electrodes are commercially available but show a large interference from I^- and S^{2-}.[1] Most of these electrodes are based on vitamin B12 derivatives,[2–3] metalloporphyrins,[4–6] organomercury compounds,[7] Schiff base complexes of metal ions,[8] phthalocyanines[9–11] and organometallic complexes.[12–14] 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. The potentiometric response of the membranes doped with these complexes is believed to be based on the coordination of analyte anion axial ligand to the metal center of the carrier molecule.[15–16] Most of the thiocyanate potentiometric sensors suffer from serious interfering affects from 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 impregnated with a new cadmium Schiff 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.

Experimental

Reagents

Reagent grade dibutylphthalate (DBP), methyltrioctyl ammonium chloride (MTOAC), dioctylphthalate (DOP), 2-nitrophenyloctylether (NPOE) and tetrahydrofuran (THF) were obtained from Merck and were used as received, except THF, which was distilled before use. PVC of high relative molecular weight was purchased from Aldrich. All other chemicals were of analytical reagent grade from Merck. Doubly distilled water was used for preparing all solutions. Adjustments of pH were made with dilute nitric acid or sodium hydroxide.

Preparation of the new thio Schiff-base complex

The thio Schiff-base ligand, 2,2-[(1,3-dimethyl-1,3propanediylidene)dinitrilo]bis-benzenethiol was prepared by the reaction of the 2-aminothiophenol (2.50 g, 0.02 mol) with acetyl acetone (1.01 g, 0.01 mol) in ethanol.[17] The thio Schiff-base ligand (3 g, 9.54 mmol) was dissolved in 100 ml of ethanol, and the solution was brought to reflux. To this hot solution was added cadmium acetate (2.54 g, 9.54 mmol) dissolved in 100 ml of ethanol. Refluxing was continued for 8 h. Upon cooling the solution, a red crystalline solid formed which was filtered, washed with ethanol, and dried *in vacuo* and purified by recrystallization from chloroform. Elemental analysis showed for $C_{17}H_{16}N_2S_2Cd$: C, 48.0; H, 3.8; N, 6.6; S, 15.09% (theoretical C, 47.86; H, 3.74; N, 6.71; S, 14.86%). Also infrared spectra of complex showed: $\nu_{C=C}$ (1617 cm^{-1},s); ν_{C-H} (2868 cm^{-1}, m: 2736 cm^{-1}, m), $\nu_{C=N}$ (1514 cm^{-1}, m); ν_{C-N} (1162 cm^{-1}, s), ν_{C-S} (1002 cm^{-1}, s) and ring vibration (1391 cm^{-1}, s; 1103 cm^{-1}, w; 768 cm^{-1}, w). Chemical structure of complex 2,2-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis-benzenethiolato cadmium(II), [CdL] is shown in Fig. 1.

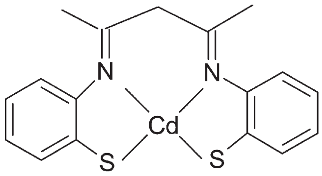

Fig. 1 Structure of complex, 2,2-[(1,3-dimethyl-1,3-propanediylidene)-dinitrilo]bis-benzenethiolato cadmium(II), [CdL] used as carrier for SCN^--ISE.

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Electrode preparation

The membrane ion-selective electrodes were prepared according to a previously reported method.[18] A mixture of PVC, plasticizer (DBP), and the membrane additive (MTOAC), total mass 200 mg was dissolved in approximately 10 ml freshly distilled THF. To this mixture was added the electroactive material [CdL], and the solution was mixed well. The resulting mixture was poured into a small flat bottom dish, 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 incorporated into a silver–silver chloride wire electrode. The electrode was then filled with an internal solution of 0.10 M KSCN. The filled electrode was conditioned by soaking in 0.10 M KSCN. The first conditioning time was approximately 5 h and then 30–40 min for successive uses.

Potential measurement and calibration

The electrochemical system for this electrode can be represented as follows:

Ag | AgCl | internal solution (0.10 M KSCN)|
PVC membrane | test solution || SCE

All potentials were measured at 25 ± 1 °C using a Metrohm Model 691 pH/mV meter. A saturated calomel electrode (SCE, Metrohm) with a fiber junction was used as the external reference electrode. Activities were calculated according to the Debye–Hückel procedure,[19] 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 1×10^{-7}–1×10^{-1} M by serial dilution at constant pH = 5. All solutions were freshly prepared by dilution from the stock standard solution, 1×10^{-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 *vs.* the logarithm of the SCN^- concentration. Potentiometric titration of 10 ml 1×10^{-3} M KSCN solution was carried out with 0.01 M $AgNO_3$ solution using the thiocyanate selective electrode as the indicator electrode in conjunction with a fiber function SCE electrode.

Results and discussion

The plasticized PVC-based membrane electrode containing the ionophore, generates a stable potential response in solution containing thiocyanate. The response of the electrode was improved by addition of lipophilic salts such as MTOAC to the membrane. This not only reduces the membrane resistance but also enhances the response behavior and selectivity and reduces interference from lipophilic sample anions.[20–21] The membrane without the ionophore displayed insignificant selectivity toward thiocyanate whereas, in the presence of the ionophore, the membrane showed remarkable selectivity for thiocyanate over most common inorganic and organic anions. The preferential response toward SCN^- is believed to be associated with the coordination of thiocyanate with the central metal ion of the carrier. It is well-known that the sensitivity and selectivity obtained for a given ionophore depends significantly on the membrane condition.[22–25] Several membrane compositions were investigated by varying the proportions of PVC, DBP (or DOP), and membrane active material, [CdL] and MTOAC. Irrespective of ionophore concentration the slope was relatively larger when the DBP/PVC weight ratio was approximately 2.0. 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 [CdL] up to 5% resulted in membranes for which slopes were larger and the linear range wider.

The potentiometric response of the membrane was greatly improved by the presence of the lipophilic cationic additive, MTOAC. Better response characteristics, *i.e.* Nernstian response and improved selectivity, were usually observed with an ionophore/MTOAC weight ratio of approximately 2.5 which corresponds to a mole ratio of approximately 2.0. The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier-based ion-selective electrodes.[26–27]

Among the different compositions studied (Table 1) responses were best for the membrane incorporating 32% PVC, 61% DBP, 2% additive and 5% [CdL]. As is obvious from Table 1, among two different plasticizer used, DBP is a more effective solvent mediator in preparing the thiocyanate ion-selective electrode. The composition was, therefore, used to study the performance of the electrode, *viz*, working concentration range, sensitivity, selectivity, life time, response time, and effect of pH. The characteristic properties of the optimized membrane are summarized in Table 2.

The influence of the concentration of the internal solution 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.

Table 1 Optimization of membrane ingredients

Percent (w/v) of various components								
No	PVC	DBP	Ionophore	DOP	MTOAC	Slope/mV $decade^{-1}$	Linear range/M	Detection limit/M
1	31	—	7	60.5	1.5	−49.0	1×10^{-5}–1×10^{-1}	1×10^{-5}
2	31	60.5	7	—	1.5	−53.6	1×10^{-5}–1×10^{-1}	1×10^{-5}
3	31.5	62	6	—	0.5	−62.2	1×10^{-5}–1×10^{-1}	5×10^{-6}
4	30	61	7	—	2	−54.8	1×10^{-5}–1×10^{-1}	1×10^{-5}
5	32	61	6	—	1	−65.4	1×10^{-5}–1×10^{-1}	5×10^{-6}
6	32	—	6	61	1	−55.0	1×10^{-4}–1×10^{-1}	5×10^{-5}
7	32	61	5	—	2	−58.9	1×10^{-6}–1×10^{-1}	5×10^{-7}
8	32	—	5	61	2	−62.0	1×10^{-5}–1×10^{-1}	1×10^{-5}
9	32	63	5	—	0.0	42.3−	5×10^{-5}–1×10^{-1}	5×10^{-5}
10	32	—	5	63	0.0	40.3−	5×10^{-4}–1×10^{-1}	1×10^{-4}

Table 2 Characteristics of optimized SCN^--ISE

Linear range/M	1×10^{-6}–1×10^{-1} M
Slope/mV decade^{-1}	−58.9
pH range	2.5–8.0.
Precision	At concentrations of 1×10^{-2} M and 1×10^{-3} M SCN^- standard deviations were of ±0.5 and ±0.7 mV respectively.
Detection limit/M	5×10^{-7}
Life time/month	2
Response time/s	5–20

The effect of the pH of the test solution (1×10^{-2}, 1×10^{-3} and 1×10^{-4} M) on the response of the membrane electrode was examined at three SCN^- concentrations. pH was adjusted with dilute nitric acid and sodium hydroxide as required. As illustrated in Fig. 2 the potentials remain constant within a pH range of approximately 2.5–8.0. Variation of the potential at $pH < 2.5$ could be related to protonation of [CdL] in the membrane phase, which results in a loss of its ability to interact with SCN^- ions. At higher $pH > 7.5$, the potential drop (negative slope) may be because of interference from hydroxide ions. In high pH media, hydroxide ion will compete with thiocyanate ion for the cation site in the membrane.

The optimum equilibration time for the membrane electrode in the presence of 1×10^{-1} M KSCN was 5 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. In the traditional procedure, the membrane is conditioned in a solution that contains a relatively high concentration of the primary ion. This ensures stable and reproducible electrode behavior and is recommended for practical use of the sensor. However, the presence of these primary ions is often the reason for the non-Nernstian response toward highly discriminated ions.[28] The calibration plot shows the linear range to be from 1×10^{-6}–1×10^{-1} M; the near-Nernstian slope is -58.9 ± 0.5 mV decade^{-1} of SCN^- concentration. The practical limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5×10^{-7} M.

The stability and reproducibility of the electrode was also tested. The standard deviation of 20 replicate measurements at three thiocyanate concentration of 1×10^{-2}, 1×10^{-3} and 1×10^{-4} M were ±0.5, ±0.7 and ±0.8 mV respectively.

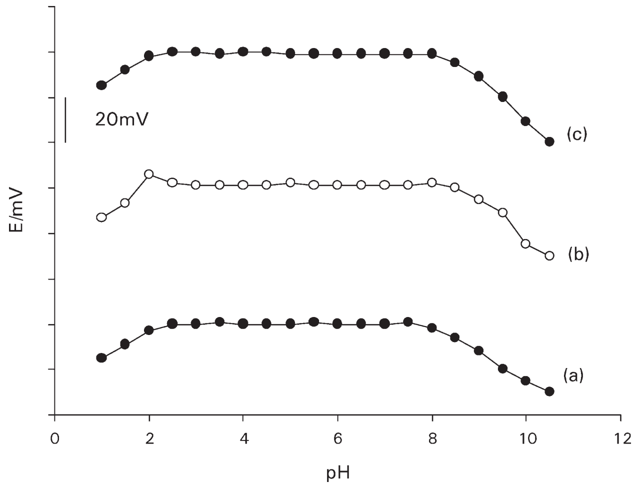

Fig. 2 The influence of pH on the potential response of the optimized SCN^--ISE: (a) 1×10^{-2} M, (b) 1×10^{-3} M, (c)1×10^{-4} M.

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 1×10^{-6} to 1×10^{-1} M. The static response time thus obtained was 5 s for 1×10^{-1}M SCN^- concentration. At lower concentrations, however, the response time was longer and reached 20 s for a SCN^- concentration of 1×10^{-5} M. The actual potential *vs.* time traces are shown in Fig. 3. 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 two months to investigate stability. During this period the electrode was in daily use and was stored in 1×10^{-4} M SCN^- solution when not in use. Before measurements the electrode was conditioned in 0.1 M KSCN for approximately 30 min. 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.

The most important characteristics of any ion-sensitive sensor 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

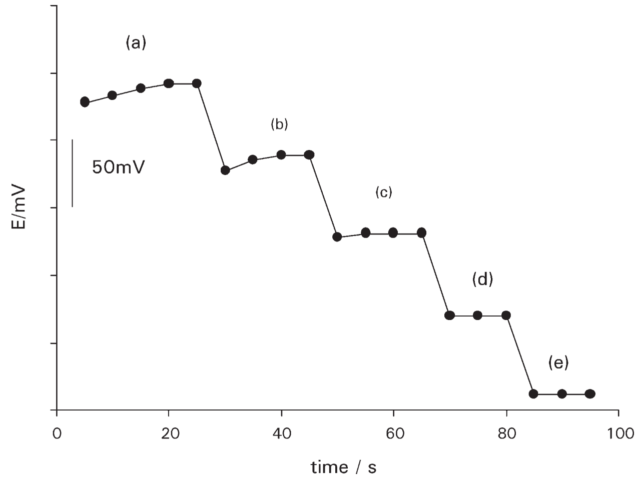

Fig. 3 Response time of the optimized SCN^--ISE for step changes in concentration of SCN^-: a) 1×10^{-5} M, b) 1×10^{-4}M, c) 1×10^{-3}M, d) 1×10^{-2} M, e) 1×10^{-1} M.

Table 3 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^-	−2.4	CO_3^{2-}	−3.6
CI^-	−4.1	MnO_4^-	−2.2
Br^-	−2.5	NO_3^-	−2.8
I^-	−2.8	SO_4^{2-}	−3.5
NO_2^-	−3.1	$S_2O_3^{2-}$	−3.2
CN^-	−4	$H_2PO_4^-$	−3.5
OAc^-	−4.1	C_{2O4}^{2-}	−4
Sal[a]	−4.2	HPO_4^{2-}	−3.7
$Cr_2O_7^{2-}$	−3.7	CrO_4^{2-}	−2.5

[a] Salicylate.

Table 4 Comparison of the potentiometric parameters of the proposed SCN^--selective electrode with the other SCN^--selective electrodes

A^-	The proposed SCN^--ISE	Ref. 30	Ref. 31[a]	Ref. 32[b]	Ref. 33
Nernstian slope, mV $decade^{-1}$	-58.9 ± 0.5	-57.8	Ionophores (I,II,III, respectively) -56.8, -58.3, -55.6	Ionophores (I,II, respectively) -60.6 ± 0.8, -57.5 ± 1.2	-58.1
Linear range, M	1×10^{-6}–1×10^{-1}	1×10^{-7}–1×10^{-1}	Ionophores (I,II,III, respectively) 1×10^{-5}–1×10^{-2} 9×10^{-6}–1×10^{-2} 1×10^{-5}–1×10^{-2}	Ionophore (I,II) 1×10^{-6}–1×10^{-1}	5×10^{-5}–1×10^{-2}
Limit of detection, M	5×10^{-7}	4.8×10^{-8}	5×10^{-6}	6×10^{-7}	4×10^{-5}
Response time, s	5–20	15–120	<10	5	5
Interferent ions	—	—	IO_4^-	I^-	NO_3^-, NO_2^-, I^-, Cl^-, ClO_4^-, Br^-

[a] Ionophores I,II,III, were di-,tetra-,and hexa-imidepyridine derivatives respectively. [b] Ionophores of I, II, were bis(2-mercaptobenzoxazolato)-mercury(II) and bis(2-pyridinethiolato)mercury(II) respectively.

the fixed interference method (FIM)[29]. The selectivity coefficient for various anions were evaluated by the mixed solution method with a fixed concentration of interference (0.10 M), and varying amounts of SCN^- concentrations. Table 3 lists the potentiometric selectivity coefficient data of the sensor for several anions relative to SCN^-. As is evident from the data in Table 3 the electrode based on [CdL] has relatively high selectivity toward SCN^- relative to anions such as salicylate, oxalate, and several common anions. The compound of [CdL] seems to show a stronger interaction with the SCN^- ion than with any of the other anions tested. It is interesting to note that the observed selectivity pattern for the SCN^--ISE significantly differs from the so-called Hofmeister selectivity sequence. From the data given in Table 3, it is immediately obvious that the SCN^--ISE is highly selective with respect to other inorganic and organic anions. This is most probably due to the weak interaction between these anions and the ionophore.

Table 4 lists the linear range, detection limit, slope, response time and selectivity coefficients of some of the other thiocyanate-selective electrodes against the proposed thiocyanate-selective electrode for comparative purposes.[30–33] As can be seen from the Table 4, the selectivity coefficients obtained for the proposed electrode are superior to those reported for other SCN^--selective electrodes listed. It is noteworthy that the limit of detection, linear range, slope and response time of the proposed electrode are also considerably improved with respect to those of the previously reported SCN^--selective electrodes.

Analytical applications

The high degree of thiocyanate selectivity exhibited by the electrode based on [CdL] carrier makes it potentially useful for monitoring concentration levels of thiocyanate in biological 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. Quantification of salivary thiocyanate provides a reliable prediction of cyanide exposure such as occurs in tobacco smoking and as a suitable index for distinguishing smokers from non-smokers. 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 spectrophotometric method.[34] The results, presented in Table 5, indicate good agreement between the potentiometric and spectrophotometric procedures.

Table 5 Determination of thiocyanate in different samples

Sample	Spectrophotometric method (SCN^-/mM)[a]	ISE (SCN^-/mM)[a]
Urine of smoker	0.77 ± 0.07	0.79 ± 0.06
Urine of non-smoker	0.32 ± 0.04	0.31 ± 0.04
Saliva of non-smoker	0.73 ± 0.06	0.74 ± 0.05
Saliva of smoker	1.73 ± 0.08	1.71 ± 0.06

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

The proposed electrode was also successfully used an indicator electrode in conjunction with SCE in the potentiometric titration of KSCN solution with $AgNO_3$ a suitable titrant. Typical results for the titration for 10.0 ml of 0.001 M KSCN with 0.01 M Ag NO_3 show that the amount of KSCN ion in solution can be accurately determined with the electrode. Therefore, the end point can be obtained by extrapolation of the linear portions of the titration plot.

Conclusions

The new electrode incorporating the 2,2-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis-benzenethiolato cadmium(II) as an ionophore showed fast response time, wide linear dynamic range and low limit detection. The high degree of thiocyanate selectivity by the electrode makes it potentially useful for monitoring concentration levels of thiocyanate in biological samples.

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