

Thiocyanate: selective membrane electrode based on macrotricyclic binuclear Cu(II)–Schiff base complex

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Abstract A highly selective PVC membrane electrode was prepared for thiocyanate (SCN^-) determination, based on macrotricyclic binuclear Cu(II)–Schiff base complex as an ionophore. The novel macrotricyclic compound (cryptand) was synthesized by condensation of 4,4'-diaminodibenzo-18-crown-6 with bis(4-formyl phenyl)terephthalate under high-dilution condition and the structure was confirmed by FT-IR, ^1H NMR, ^{13}C NMR and MS studies. The Cu(II) complex of the compound was prepared and was examined for use as anion-selective electrode as a carrier which displays an anti-Hofmeister selectivity sequence in following order: $\text{SCN}^- > \text{ClO}_4^- > \text{NO}_3^- > \text{CN}^- > \text{I}^- > \text{CO}_3^{2-} > \text{NO}_2^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-}$ with a preference for thiocyanate ion over many common anions. The electrode has a linear dynamic range between 1.0×10^{-7} and 1.0×10^{-1} M, with a Nernstian slope of -58.9 mV decade $^{-1}$ and detection limit of 3.1×10^{-8} M. The working pH range of the sensor was found to be in the range of 3.0–8.0. It exhibits a fast response time of 20 s and has a lifetime of about 2 months. Application of the electrode for determination of thiocyanate in waste water samples and in human urine samples have also been demonstrated.

Keywords Anion selective electrode · Binuclear Cu(II) complex · Thiocyanate · PVC-membrane · Macrotricyclic compound

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Introduction

Anions play highly important roles in an extensive range of biological, medicinal and environmental processes [1], and because of their significance, the development of analytical methods for anions has been increasing in importance over the last few years. Although there are several methods for anion determination like spectrophotometry, spectrofluorimetry, Raman spectroscopy, capillary zone electrophoresis, gas chromatography, electrochemistry and ion chromatography [2–6], the carrier-based ion-selective electrodes (ISEs) are mainly used for routine applications because of numerous advantages like high selectivity and sensitivity, simple procedures with a relatively rapid response, long-term stability, wide linear dynamic range and are comparatively inexpensive [7, 8]. They can be widely applied for determining the anion from different samples. There are only a few examples on the transport of anions through liquid membranes. These mainly involve the use of quaternary ammonium or phosphonium salts as anion carriers [9] and they always display the classical Hofmeister selectivity sequence which reflects the hydrophobicity of the anions (i.e., the more lipophilic anions give better responses): perchlorate > thiocyanate > iodide \approx salicylate > nitrate > bromide > nitrite > chloride > sulfate. It is difficult to prepare useful electrodes for anions behind perchlorate in the Hofmeister selectivity sequence. Thus, research on anti-Hofmeister sensing materials with high selectivity for given anions is an expeditiously expanding domain in chemical sensors. Recently, electrodes using plasticized poly(vinyl chloride) (PVC) membranes with metalloporphyrins [10–13], metallophthalocyanines [14, 15], organometallic derivatives [16–18], aza-substituted macrocyclic ligands [19–21] and Schiff base metal complexes [22–25] have been observed to show such specific

metal ligand interactions. ISEs based on these metal ligand interactions have been reported for the determination of anions which demonstrated potentiometric anion selectivity sequences that were remarkably different from the Hofmeister pattern. These deviations can be attributed to specific interactions between the central metal and the analyte anion.

Binuclear metallic complexes may become a new promising class of carriers for anion electrodes because of the higher lipophilicity as compared to mononuclear complexes. Moreover there are very few reports on binuclear metal complex as a carrier in an anion selective electrode [26–29]. This special property is advantageous in increasing the solubility of ionophore in membrane and hence can be efficiently used to improve the interaction towards an anion like SCN^- of the binuclear complex electrode.

Monitoring and detection of SCN^- have received great attention in recent years due to its harm to aquatic and human life. At present, the most preferred detection method is potentiometric detection based on ISEs.

Macrotricyclic compounds (cryptands) have found application as neutral carriers in preparation of ISEs for many cations [30–32]. However, there are only a few reports wherein cryptands have found application as ISE for anions but there are no reports of SCN^- detection using cryptand.

In the present work, a binuclear copper(II) complex of a novel macrotricyclic Schiff base synthesized in our laboratory have been incorporated into a plasticized PVC membrane with 2-nitrophenyloctylether (O-NPOE) as plasticizer to prepare highly selective and sensitive thiocyanate electrode. We found that this electrode displayed excellent potentiometric response characteristics such as a wide linear range, low detection, fast response and good selectivity towards thiocyanate over other anions.

Experimental

Reagents and materials

All reagents and chemicals used were of analytical grade. Milli-Q water was used for preparing the stock solution of metal salts. Dilutions of the stock solution were also done by Milli-Q water. O-NPOE was purchased from Merck. Polyvinyl chloride (PVC) was obtained from G.S.C. (India) and SCN^- was used as potassium thiocyanate for membrane sensor studies.

Apparatus

The FT-IR spectra were recorded on Bruker Tensor 27 FT-IR spectrometer as KBr pellets. The FAB-MS were

recorded on a Jeol/SX/102/Da-600 mass spectrometer data system using Argon/Xenon as the accelerating gas. m-Nitro benzyl alcohol (NBA) was used as a matrix with the peak at m/z 136, 137, 154, 289 and 307. EI-MS were recorded on GC-MS SHIMADZU QP 5050. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 125 MHz respectively on a Bruker DRX 400 spectrophotometer in CDCl_3 with tetra methyl silane (TMS) as a internal standard. A Meter Lab Model PHM 95 pH/ION Meter with a saturated calomel electrode as reference electrode was used for potential measurements.

Synthesis of the ionophore

Preparation of terephthaloyl dichloride (1)

A mixture of terephthalic acid (5 g, 30 mmol) and PCl_5 (12.48 g, 60 mmol) were placed in 100 mL single neck flask equipped with reflux condenser. The mixture was refluxed for 4 h and after completion of the reaction, the by-product, phosphorus oxy chloride (bp, 107 °C) was distilled off and residual viscous liquid was allowed to cool down at room temperature to obtain a white solid crystalline product mp 81 °C EI-MS m/z 203 ($M + 1$).

Synthesis of bis(4-formyl phenyl)terephthalate (2)

A mixture of terephthaloyl dichloride (2.5 g, 12 mmol) and 4-hydroxy benzaldehyde (3.0 g, 24 mmol), triethylamine in diethyl ether was stirred at room temperature (25 °C) for about 4 h. The resulting mixture was washed with dilute HCl and the organic layer was separated and the solvent was removed by vacuum distillation to get white crystalline product. EI-MS m/z 374 ($M + 1$).

Preparation of Schiff-base macrotricyclic compound (3)

The novel Schiff base macrotricyclic compound was prepared by condensation of 4,4'-diamino-dibenzo-18-crown-6 with bis(4-formyl phenyl)terephthalate under high-dilution condition.

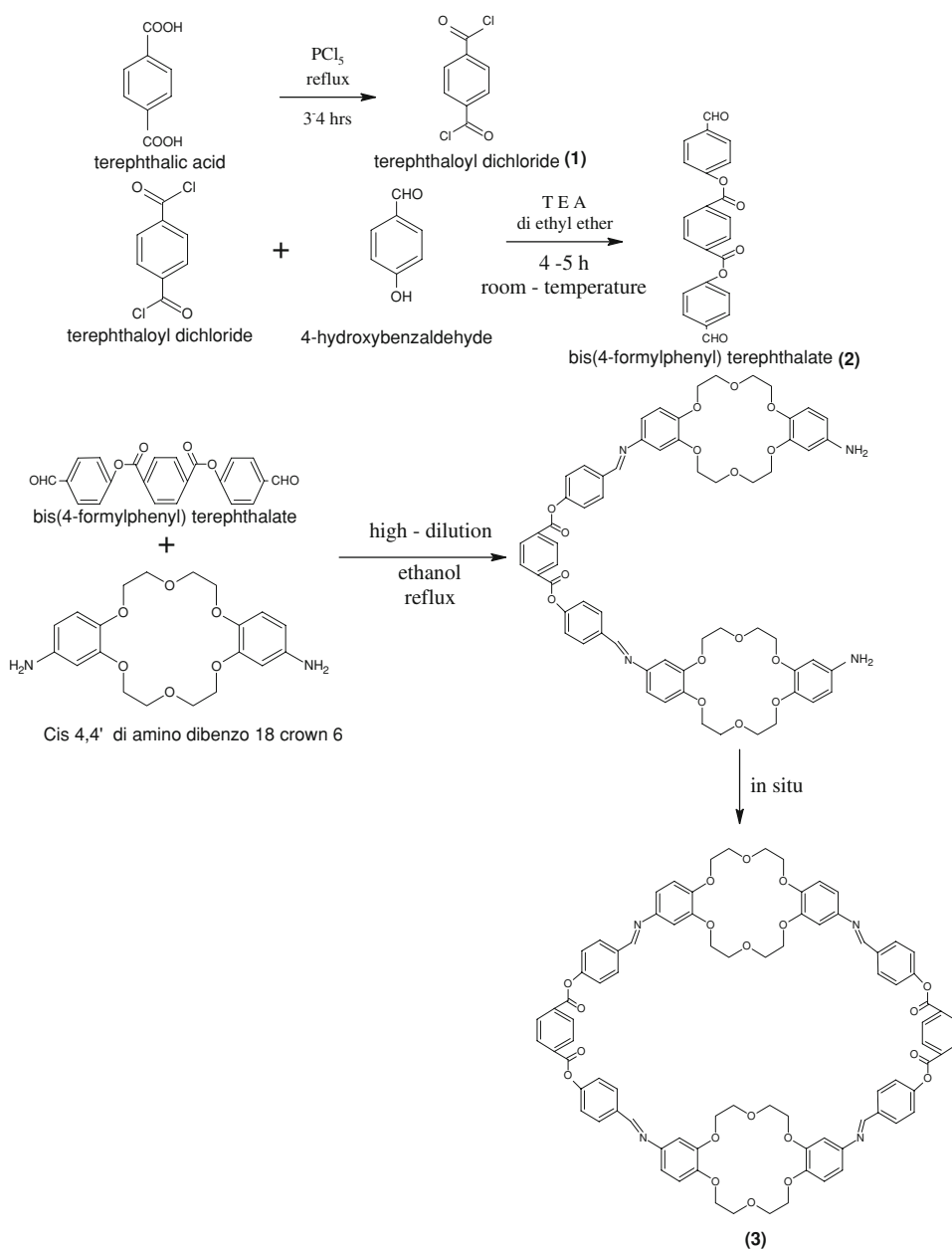
An ethanolic solution of bis (4-formyl phenyl) terephthalate (0.035 g, 2.5 mmol) was added drop wise to a solution of 4,4'-diamino-dibenzo-18-crown-6 (2 g, 5 mmol) in ethanol (700 mL) and the resulting mixture was vigorously stirred and refluxed for 6 h. The second portion of bis(4-formyl phenyl)terephthalate (0.035 gm, 2.5 mmol) in 50 mL ethanol was added drop wise with vigorous stirring and refluxed for another 8 h. After completion of the reaction, ethanol was distilled out using rotary

evaporator. The product mixture was subjected to column chromatography toluene/methanol (9:1) to obtain product as light yellow solid. mp 215 °C FT-IR (KBr) 1630, 1250, 1123 cm^{-1} : ^1H NMR (400 MHz, CDCl_3 , Me_4Si): δ 8.8 (s, 4H, $-\text{N}=\text{CH}$), 6.6–7.2 (m, 12H, Ar-H), 7.4–7.6 (m, 24H, Ar-H), 4.2–4.0 (m, 16H, OCH_2), 3.4–3.2 (m, 16H, OCH_2) ^{13}C NMR (125 MHz, CDCl_3 , Me_4Si) 163.8, 162.6, 145.2, 142.2, 134.9, 130.0, 128.8, 121.3, 116.1, 115.1, 106.9, 72.8, 70.4. FAB-MS observed m/z 1457 (M^+) Elemental analysis calculated for $\text{C}_{84}\text{H}_{72}\text{N}_4\text{O}_{20}$ %C 69.18, %H 4.94, %N 3.84 found %C 69.42, %H 4.87, %N 3.92. The synthetic protocol is given in Scheme 1.

Synthesis of the complex

The Schiff-base ligand (2.91 g, 2.0 mmol) was dissolved in 50 mL of ethanol and the solution was brought to reflux. To this hot solution was added cupric acetate (0.72 g, 4.0 mmol) dissolved in 50 mL of ethanol. Refluxing was continued for 8 h. Upon cooling, a green solution was obtained which was further evaporated at room temperature to obtain light green solid as the desired solid complex. The structure of the complex was studied by mass spectral analysis. The FAB-MS of the complex showed a peak at m/z 1584 (M^+) which indicate that the macrotricyclic

Scheme 1 Synthetic protocol of Schiff base macrotricyclic compound



compound (**3**) is forming a binuclear complex with Cu^{2+} . The structure of the binuclear complex was confirmed by FT-IR spectroscopy which also provided valuable information about the coordination sites which are taking part in the chelation. On comparing the absorption bands in the infrared spectra it was found that some of the characteristic peaks were shifted in the complex when compared to the ligand. It was found that the strong bands located at 1580 cm^{-1} assigned to the $\nu(\text{C}=\text{N})$ stretching vibration of Schiff base linkage in the free ligand was shifted by 15 cm^{-1} to lower wavenumber confirming the bonding of metal to the ligand through the nitrogen atoms of the azomethine linkage.

Electrode preparation

The optimum composition for the preparation of desired electrode was found to be 5% ionophore, 31% PVC and 64% O-NPOE. The mixture of the components that make up to a total of 100 mg was dissolved in dry freshly distilled 3 mL THF. The resulting mixture was slowly poured on a small flat bottom dish of 2 cm diameter at room temperature ($25\text{ }^\circ\text{C}$). The master membrane developed was sectioned appropriately and attached with electrode assembly with the use of araldite. The assembly was filled with an internal solution of $1.0 \times 10^{-3}\text{ M SCN}^-$. The filled electrode was conditioned by soaking in $1.0 \times 10^{-3}\text{ M SCN}^-$ solution for 24 h.

Potential measurement

The following cell assembly was set up for electrochemical measurement. All the measurement was made at $25 \pm 1\text{ }^\circ\text{C}$.

$\text{Ag-AgCl}/3\text{M KCl}/1.0 \times 10^{-3}\text{M SCN}^-/$

PVC membrane/test solution/ $\text{KCl}/\text{Hg-Hg}_2\text{Cl}_2$

Results and discussion

The electrode based on the metal-ligand complex in plasticized membrane exhibited selectivity behavior deviating from the lipophilicity based Hofmeister sequence and gave a highly selective response towards SCN^- . Such unusual response can be attributed to some strong interaction between the central metal in the carrier and the anion. In preliminary experiments, the Cu(II) -macrotricyclic Schiff base complex was tested for its selectivity towards different anions by UV-vis spectral analysis. It was found that noticeable shift was observed only in the case of thiocyanate anion, whereas for other anions the shifts were negligible (Table 1). The spectral change of ionophore on

Table 1 Change in UV-vis spectra of Cu-complex ($1 \times 10^{-5}\text{ M}$) on interaction with different anions [A^-] = $2 \times 10^{-5}\text{ M}$

Anion examined	Shift in λ_{max} (nm)
SCN^-	16
ClO_4^-	6
NO_3^-	5
CN^-	5
I^-	4

interaction with thiocyanate is shown in Fig. 1. Similar studies were carried out using the macrotricyclic Schiff base ligand which did not show any shift in the spectra with the addition of different concentration of SCN^- . A bathochromic shift of 16 nm in the spectra in presence of Cu in the structure of the complex gave evidence of coordination of central metal ion with the analyte anion (SCN^-). The Response characteristics of the optimized ion selective electrode no. 4 towards SCN^- is given in Table 2.

Effect of membrane composition

It is recognized that sensitivity and selectivity of the ion selective electrode depend not only on the nature of the carrier used but also extensively on its membrane composition as well as plasticizer/polyvinyl chloride (PVC) ratio. The presence of the lipophilic site in composition of membrane reduces the ohmic resistance thereby improve extraction capacity of the membrane. We investigated the influence of membrane composition on the potential response of the thiocyanate sensor. Different aspects of membrane were optimized and results were summarized in the Table 3. Among the different compositions studied, the membrane in absence of ionophore displayed insignificant selectivity towards anion (SCN^-), whereas in the presence of ionophore the membrane shows remarkable selectivity for anion (SCN^-). The membrane optimized with ingredients 5% ionophore 31% PVC and 64% O-NPOE gave the best response characteristics. The potential response of

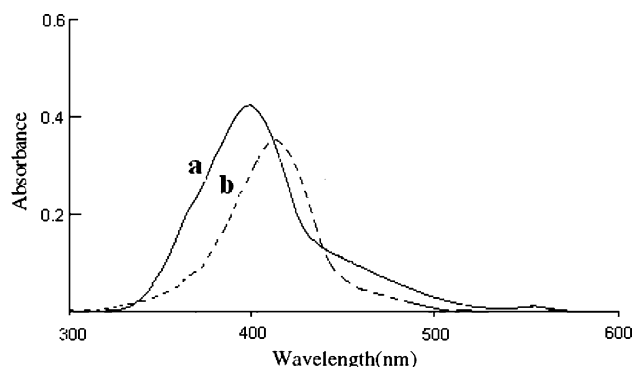


Fig. 1 UV-vis spectra of the Cu complex ($1 \times 10^{-5}\text{ M}$) the absence (a) and presence (b) of thiocyanate ($2 \times 10^{-5}\text{ M}$)

Table 2 Characteristics of the optimized ion selective electrode

Properties	Values/range
Slope	58.9 mV decade ⁻¹
Linear range	1.0 × 10 ⁻⁷ –1.0 × 10 ⁻¹ M SCN ⁻
pH range	3.0–8.0
Detection limit	3.1 × 10 ⁻⁸ M
Response time	≈ 20 s
Standard deviation	±0.5 mV
Lifetime of the electrode	90 days
Optimized membrane composition	PVC (31%), O-NPOE (64%), O-NPOE/PVC weight ratio = 2.06
Conditioning time	1.0 × 10 ⁻³ M SCN ⁻ solution for 24 h

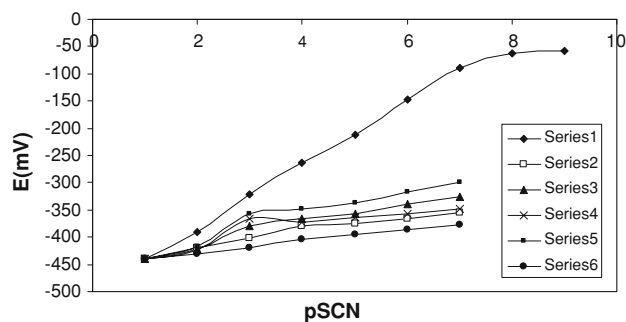
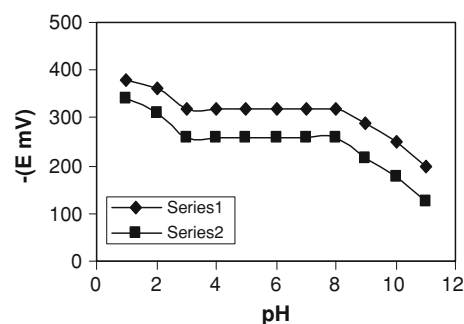
the all the membrane sensors were measured in the range 1.0 × 10⁻¹ M–1.0 × 10⁻⁹ M.

Response characteristics of the electrode

After equilibration in 1.0 × 10⁻³ M SCN⁻ solution for 24 h, the electrode would generate a stable potential in contact with thiocyanate solution. Response characteristic of the electrode was examined in the range of 1.0 × 10⁻¹ M–1.0 × 10⁻⁹ M by serial dilution. All the solutions were freshly prepared by dilution from the standard stock solution. The solutions were stirred and the potential readings were recorded when they became stable. The electrode showed a linear response to the concentration of SCN⁻ in the range of 1.0 × 10⁻¹ M–1.0 × 10⁻⁷ M (Fig. 2). The slope of the calibration graph was 57.81 mV decade⁻¹ and the limit of detection determined from the intersection of the calibration graph was found to be 3.1 × 10⁻⁸ M.

Effect of pH

The potential response of the electrode was found sensitive towards pH change. The effect of pH of the test solution on the response of the electrode was examined over a range of 2.0–13.0 at 1.0 × 10⁻³ (series 1) to 1.0 × 10⁻⁴ M (series 2) anion concentration as illustrated in the Fig. 3. The pH

**Fig. 2** Potential response of SCN⁻ ion selective electrode series (1) SCN⁻, (2) SO₄²⁻, (3) NO₃⁻, (4) NO₂⁻, (5) ClO₄⁻, (6) CO₃²⁻**Fig. 3** Effect of pH on the potential response at concentration of SCN⁻ 1.0 × 10⁻³ (series 1) and 1.0 × 10⁻⁴ M (series 2)

adjustments were carried out by 0.1 M phosphoric acid and sodium hydroxide solution. The potential remain constant within the range of approximately pH 3–8. Variation of the potential under pH 3 could be related to protonation of the ionophore in the membrane which result in loss of its interaction with the anion. And at pH above 8 the potentiometric response was found to be poor towards anion because of coordination competition between anion (SCN⁻) and OH⁻. Thus the prepared anion selective electrode is applicable over a wide pH range of 3.0–8.0, which is wider range as compared to other SCN⁻ selective electrodes.

Effect of internal solution

The effect of the internal solution concentration on the potential response of the electrode was investigated. The

Table 3 Composition (%) of membranes and response characteristics of the electrode

Membrane no.	PVC	O-NPOE	Ionophore	Slope (mV decade ⁻¹)	Liner range (M)
1	36	64	0	11.3	–
2	32	62	6	57.10	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁷
3	30	63	7	56.62	1.0 × 10 ⁻¹ –5.0 × 10 ⁻⁷
4	31	64	5	57.81	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁷
5	30	65	5	56.10	1.0 × 10 ⁻¹ –8.0 × 10 ⁻⁷
6	28	67	5	55.10	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁶

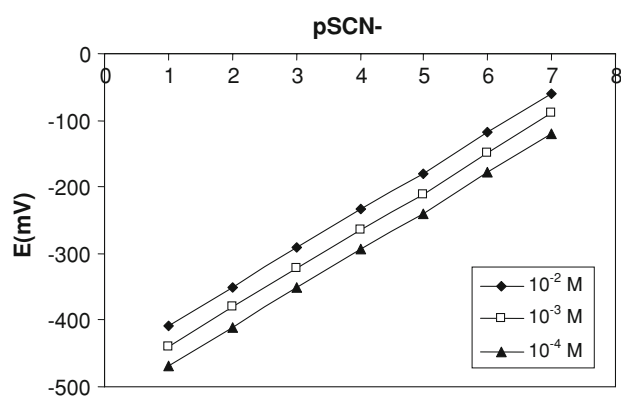


Fig. 4 Effect of internal solution (1.0×10^{-2} M– 1.0×10^{-4} M) on the potential response of the SCN^- selective electrode

SCN^- concentration was changed from 1.0×10^{-2} M– 1.0×10^{-4} . It was found that the concentration of the internal solution had negligible effect on the potential response of the electrode which can be seen in Fig. 4. A 1.0×10^{-3} M SCN^- solution was thus used as internal solution for the further studies.

Response time of the electrode

Response time is one of the most important characteristic of the ion selective electrode. To measure response time, the electrode was first dipped in to 0.1–0.01 M concentration solution of SCN^- and was then immediately shifted to another solution in which the concentration of the ion solution was tenfold. After dipping in the second solution the potential was noted in the interval of 5 s and the graph of potential against time was plotted as shown in Fig. 5. The time taken by the electrode to obtain stable potential is the response time of the electrode which is 20 s for the proposed electrode.

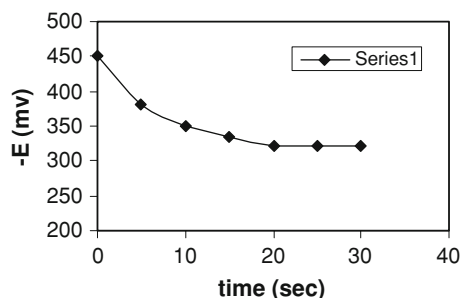


Fig. 5 Dynamic response of SCN^- selective electrode from concentration 0.1 M to 0.001 M

Life time of the SCN^- selective electrode

The electrode was tested a period of 3 months to investigate the stability (life time). During this period the electrode was stored in 1.0×10^{-3} M SCN^- solution when not in use. Before each measurement the electrode was conditioned for approximately 30 min, and the response of the anion selective electrode was examined at the regular intervals. Results shown in Table 4 indicate that the electrode displayed no significant change in the performance in the terms of slope and linearity for a long period of about 90 days.

Effect of non aqueous media

The working of the electrode in different solvents was studied using methanol–water, ethanol–water and acetone–water mixture. The non-aqueous content was varied between 10 and 30% (v/v). Results summarized in Table 5 showed that the electrode can be applied in solutions having up to 20% non aqueous content above which the slope and the working concentration range is reduced and potential showed drift probably due to leaching of the membrane ingredients.

Selectivity

The most important characteristic of any ion-sensitive sensor is its relative response to the primary ion over other ions present in solution, which is usually expressed in terms of selectivity coefficient. In the present work selectivity coefficient of the anion selective electrode towards different anions were evaluated by the match potential method (MPM) [33] which is totally independent of the Nicolski–Eisenman equation. A specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate

Table 4 Stability and reproducibility of SCN^- selective electrode

Time (days)	Slope (mV decade ⁻¹)	Liner range (M)
1	57.81 ± 0.5	1.0×10^{-1} – 1.0×10^{-7}
7	57.81 ± 0.5	1.0×10^{-1} – 1.0×10^{-7}
14	57.81 ± 0.5	1.0×10^{-1} – 1.0×10^{-7}
21	57.81 ± 0.5	1.0×10^{-1} – 1.0×10^{-7}
35	57.80 ± 0.5	1.0×10^{-1} – 1.0×10^{-7}
49	57.32 ± 0.7	1.0×10^{-1} – 1.0×10^{-7}
60	57.15 ± 1.0	1.0×10^{-1} – 7.0×10^{-7}
70	56.83 ± 1.3	1.0×10^{-1} – 1.0×10^{-6}
90	56.29 ± 1.5	1.0×10^{-1} – 1.0×10^{-6}

Table 5 Effect of partially non aqueous media on the response of SCN⁻ selective electrode

Non aqueous content % (V/V)	Working concentration range (M)	Slope (mV decade ⁻¹)
0	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁷	57.8
<i>Ethanol</i>		
10	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁷	57.8
20	1.0 × 10 ⁻¹ –2.0 × 10 ⁻⁷	57.3
30	1.0 × 10 ⁻¹ –3.0 × 10 ⁻⁶	56.5
<i>Methanol</i>		
10	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁷	57.8
20	1.0 × 10 ⁻¹ –2.5 × 10 ⁻⁷	57.1
30	1.0 × 10 ⁻¹ –3.0 × 10 ⁻⁶	56.1
<i>Acetone</i>		
10	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁷	57.8
20	1.0 × 10 ⁻¹ –4.0 × 10 ⁻⁷	56.9
30	1.0 × 10 ⁻¹ –5.0 × 10 ⁻⁶	55.8

experiment, interfering ions (B) are added to an identical reference solution, until the same potential obtained. Its value can be determined from the following equation,

$$K_{A,B}^{\text{pot}} = \frac{\Delta aA}{a_B} = \frac{a'A - aA}{a_B}$$

Specific activity (concentration) of the primary ion ($a_{\text{SCN}^-} = 1.0 \times 10^{-6}$ M) is added to reference solution ($a'_{\text{SCN}^-} = 5.0 \times 10^{-6}$ M) and potential change (ΔE) is measured. In a separate experiment the interfering ion activity (concentration) ($a_B = 1.0 \times 10^{-5}$ – 1.0×10^{-1}) was added to an identical reference solution until the same potential change (ΔE) is recorded. All the interference studies were carried out at pH 6. The resulting selectivity coefficients for different interfering ions are given in the Table 6. The results indicate that the electrode is selective to thiocyanate over a number of other inorganic anions. It is interesting to note that observed selectivity pattern for the thiocyanate selective electrode was found to be as

Table 6 Selectivity coefficient values for SCN⁻

Interfering anion	Selectivity coefficient
ClO ₄ ⁻	-1.34
NO ₃ ⁻	-1.72
NO ₂ ⁻	-3.22
SO ₄ ²⁻	-5.21
CO ₃ ²⁻	-2.72
I ⁻	-2.10
Cl ⁻	-4.68
Br ⁻	-4.58
CN ⁻	-1.98

follows: SCN⁻ > ClO₄⁻ > NO₃⁻ > CN⁻ > I⁻ > CO₃²⁻ > NO₂⁻ > Br⁻ > Cl⁻ > SO₄²⁻ which is significantly different from the so-called Hofmeister selectivity sequence. Table 7 display comparison of the proposed anion selective electrode with earlier reported anion selective electrode.

Mechanism to thiocyanate response

The PVC membrane electrodes incorporating some Schiff-base metallic compound as a carrier display an anti Hofmeister selectivity which mainly depends on the specific interaction between the central metal and the analyte anion. It is possible to study the interaction between the central metal of carriers and SCN⁻ with UV–visible spectroscopy. The UV–visible absorption spectra in chloroform of binuclear Cu(II)–Schiff base complex in the presence and absence SCN⁻ is given in the Fig. 1. The considerable bathochromic shift of 16 nm in spectrum in the presence of SCN⁻ is due to coordination of the central metal with the analyte ion SCN⁻. The binuclear complex possesses higher lipophilicity than mononuclear complex, which is favorable to increase the solubility of ionophore in membrane, thus interaction towards SCN⁻ from binuclear compound based electrode is enhanced.

Analytical application

The thiocyanate selective electrode fabricated is potentially useful for determination of thiocyanate in biological samples. The electrode was tested by determining thiocyanate in human urine. Measurement was carried out on different urine samples taken from smokers and non-smokers. The sample was diluted tenfold with phosphate buffer solution of pH 6 before measurement. Experimental results show that the urinary thiocyanate concentration is higher for smokers than for non smokers. An attempt was also made to determine SCN⁻ in industrial waste water sample. Table 8 summarized thiocyanate concentration in human urine by the proposed electrode as well as by reported colorimetric method [34].

Conclusion

The results of this study showed that the ion selective electrode based on Cu(II)–Schiff base binuclear complex display many advantages like fast response, high selectivity, fair stability and reproducibility and low detection limit. And the study also displayed that selectivity for SCN⁻ is related to the unique interaction between the central metal Cu(II) and SCN⁻; which was supported UV–vis spectroscopy. The electrode could be used to the

Table 7 Comparison of the potentiometric parameters of the proposed thiocyanate-selective electrode with other reported thiocyanate-selective electrodes

Ionophore	Linear range (M)	Limit of detection (M)	Slope (mV decade ⁻¹)	Interferents (log K > -3.0)	Reference
Mn(II) porphyrin	1×10^{-1} – 10^{-2}	2.5×10^{-5}	-64	Sal ⁻ , IO ₄ ⁻	[35]
Co(II) porphyrin	1×10^{-4} – 10^{-1}	3.0×10^{-5}	-55	NO ₂ ⁻ , ClO ₄ ⁻	[36]
Co(II) and Mn(II) phthalocyanine	1×10^{-6} – 10^{-1}	3.0×10^{-6}	-57.5	Sal ⁻ , I ⁻ , N ₃ ⁻	[37]
Ag(I)-thiourea complex	3×10^{-4} – 10^{-2}	1.0×10^{-4}	-41.5	S ₂ O ₃ ⁻ , Br ⁻ , I ⁻	[38]
Imidepyridine derivatives	9×10^{-6} – 10^{-2}	5.0×10^{-6}	-55.6	IO ₄ ⁻	[39]
Bis-furaldehyde Schiff base copper(II) complex	5×10^{-6} – 10^{-1}	2.0×10^{-6}	-57.5	I ⁻ , Sal ⁻ , ClO ₄ ⁻	[40]
Cooper-1,8-dimethyl-1,3,6,8,10,13-aza cyclotetradecane complex	7×10^{-6} – 10^{-1}	4.0×10^{-6}	-57.2	ClO ₄ ⁻ , CN ⁻	[41]
Bis-bebzion Schiff base binuclear copper(II) complex as neutral carrier	8.5×10^{-7} – 6.8×10^{-1}	5.0×10^{-7}	-59.0	ClO ₄ ⁻ , Sal ⁻ , I ⁻	[27]
Proposed SCN ⁻ selective electrode	1×10^{-7} – 10^{-1}	3.1×10^{-8}	-57.81	ClO ₄ ⁻ , N O ₃ ⁻ , NO ₂ ⁻	

Table 8 Determination of thiocyanate in different samples

Sample	ISE (mM)	Colorimetric method (SCN ⁻ , mM)
Urine of non-smoker	0.25 ± 0.03	0.23 ± 0.04
Urine of smoker	0.79 ± 0.04	0.82 ± 0.05
Wastewater	3.26 ± 0.07	3.24 ± 0.07

direct determination of the SCN⁻ content in waste water and human urine samples.

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