

Full Paper

Determination of Thiocyanate Ion by Ion-selective Electrode Using Schiff Base Complex of Cu(II) as an Ionophore

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Received: 4 April 2012 / Accepted: 21 April 2012 / Published online: 30 April 2012

Abstract- This study is related with the determination of thiocyanate anion by using 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxahexadec-1(17),14,15-triene-2,13 diimencopper(II) as ionophore. The membrane sensor with composition of 37% PVC, 60%, BES, 2% HTBP and 1% ionophore, exhibits a Nernstian response for thiocyanate ion, with a wide concentration range of 4.4×10^{-8} – 1.0×10^{-1} M, low detection limit (1.0×10^{-8} M) and slope of 60.5 ± 0.3 mV decade⁻¹ of activity within pH range of 2.5–8.5 and fast response time of 5s. The sensor was also found to work satisfactorily in partially non-aqueous media up to 30% (v/v) content of methanol, ethanol or acetone and could be used for a period of 2 months without any change in response characteristics.

Keywords- Thiocyanate Ion, Ion-selective electrode, Schiff Base, Potentiometry

1. INTRODUCTION

Anions play a very important part in many essential chemical and biological processes. For example DNA, ATP and most of the enzyme substrates and co-factors are present under anionic forms [1, 2]. Today, many industrial processes and wastes increase the concentration

of anions present in the environment. The presence of these anions is crucial in medical and environmental concerns. High concentration of anions in organisms or a misregulation of anion transport can have harmful effects on human health and can be the origin of a number of diseases such as cancers. For example, problems with the transport of such a simple anion as chloride cause illnesses like cystic fibrosis [3, 4] and excessive phosphate concentrations provoke disorders of the calcium distribution within human organisms [5].

Potentiometric sensors are attractive devices for continuous water quality monitoring, either as in situ probes or as chemical analysis systems. The development of a good sensitive sensor for thiocyanate ion has long been a subject of concern to analytical chemists and lot of efforts has been made in this direction in the last four decades.

Thiocyanate finds many industrial applications and though not as toxic as cyanide, it is harmful to aquatic life. Thiocyanate is known to be an important part in the biosynthesis of hypothyronine by lactoperoxidase. Thus the complete absence of thiocyanate or reduced thiocyanate in the human body is damaging to the human host defense system. Transition metal macro cyclic complexes have received a great attention because of their use in anion selective electrodes [6-18].

The development of the field of analytical chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as anionic receptor for biologically important species [19, 20]. Thus a new Schiff base complex of copper was synthesized and used for the fabrication of PVC based thiocyanate selective sensor.

2. EXPERIMENTAL

2.1. Reagents and Equipments

Most of the metal salts, 5-methyl-2-hydroxybenzene-1,3-dial, 1,2-dichloro ethane, and o-aminophenol were purchased from E. Merck and were used as received. High molecular weight pure poly(vinyl chloride) i.e. PVC-powder was purchased from Sigma Aldrich. Various additives/plasticizers viz. bis(2-ethylhexyl)sebacate (BES), dimethylsebacate (DMS), acetophenone (AP), benzyl acetate (BA), bis(2-ethylhexyl)sebacate (DOS), Oleic acid (OA) and hexadecyltrimethyl-ammonium bromide (HTAB) was bought from Reidel (India). Triply distilled water was used throughout. All potentiometric measurements were made at $25 \pm 1^\circ\text{C}$ with an Equiptronic-India Digital Potentiometer using SCN^- selective membrane sensor in conjunction with an standard calomel electrode containing 10% (w/w) potassium nitrate solution in the outer compartment. pH measurements were made on a digital pH meter (Elico-LI-Model-120 pH meter).

2.2. Synthesis of Ionophore

The ligand 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxahexadec-1(17),14,15-triene-2,13-diimine (L) was synthesized according to modify procedure already published [19] and the brief synthesis is given as below:

A solution of compound 1,5-Bis(*o*-aminophenoxy)-3-thiapentane (2 mmol) in dry CH_2Cl_2 (35 mL) was added to a vigorously stirring solution of 5-methyl-2-hydroxybenzene-1,3-dial (2 mmol) in dry CH_2Cl_2 (35 mL) at room temperature. The reaction mixture was stirred for a further 25 min and washed with 1:1 mixture of bicarbonate and water (40 mL each). The organic layer was dried over magnesium sulfate, and the solvent was evaporated to give an oily product. The crude was purified by column chromatography, using petroleum ether (bp=60-80°C)/ethyl acetate as eluent. The pure product was obtained as a pale yellow liquid; bp=146-150 (0.52 mg, 65% yield). A pale yellow liquid obtained than reacted with etanolic solution of several metal nitrates. The stability of ligand metal complex was calculated in terms of formation constant.

The physical data of the ligand are given below:

Molecular formula: $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2$

^1H NMR (CDCl_3 , ppm): 3.31 (t, 4H, $J=8.4$ Hz, CH_2), 3.84 (s, 3H methyl), 4.34 (s, 2H, $J=8.5$ Hz, CH_2), 7.04 (s, 8H aromatic), 7.1 (s, 2H aromatic), 8.2 (s, 2H, imminic).

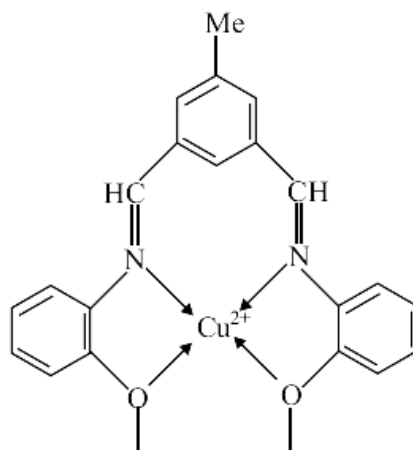


Fig. 1. 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxahexadec-1(17),14,15-triene-2,13-diimencopper(II) (CuL)

2.3. Formation constant

Formation constant of the ion-ionophore complex is very important parameter that dictates the practical stability and selectivity of the metal ligand complex. In this work the complexation between metal cations and the ionophore were measured in terms of formation

constant (K_f) using molar conductance ratio [21] (equation 1 and 2) in acetonitrile solution at $25 \pm 1^\circ\text{C}$.

$$K_f = \frac{[\text{ML}^+]}{[\text{M}^+][\text{L}]} \times \frac{(\Lambda_M - \Lambda_{\text{obs}})}{(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]} \quad (1)$$

Where

$$[\text{L}] = C_L - \frac{C_M(\Lambda_M - \Lambda_{\text{obs}})}{(\Lambda_M - \Lambda_{\text{ML}})} \quad (2)$$

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the ionophore added, and C_M the analytical concentration of the cation. The complex formation constants, K_f , and the molar conductance of complex, Λ_{obs} , were obtained by using a nonlinear least squares program KINFIT [22], and the results are summarized in Table 1. The values of formation constant in table 1 indicate that the ligand 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxa heptadec-1(17),14,15- triene-2,13-diimene forms a stable complex with Cu^{2+} ion as compared to other tested cations. Hence the copper complex of the ligand 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxa heptadec-1(17),14,15- triene-2,13-diimene-copper (CuL) was used for the further studies.

2.4. Fabrication of Electrode

The PVC-based membranes of Cu^{2+} complex with ligand 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxa heptadec-1(17),14,15-triene-2,13-diimene have been prepared by dissolving a mixture of 32% PVC, 64% plasticizer (BES, DMS, AP, BA, DOS respectively), and 3% HTAB, and 1% ionophore in 20 mL THF [23]. The components were added in terms of weight percentage. After complete evaporation of THF a membrane sheet about 0.5 mm of thickness and 5 mm diameter was cut away and glued at one end of a glass tube with the help of araldite to avoid leakage. The membrane electrode was finally conditioned by soaking in a 0.1 M NaCNS solutions for 2 days. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as an external reference electrode.

The Emf measurements were carried out with the cell assembly given below:

Internal reference calomel electrode	Internal reference solution (0.01 M SCN^-)	SCN^- ion Selective Membrane	Test solution of SCN^- ion	External reference Calomel electrode
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Potential differences between the ion selective electrodes and the double junction calomel electrodes were measured with Equiptronic-India Digital Potentiometer at $25\pm 1^\circ\text{C}$. Several membranes incorporating CuL as ionic carrier was made to study the behavior of best optimized membrane and the one which generated the best Potentiometric response was further studied in detail for selectivity, pH range, non-aqueous effect, and the determination of thiocyanate ion in different samples.

Table 1. Formation constant of metal ions-ligand

Cation	Log K_f
Cu^{2+}	6.32 ± 0.30
Co^{2+}	3.12 ± 0.30
Ni^{2+}	3.10 ± 0.30
Zn^{2+}	2.92 ± 0.30
Cd^{2+}	2.35 ± 0.30
Hg^{2+}	2.26 ± 0.30
Ca^{2+}	1.86 ± 0.30
Mg^{2+}	1.65 ± 0.30
Pb^{2+}	1.38 ± 0.30
Na^+	1.19 ± 0.30
K^+	1.69 ± 0.30
Al^{3+}	2.76 ± 0.30
Ag^+	1.73 ± 0.30
Eu^{3+}	3.86 ± 0.30
Sm^{3+}	3.80 ± 0.30
Lu^{3+}	3.72 ± 0.30
La^{3+}	3.63 ± 0.30

3. RESULT AND DISSCUSION

The proposed ligand 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxa heptadec-1(17),14,15- triene-2,13-diimene (L) act as tetradentate ligand and forms square planer complex with Cu^{2+} ion. The central metal atom in the complex is to increase the coordination number to five or six by interact with anions or polar solvent molecule. The electron density around central metal atom is depends on the ability of electron donor atom present in the ligand.

3.1. Membrane Optimization

The response characteristics of membrane sensors are highly depend on the ionic carrier, as well as on other membrane components. The presence of lipophilic plasticizers improved the selectivity, sensitivity and other response characteristics of membrane electrode, the positively charged additives reduces the ohmic resistance and improved the potentiometric behavior of ion selective electrode, and polymeric matrix provide the mechanical strength to the membrane electrode [24, 25]. In the present study several polymeric membranes with varying composition were prepared, after several experiments it has found that the membrane sensor with the composition of ionophore: Plasticizer: HTAB: PVC of 1: 60: 2: 37, shows the best performance. All the components were added in weight percentage (Table 2). The data in Table 2 indicates that the plasticizer BES provide the best environment for the complexation between ion and ligand and dissolve the membrane components.

Table 2. Membrane optimization with different plasticizers

Membrane No.	Composition of membrane (%)						HTAB	Iono-phore	PVC	Working Concentration Range (M)	Slope(mV decade ⁻¹ of activity)	Response Time (sec)
	BES	DMS	AP	BA	DOS	OA						
1	60						2	1	37	4.4×10^{-8} - 1.0×10^{-1}	-60.5 ± 0.30	5
2		60					2	1	37	1.5×10^{-7} - 1.0×10^{-1}	-59.00 ± 0.3	14
3			60				2	1	37	2.6×10^{-7} - 1.0×10^{-2}	-58.00 ± 0.1	16
4				60			2	1	37	2.2×10^{-9} - 1.0×10^{-1}	-57.80 ± 0.3	17
5					60		2	1	37	1.4×10^{-9} - 1.0×10^{-1}	-59.50 ± 0.1	20
6						60	2	1	37	2.8×10^{-9} - 1.0×10^{-1}	-60.50 ± 0.3	22
7. Without plasticizer							2	1	37	3.2×10^{-5} - 1.0×10^{-1}	-29.02 ± 0.3	38

3.2. Effect of internal solution

The influence of the concentration of internal solution on the potential response of the electrode assembly was studied and the results shows that the variation of the concentration of the internal solution do not cause any significant difference in the potential response of the electrode, except a change in the intercept of the resulting Nernstian plots. After immense studies of internal solution with different concentration, it was found that the best results have

been obtained with internal solution of activity 0.01 M. Therefore an internal solution of the same concentration was taken as reference solution [26].

3.3. Effect of plasticizer and working concentration range

Plasticizer is one of the key components of membrane selective electrode which increases the selectivity, sensitivity and stability of membrane sensor [27]. In the present study various membranes with different plasticizers was fabricated and their response characteristics were evaluated. After extensive studies of experimental data's it was observed that the membrane with plasticizer BES gives the best response characteristics. This is because of high polarity of BES as compared to the other plasticizers (Fig. 2). The polarity of plasticizer may affect the mobility of ionophore and its metal complex, which may change the detection limit of the membrane sensor. Experimental result using proposed membrane sensor shows that the detection limit of membrane electrodes decreases as the dielectric constant of plasticizer decreases

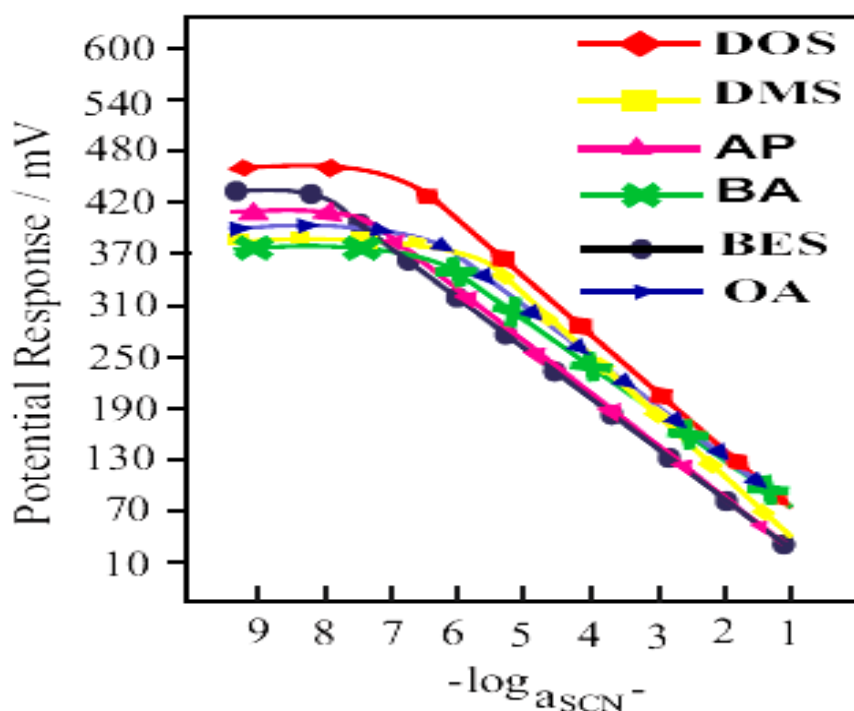


Fig. 2. Calibration plot of the thiocyanide ion-selective electrode with CuL

3.4. Selectivity coefficient

Response of the ion-selective membrane sensor is provided by the presence of lipophilic ionic sites and electro active material. If membrane, contain sufficient amount of

electroactive material, the complexation of the target ion by the ligand and membrane-solution ionic exchange determines membrane selectivity .

In the present study, the selectivity of membrane sensor was detected by Fixed Interference Method (FIM) (IUPAC recommendation), and the results were presented in terms of potentiometric selectivity coefficients ($-\log K_{SCN^-, A^{n-}}^{POT}$) which has been measured at 1×10^{-3} M concentration of metal ions using the modified the Nicolsky equation (Eq. 3) [28]

$$K_{SCN^-, A^{n-}}^{POT} = \frac{a_{SCN^-}}{a_{A^{n-}}^{z_{SCN^-}/z_{A^{n-}}}} \quad (3)$$

Where a_{SCN^-} is the activity of the primary ion and $a_{A^{n-}}$ is the activity of other metal ions z_{SCN^-} and $z_{A^{n-}}$ are their respective charges. The selectivity coefficient pattern (Table 3) clearly indicates that the electrodes are efficiently selective to SCN^- ions.

Table 3. Selectivity Coefficient values calculated by Fixed Interference Method

Interfering Ions	Selectivity Coefficient $\left[-\log K_{SCN^-, A^{n-}}^{Pot} \right]$
Fixed Interference Method (FIM)	
CN ⁻	3.38
Cl ⁻	4.23
I ⁻	4.82
NO ₃ ⁻	3.86
NO ₂ ⁻	3.83
AcO ⁻	5.76
SO ₄ ²⁻	2.71
ClO ₄ ⁻	2.65
C ₂ O ₄ ²⁻	2.46
CO ₃ ²⁻	2.32
PO ₄ ³⁻	2.92

3.5. Response time and life time

Response time of ion-selective electrode is a very important factor. The response time is defined as the time taken to reach a static potential in the measurements. It is determined after the potential of one metal ion solution becomes constant and then the similar measurements are carried out in another solution of same metal ion with 10 fold change (lower or higher) in concentration. In present study, the practical response time (5 s) was recorded by changing the metal ion concentration in solution over a concentration range of 1.0×10^{-1} to 1.0×10^{-8} M, from lower to higher direction and then higher to lower direction. Experimental results revealed that potentiometric response of the sensor was reversible, although the time needed to reach the equilibrium values was longer than that for the low-to-high sample concentration procedure (Fig. 3).

3.6. pH and non-aqueous effect

The presence of hydrogen ion in the solution may affect the ion exchange kinetics between the solution and membrane phase. In present study the effect of pH on potential response of the electrode was observed in the range of 1-10 (Fig. 4). The data shown in figure 4 indicates that the potential of the electrode remains almost constant in the pH range of 2.5-8.5, therefore this range was taken as the pH range of electrode assembly. The change in potential at higher pH (> 8.5) may be due to the competition kinetics between target ion and hydroxide ion.

In addition to this the electrode was also used in non-aqueous media contain methanol-water, ethanol-water and acetone-water sample. After extensive studies it was observed the proposed electrode is uncreated up to 30% (v/v) solution of these non-aqueous components. However after this composition the concentration range and detection limits decreases (Table 4), this may be due to the interference caused by non-aqueous components.

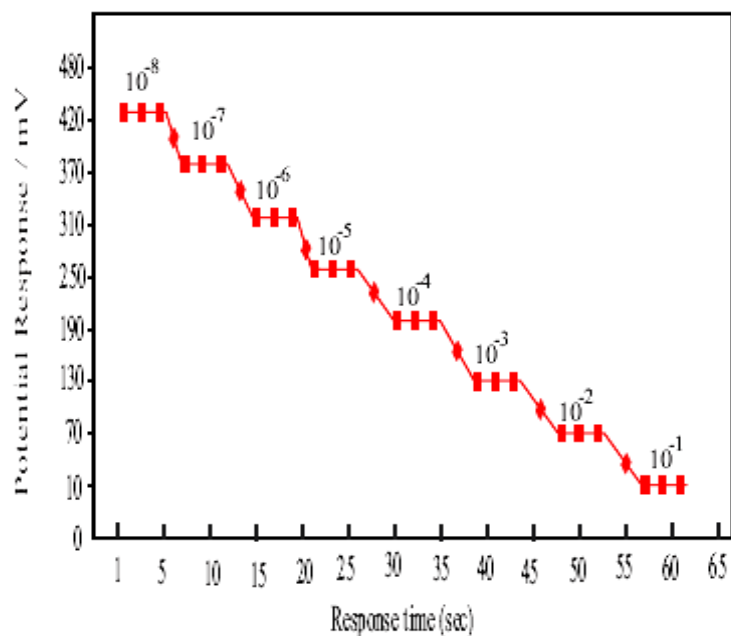


Fig. 3. Response time curve for sensor no. 1

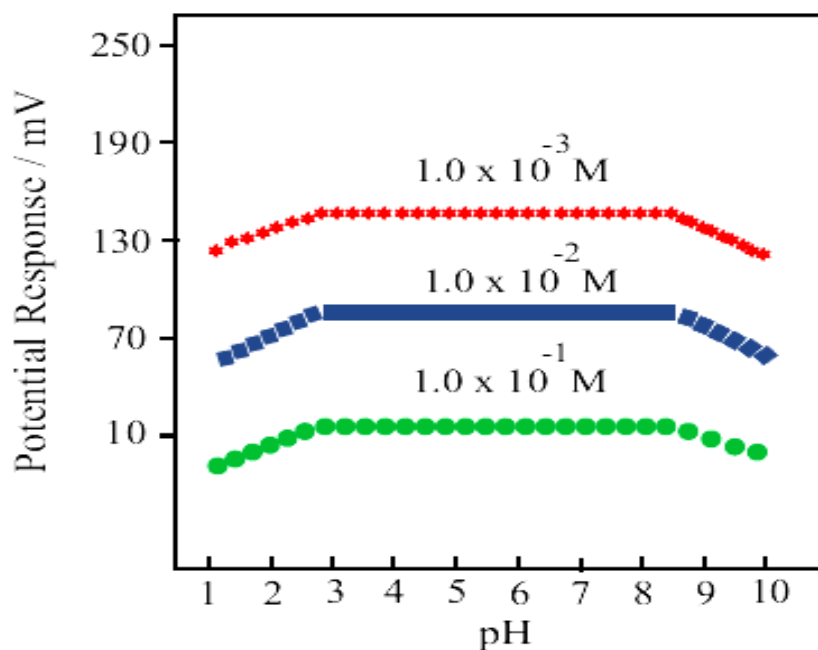


Fig. 4. Effect of pH on potential for sensor no. 1

3.7. Comparison Study

The performance characteristics of the proposed electrode and those of some best reported electrodes were compared and it was found that the proposed electrode has wide concentration range, fast response time (5 s), lower detection limit, wide pH range (2.5-8.5) and long life time (5 months). The proposed electrode show lower detection limit with respect to the previously reported sensor (Table 5).

3.8. Analytical applications

3.8.1. Titration

The practical utility of the proposed membrane sensor was investigated by using it as indicator electrode for the titration of 40 ml of 1.0×10^{-3} M SCN^- with 1.0×10^{-2} M ternary mixtures of silver nitrate, thallium nitrate and lead nitrate solutions, and the curve obtained is shown in Fig. 5. The curves are of standard sigmoid type indicating the sufficient selectivity of the proposed electrode for SCN^- ion.

Table 4. Effect of partially non-aqueous medium on the working of SCN^- sensor (No.1)

Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Working Conc. Range (M)	Response time (Sec)
0	-60.5±0.3	4.4×10^{-8} - 1.0×10^{-1}	5:00
Methanol			
10	-60.4±0.3	4.1×10^{-8} - 1.0×10^{-1}	5:00
15	-60.4±0.3	4.1×10^{-8} - 1.0×10^{-1}	5:00
25	-60.2±0.3	4.0×10^{-8} - 1.0×10^{-1}	5:00
30	-60.0±0.3	4.0×10^{-8} - 1.0×10^{-1}	6:00
35	-53.30±0.3	3.0×10^{-6} - 1.0×10^{-1}	12:00
Ethanol			
10	-60.2±0.3	4.0×10^{-8} - 1.0×10^{-1}	5:00
15	-60.2±0.3	4.0×10^{-8} - 1.0×10^{-1}	5:00
25	-60.0±0.3	3.8×10^{-8} - 1.0×10^{-1}	6:00
30	-59.8±0.3	3.6×10^{-8} - 1.0×10^{-1}	6:00
35	-52.80±0.3	3.2×10^{-6} - 1.0×10^{-1}	12:00
Acetone			
10	-60.6±0.3	4.2×10^{-8} - 1.0×10^{-1}	5:00
15	-60.4±0.3	4.2×10^{-8} - 1.0×10^{-1}	5:00
25	-60.1±0.3	4.1×10^{-8} - 1.0×10^{-1}	5:00
30	-60.2±0.3	4.1×10^{-8} - 1.0×10^{-1}	6:00
35	-54.50±0.3	3.4×10^{-6} - 1.0×10^{-1}	10:00

3.8.2. Determination of thiocyanate ion in different samples

In addition the proposed sensor no. 1 was also used for the determination of SCN^- in different samples such as tap water, river water and urine. The test solution of these samples was used without any modification at pH 9.6. The pH of the solution was adjusted by

addition of NaOH. The obtained values were also compared with the values obtained by AAS and ICP (Table 6).

Table 5. Comparison of the reported Thiocyanate-selective electrodes with proposed electrode

Ionophore	Conc. Range (M)	Detection limit (M)	Slope mV/decay	pH range	Reference no.
surfactant modified zeolite (SMZ),	$1.0 \times 10^{-6} - 1.01 \times 10^{-1}$	8.33×10^{-7}	-58.9 ± 0.90	2.0-8.0	29
Tetra-midopyridine	$6.0 \times 10^{-6} - 1.0 \times 10^{-2}$	5.0×10^{-6}	-56.3	2.0-8.0	7
Cu(II) ₂ BBSTA	$9.0 \times 10^{-7} - 1.0 \times 10^{-1}$	7.0×10^{-7}	-57.0	5.0	8
Zn(BDSH)	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	7.0×10^{-7}	-56.5	3.5-8.5	9
Rh[(trpy)(bpy)Cl](PF ₆)	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	4.0×10^{-6}	-58.7	3.0-8.0	10
CCT	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	5.0×10^{-7}	-57.6	3.9-9.2	11
Calix[4]arene	$3.0 \times 10^{-5} - 1.0 \times 10^{-1}$	2.5×10^{-5}	-52.0	2.0-3.0	12
3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxoheptadec-1(17),14,15-triene-2,13-diimino-copper(II)	$4.4 \times 10^{-8} - 1.0 \times 10^{-1}$	1.0×10^{-8}	-60.5 ± 0.3	2.5-8.5	This Work

Table 6. Determination of thiocyanate ion in different water samples

Sample	Proposed Sensor (ppm) ^a	AAS (ppm) ^a	ICP (ppm) ^a
Tape Water	0.031	0.032	0.032
Hindon river	0.065	0.067	0.067
Urine	0.056	0.057	0.056

^aAverage of three replicate measurements

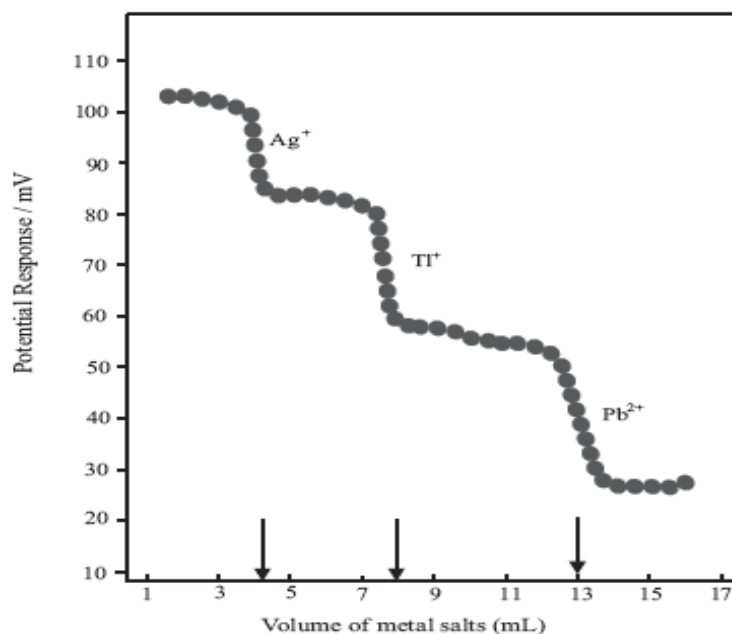


Fig. 5. Potentiometric titration curve of 10^{-3} M SCN^- ion solution with $\text{Pb}(\text{NO}_3)_2$, AgNO_3 and TlNO_3 solutions

4. CONCLUSION

A copper complex 3,12-diaza-4,5,10,11-dibenzo-16-methyl-6,9-dioxo heptadec-1(17),14,15-triene-2,13-diimene was synthesized and used as an ionophore for the direct determination of thiocyanate anion in different samples. The proposed membrane electrode has good potentiometric figures of merit for the determination of thiocyanate ions, including high sensitivity, wide concentration range (4.4×10^{-8} – 1.0×10^{-1} M), low detection limit (1.0×10^{-8} M), and fast response time (5s), with a slope of -60.5 ± 0.3 mV/decade of activity within the pH range of 2.5–8.5. The proposed membrane electrode was also successfully applied as an indicator electrode for the titration of thiocyanate ion with a standard solution of AgNO_3 , TlNO_3 and $\text{Pb}(\text{NO}_3)_2$ solutions (1.0×10^{-2} M).

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