Full Paper

Thallium (I) Selective Membrane Sensor Using Newly Synthesized Podand Derivative of Catechol and Quinoline

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Abstract- The podand chelate, 1,2-bis[$2^{'}$-($8^{''}$-oxyquinoline)ethoxy]-benzene have been synthesized and used as a neutral ionophore to construct an ion selective electrode for the potentiometric determination of thallium ions. Due to the decisive role of solvent mediators, the membranes was fabricated with the plasticizers *o*-NPOE, DBP, DBBP, TEP, OA, DOP, CN respectively and anionic additive NaTPB. The best of the results were obtained with the membrane electrode composition of *o*-NPOE:PVC:Ionophore:NaTPB (58%:34%:5%:3%). This sensor exhibits Nernstian response with slope 58.7 ± 0.3 mV decade^{-1} of activity in concentration range 2.0×10^{-9} to 1.0×10^{-1} M Tl(I), performs satisfactorily over wide pH range (2.5-12), with a fast response time (5 s). The sensor was also found to work satisfactorily in partially non-aqueous media up to 40% content of methanol, ethanol, acetone and acetonitrile solution. The Tl(I)-selective electrode was used as an indicator electrode for the titration of TlNO$_3$ with EDTA and KI solution. The selectivity coefficients determined by using fixed interference method (FIM) indicate high selectivity for Tl (I).

Keywords- Sensor, Potentiometry, Ionophore, Podand, Thallium

1. INTRODUCTION

Thallium is a soft ductile metal belongs to the 13th group of the periodic table. The name thallium derived from the green color its salts give to Bunsen burner flame. The green spectral line is used in forensic chemistry and toxicology, to detect thallium poisoning. Pure thallium is a bluish-white metal that is found in trace amounts in the earth's crust. It stays in the air, water, and soil for a long time and is not broken down [1]. Some thallium compounds are removed from the atmosphere in rain and snow. It's absorbed by plants and enters the food chain. It builds up in fish and shellfish. Thallium and its compounds are extremely toxicit, its toxic being higher than that of Hg, Cd, Pb, Zn and Cu, and only inferior to that of methyl mercury [2]. Agatha Christie made use of thallium's toxicity in her novel The Pale Horse. One symptom the victims experienced, including one of the amateur investigators, was that their hair came out in clumps. The maximum allowable concentration of thallium is 0.1 mg per m^2. Thallium is accumulated in the body in monovalent form, becoming enriched in the hair and skin; it is excreted through kidney and intestines and remains in the body for about 14 days [3].

Thallium usually exists in two oxidation states in nature: Tl(I) and Tl(III). Thallous compounds are quite similar to the compounds of alkali metals, are highly soluble, and can be easily absorbed by plants [4]. The Tl(I) is more stable and more dominate form of thallium in natural water, because the standard redox potential of Tl^{3+}/Tl^+ is 1.28 V, so Tl(I) can only be oxidized to Tl(III) by a strong oxidant, such as bromic water or MnO_2.

The release of thallium into the environment in the case of smelting of lead, copper and zinc ores, the combustion of fossil fuels, oil refining, and other industrial activities, has become one of the major subjects of study now a day. There are lots of technique for the determination of thallium metal ion such as atomic absorption spectroscopy, (AAS), ICP-MS [4], ICP-AES [5], gravimetric determination [6], and isotopic dilution mass spectroscopy [7, 8] are available in the literature, but all these methods are time consuming, involving sample manipulations, relatively expensive and required large infrastructure back up. The simplicity, low cost, fast response time and small infrastructure make the ion-selective electrode a convenient method in this regard. On extensive literature survey we found that few ionophore such as Calix[6]arene-hexaacetic [9], 2′-amino-1,3,5′-trioxospiro[indane-2,4′(5′H)-3′-cyano-indeno(1,2-b)]pyran [10], *N,N′*-dioctylethylene diamine-*N,N′*-disuccinic acid, *meso*-alkyl substituted calix[4]pyrroles [11], *meso*-octamethylcalix[4]pyrrole (**L1**), *meso*-octaethylcalix[4]pyrrole (**L2**) and *meso* tetraspiro cyclohexylcalix [4]pyrrole (**L3**) [12], 4′–nitrobenzo –18–crown–6 [13] has been used for the selective determination of thallium. But all of these reported electrodes have low selectivity, low concentration range, small pH range and high detection limit.

In this research, we report the use of 1,2-bis[2′-(8″-oxyquinoline)ethoxy]-benzene as an ionophore in construction of highly sensitive and selective polyvinyl chloride (PVC)

membrane sensor for the determination of ultra trace amounts of Tl (I) cation in different real and environmental samples.

The electrode exhibited Nernstian responses to thallium (I) ion over a wide concentration rang with low detection limit. The electrode possess fast response time, appropriate lifetime and most importantly good selectivity toward Tl(I) relative to variety of other common inorganic cations.

2. EXPERIMENTAL SECTION

2.1. Reagents

All the analytical grade reagent, di-butyl phthalate (DBP), di-octyl phthalate (DOP), o-nitrophenyl octylether (*o*-NPOE), tri-n-butylphosphate (TBP), dibutyl-butylphosphonate (DBBP), oleic acid (OA), and 1-chloronaphthalene (CN) were purchased from Aldrich Sigma (Wisconsin, USA). Chatechol, 8-hydroxyquinoline and 1,2-dichloroethane were purchased from Merck. High molecular weight poly(vinyl chloride), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), ethanol, chloroform, acetone and potassium carbonate were purchased from Reidel (India) All metal nitrates were brought from Indian Rare Earth Chemicals Ltd. India. All the reagents were of highest pure grade and used without further purification. Standard solutions were freshly prepared in deionized water.

2.2. Instruments Used

All potentiometric measurements were made at $25\pm1^{\circ}$C with a digital potentiometer (Equiptronics EQ-602, Mumbai, India) using Tl(I) selective membrane sensor in conjunction with an ECIL, India double junction Ag/AgCl reference electrode (Model 90-02) containing 10% (w/w) potassium nitrate solution in the outer compartment
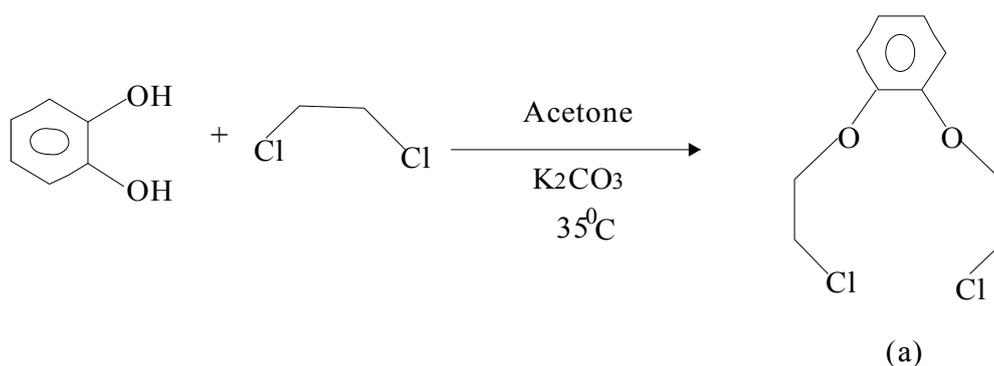
2.3. Synthesis of ionophore

In first step 1,2-bis[(2'-chloro)ethoxy]benzene (a) (scheme-1) was synthesized by stirring a solution of chatechol (1.0 mmole) (in 15 mL acetone) and 0.1 M K_2CO_3 (10 mL) with 1,2-dicholoroethane (1 mmol in 15 mL acetone) in reflux for 70 min, resulting in a colorless liquid. Evaporation of the solution in vacuum gave viscous liquid which on crystallization gives colorless crystals (72% yield). The ionophore (scheme-2) was synthesized by stirring the compound (a) (1.0 mmole) (in 20 mL acetone) and 0.1 M K_2CO_3 (10 mL) with 1,2-dicholoroethane (1 mmol in 20 mL acetone) in reflux for 90 min, resulting in a yellow oily liquid. Evaporation of the solution in vacuum gave viscous liquid. The ligand was obtained as light yellow micro crystals. The micro crystals were filtered off, washed with 5 mL of cooled absolute ethanol and then recrystallized from acetone-/chloroform (2:1, v/v).

The analytical and physical data of the ionophore is given below.

Molecular formula: $C_{28}H_{24}N_2O_4$, yield: 62%.

Analysis: ^{1}H-NMR (CDCl$_3$, ppm): $\delta = 7.36$ (d, 2H, aromatic), 7.21 (d, 2H, aromatic), 6.85 (d, 2H, aromatic), 6.76 (s, 4H, aromatic), 6.73 (d, 4H, aromatic), 6.71 (s, 2H, aromatic), 3.80 (t, 4H, CH2 aliphatic), 3.13 (t, 4H, CH2 aliphatic).

^{13}C-NMR (CD$_3$CN, ppm): $\delta = $ (24 C aromatic); 172.53, 172.31, 171.89, 171.46, 170.75, 169.28, 167.65, 167.62, 165.85, 164.43, 162.86, 160.37, 146.45, 144.92, 143.46, 133.25, 132.76, 132.32, 121.73, 121.56, 119.96, 119.02, 109.95, 109.73; (4C aliphatic); 58.93, 57.6, 32.94, 31.82.

Scheme 1. Synthesis of 1,2-bis[(2′-chloro)ethoxy]benzene

1,2-bis[2′ -(8″ -oxyquinoline)ethoxy]-benzene
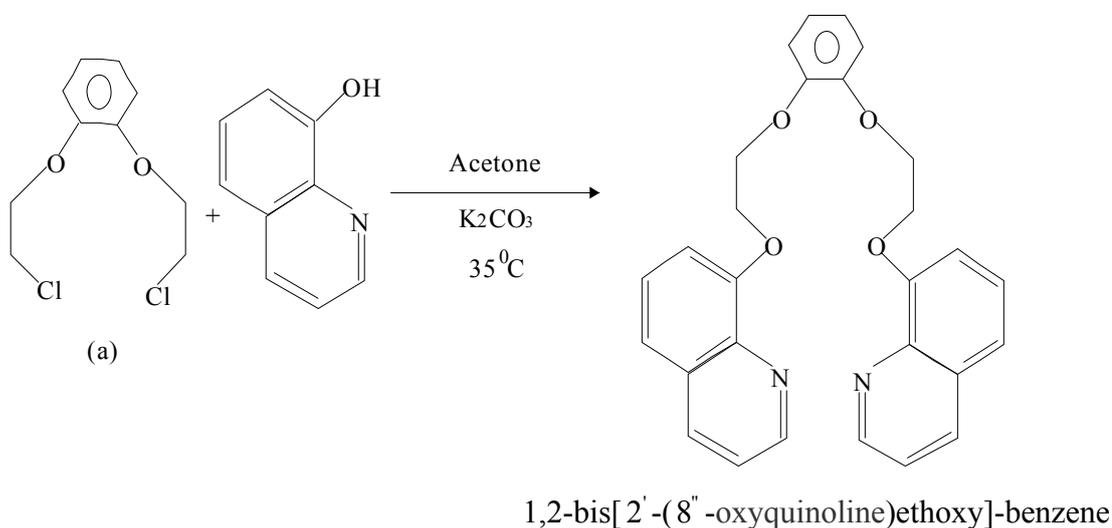
Scheme 2. Synthesis of ionophore (1,2-bis[2′ -(8″ -oxyquinoline)ethoxy]-benzene

2.4. Electrode preparation

The membranes have been fabricated as suggested by Craggs et al. [14]. The PVC-based membranes have been fabricated by dissolving a mixture of 34% PVC, 58% plasticizer (o-NPOE, DBBP, DBP, TBP, 1-CN, OA, DOP respectively), 3% NaTPB, and 5% ionophore in THF. The components were added in terms of weight percentage. The viscosity of the solution and solvent evaporation was carefully controlled to obtain membrane with reproducible characteristics and uniform thickness otherwise the response of the membrane sensors have shown a significant variation. The membranes of 0.5 mm of thickness and 8 mm diameter were removed from the glass plate and glued to one end of a Pyrex glass tube with the help of araldite and M-seal.

The membrane electrode was finally conditioned by soaking in a 0.1 M TlNO$_3$ solution for 4 days. A saturated silver electrode was inserted in the tube for electrical contact and another saturated silver electrode was used as an external reference electrode. The ionic strength of various solutions was maintained with the help of saturated solution of KCl. When membrane was not in used, it kept in 0.1 M TlNO$_3$ solutions to avoid damage by cracking.

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

Internal reference Silver electrode	Internal reference solution(0.1 M Tl$^+$)	Tl$^+$ion Selective Membrane	Test solution of Tl$^+$ ion	External reference Silver electrode

3. RESULTS AND DISCUSSION

In this experiment 1,2-bis[$2^{'}$-($8^{''}$-oxyquinoline)ethoxy]-benzene was used as ionophore to prepare Tl(I) selective membrane electrode in a poly(vinylchloride) matrix. The response characteristics of Tl(I)-ISEs based on proposed ionophore were tested as a function of the membrane composition and nature of plasticizer and amount of ionophore, and the results are compiled in Table 1. The best results are obtained with the sensor prepared by using different plasticizers in the composition of Plasticizer: NaTPB: ionophore: PVC of 58: 5: 3: 34 (%, w/w). The potential response of the membrane electrodes of the proposed ionophore with different plasticizers towards Tl(I) cation is shown in Fig. 1. Based on the generally adopted ion-selective response formalism, the internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable. The effect of concentrations on the potential response of Tl(I) ion selective sensor were studied. The concentration was

varied from 1.0×10^{-4} to 1.0×10^{-1} M and the results corroborate that the variation of the concentration of the internal solution does not cause any significant difference in the potential response of the electrode, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-1} M concentration of internal solution is quite appropriate for smooth functioning of the electrode assembly.

3.1. Effect of plasticizers

The nature of plasticizer has been found to improve the sensitivity and stability of membrane sensor due to characteristics such as lipophilicity, high molecular weight, low pressure and high capacity to dissolve the substrate and other additives present in the polymeric membrane[15]. Hence several membranes of varying compositions and different plasticizers o-NPOE, DBP, DBBP, TEP, DOP, CN and OA in PVC matrix were prepared. The result presented in Table 1 and Fig. 1 indicates that *o*-NPOE plasticized the membrane, dissolve the ion association complexes and adjust both permittivity and ion exchanger sites mobility to give highest possible selectivity and sensitivity. The values of detection limit obtained, with respect to ionophore and different plasticizers has followed the order: *o*-NPOE (1.0×10^{-9}) > DBP $(3.1 \times 10^{-9}$M) > TBP $(1.0 \times 10^{-8}$M) > BBBP $(4.1 \times 10^{-8}$M) > DOP $(2.0 \times 10^{-7}$M) > OA $(7.2 \times 10^{-7}$ M) > CN $(3.1 \times 10^{-6}$M). The observed result clearly indicate that the value of dielectric constant of plasticizer decreases, the detection limit of sensor also decreases.

3.2. Working concentration range and slope

The results presented in Table 1 and Fig. 1, indicate that the best sensor (no. 1) based on ionophore 1,2-bis[$2^{'}$-($8^{'}$-oxyquinoline)ethoxy]-benzene exhibits Nernstian slope of 58.7 ± 0.3 mV decade $^{-1}$ of activity, over a wide concentration range of 2×10^{-9} 1×10^{-1} M with detection limit 1.0×10^{-9}. The most sensible value of slope and working concentration range correspond to sensor (no. 1) indicates that the solvent medium of *o*-NPOE is probably providing the best complexation environment between Tl(I) ion and their respective carriers.
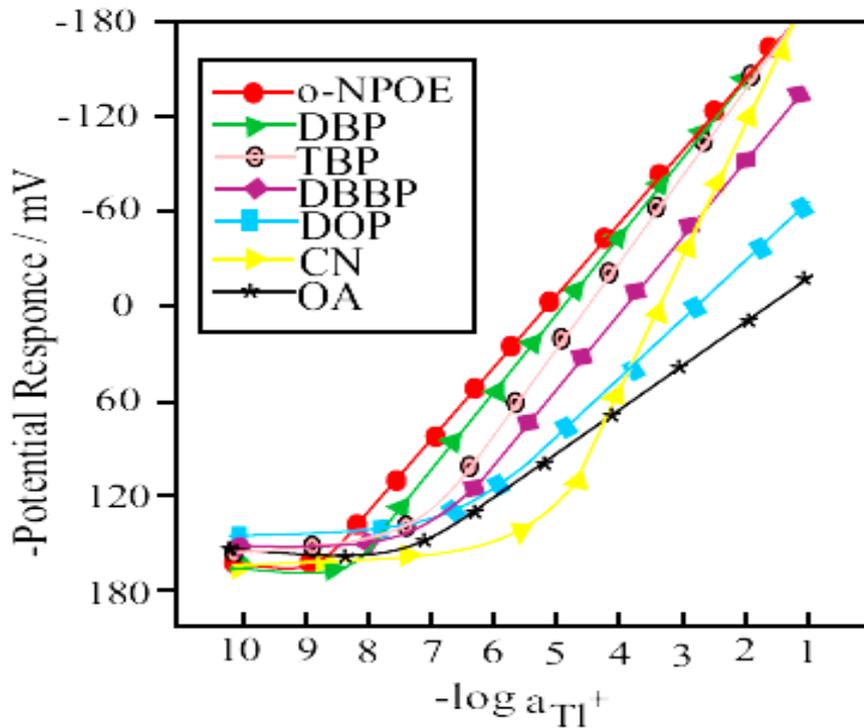
Fig. 1. Variation of potential of PVC based membrane with solvent mediators *o*-NPOE, DBP, TBP, DBBP, DOP, CN, OA respectively with Tl(I) concentration

3.3. Determination of formation constant

Formation constant (K_f) indicates the complexation between metal cations with the ionophore and dictates the practical selectivity of the sensor. In the present study the formation constant was measured using molar conductance ratio (equation 1 and 2) in acetonitrile solution at $25 \pm 1.0\ ^oC$ [16].

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

where

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

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 thesolution during titration, C_L the analytical concentration of the ionophoreadded, 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 [17], and the results are summarized in Table 2.

Table 1. Optimization of membrane composition of thallium(I)-selective sensor

Sensor No.	Membrane Composition (%, w/w)				Linear working range (M)[a]	Slope (mV/dec. of activity)[a]	Response Time (sec)	Life time (months)
	PVC	Additive	Plasticizer	Ionophore				
1	34	5, NaTPB	58,*o*-NPOE	3	2×10^{-9} - 1×10^{-1}	58.7±0.3	5	7
2	34	5, NaTPB	58, DBP	3	6×10^{-9} - 1×10^{-1}	57.4±0.3	10	1
3	34	5, NaTPB	58, TBP	3	3×10^{-8} - 1×10^{-1}	56.6±0.3	12	3
4	34	5, NaTPB	58, DBBP	3	6×10^{-8} - 1×10^{-1}	55.5±0.3	14	1
5	34	5, NaTPB	58, DOP	3	1×10^{-7} - 1×10^{-1}	54.8±0.3	12	5
6	34	5, NaTPB	58, CN	3	5×10^{-6} - 1×10^{-1}	59.1±0.3	08	4
7	34	5, NaTPB	58, OA	3	8×10^{-8} - 1×10^{-1}	33.8±0.3	16	4

[a] Mean value ± standard deviation (three measurements)

3.4. Response time and life time of proposed electrode

Response time is an important factor for a sensor to become sensitive. In this study, the practical response time has been recorded (for sensor no. 1-7) to reach a potential with in ±1 mVof the final equilibrium value, after successive immersion in a series of Tl(I) ion solution, each one having a 10-fold difference in concentration. Thus, the response time measured was 5s (Fig. 2) over the entire concentration range for sensor no. 1. The potentials were sustained for at least 5 min, and the standard deviation of 10 identical measurements was ≤0.5 mV at several concentrations of Tl(I) ions.

The high lipophilicity of ionophore and plasticizer ensure stable potentials and longer life time for the membrane. The loss of a plasticizer carrier or ionic sites from the polymeric film due to leaching into the sample solution is the primary reason for limited lifetimes of carrier-based sensors. Thus, the lifetime of a sensor based on ionophores in solvent polymeric

membranes depends on the distribution coefficient of the ionophores and plasticizers between the aqueous and membrane phases [18]. The long term stability of the electrode was studied by periodically re-calibrating in standard solutions and collecting the response slope. The slope of the electrode response was reproducible over a period of at least 7 months. Thus, the proposed sensor could be used for 7 months without any considerable change in its response characteristics towards Thallium cation.

Table 2. Formation constant of metal ions-ligand

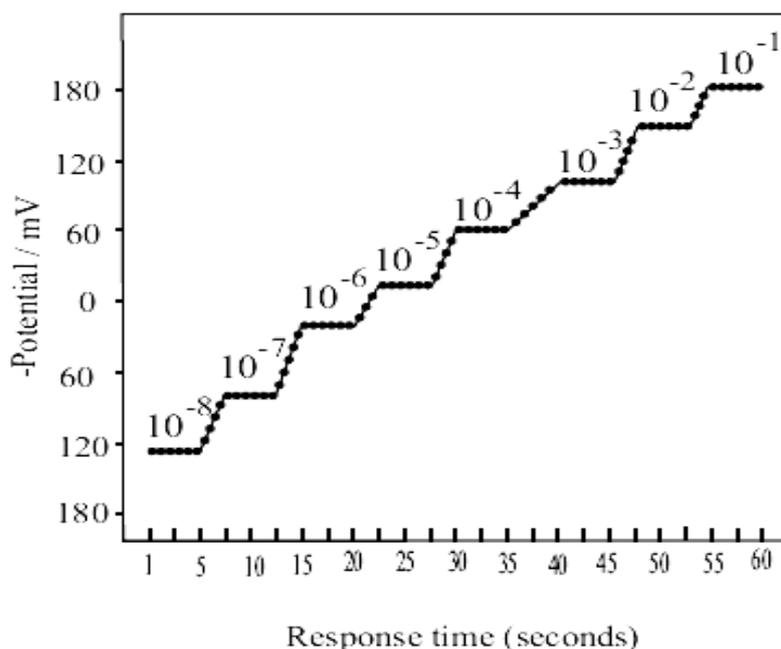| Metal ions	Formation constants (log K_f)
Tl^+	7.2
Al^{3+}	5.3
Mg^{2+}	5.2
Pb^{2+}	4.6
Cd^{2+}	3.2
K^+	3.0
Zn^{2+}	2.9
Cu^{2+}	2.7
Mn^{2+}	2.6
Co^{2+}	2.5
Ca^{2+}	2.3
Ni^{2+}	2.2
Ba^{2+}	2.0
Hg^{2+}	1.8
Ag^+	1.9
Fe^{3+}	1.8

Fig. 2. Dynamic response time curve *vs.* potential response for Tl(I)-selective ion-selective electrode

3.5. pH and non-aqueous effect

The effect of pH on the potential response of sensors was measured in the pH range 0 – 14 for 1×10^{-3} and 1×10^{-4} M Tl(I) solutions (Fig. 3). The pH of the tested solution was adjusted by the addition of nitric acid or hexamine. Fig. 3 indicates that the potential is independent with in the pH range of 2.5-12 for sensor no. 1 based on proposed ionophore. Therefore, the pH range 2.5–12 was taken as the working pH range of the sensor assembly (no.1). The sharp change in potential at pH > 12 may be due to the formation of some hydroxyl complexes of the charge transport process by the membrane thereby causing interference.

The performance of proposed membrane sensor no. 1 was further observed in non-aqueous medium, *i.e.* methanol-water, ethanol-water, acetone-water and acetonitrile-water mixture. The results obtained are compiled in Table 3 and indicate that up to 40% (v/v) solution of non-aqueous content no significant change in the slope and working concentration range of the proposed sensor no. 1 were observed. But above 40% of non-aqueous content, electrode sensor showed potential drift with time.
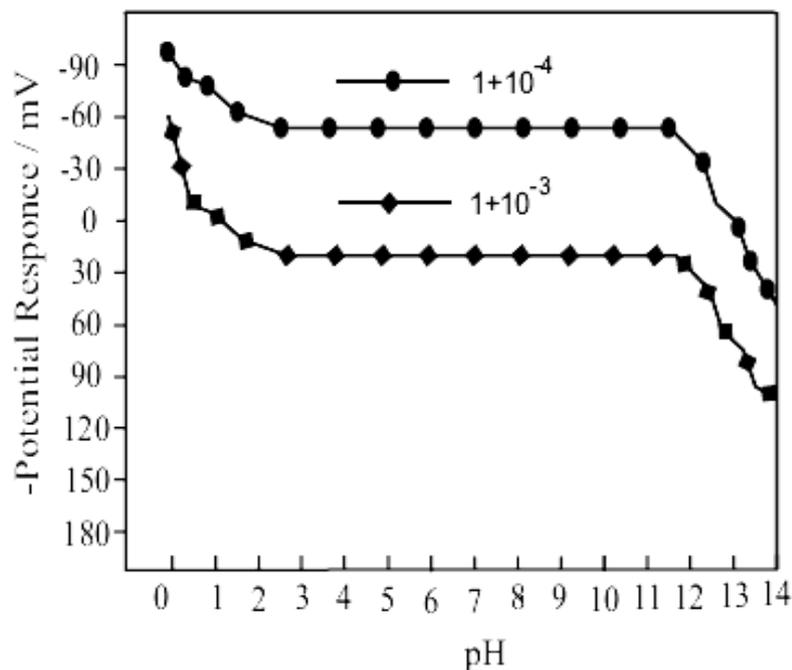
Fig. 3. Effect of pH variation on the Tl(I)-selective electrode

3.6. Potentiometric selectivity

In the present study, the selectivity of membrane sensor was detected by Fixed Interference Method (FIM), and the results was presented in terms of potentiometric selectivity coefficients $\left(K^{Pot}_{Tl^+,M^{n+}} \right)$ which has been measured at 1×10^{-2} M concentration of interfering ions (IUPAC recommendation) using equation (Eq. 3) [19].

$$K^{POT}_{Tl^+,M^{n+}} = \frac{a_{Tl^+}}{a_{M^{n+}}^{z_{Tl^+}/z_{M^{n+}}}} \tag{3}$$

Where a_{Tl^+} is the activity of the primary ion and $a_{M^{n+}}$ is the activity of interfering ion z_{Tl^+} and $z_{M^{n+}}$ are their respective charges. The selectivity Coefficient pattern (Table 4) clearly indicates that the electrodes are efficiently selective to Tl(I) ions. Value of selectivity coefficient equal to 1.0 indicates that the sensor responds equally to primary as well as interfering ions. However, values smaller then 1.0 indicate that membrane sensor is responding more to primary ion than to interfering ions and in such a cases the sensor is said to be selective to primary ion over interfering ion. Further, smaller is the selectivity coefficient, higher is the selectivity order. The value of selectivity coefficient presented in Table 4 shows that selectivity coefficient values for the present sensor are much smaller than

1.0 over a number of studied mono, di and trivalent cations. Hence, the sensor (no.1) is sufficiently selective over these ions and can therefore be used to estimate thallium in the presence of these ions by direct potentiometry. A number of metal ion selective electrodes were prepared by using the given ionophore, but after extensive work it has cleared that the present ionophoric membrane electrode is extremely selective to Tl (I) cation (Fig. 4).

Table 3. Effect of partially non-aqueous medium on the working of Tl(I) sensor (No.1)

Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Working Conc. range(M)	Response time (seconds)
0	58.70±0.3	$2.0\times10^{-9}-1.0\times10^{-1}$	5
Methanol			
10	58.05±0.3	$1.9\times10^{-9}-1.0\times10^{-1}$	5
20	58.00±0.3	$1.7\times10^{-9}-1.0\times10^{-1}$	6
30	58.40±0.3	$1.2\times10^{-9}-1.0\times10^{-1}$	5
40	58.05±0.3	$1.1\times10^{-9}-1.0\times10^{-1}$	6
Ethanol			
10	58.05±1.0	$1.8\times10^{-9}-1.0\times10^{-1}$	6
20	58.50±1.0	$1.5\times10^{-9}-1.0\times10^{-1}$	5
30	58.01±1.0	$1.3\times10^{-9}-1.0\times10^{-1}$	5
40	58.00±1.0	$1.1\times10^{-9}-1.0\times10^{-1}$	7
Acetone			
10	58.00±1.0	$1.5\times10^{-9}-1.0\times10^{-1}$	5
20	58.09±1.0	$1.0\times10^{-9}-1.0\times10^{-1}$	5
30	57.99±1.0	$1.1\times10^{-9}-1.0\times10^{-1}$	6
40	58.50±1.0	$1.9\times10^{-9}-1.0\times10^{-1}$	7
Acetonitrile			
10	58.50±1.0	$1.0\times10^{-9}-1.0\times10^{-1}$	5
20	58.1 ±1.0	$1.8\times10^{-9}-1.0\times10^{-1}$	5
30	57.90±1.0	$1.3\times10^{-9}-1.0\times10^{-1}$	5
40	58.01±1.0	$1.6\times10^{-9}-1.0\times10^{-1}$	6

Table 4. Selectivity coefficient values sensors

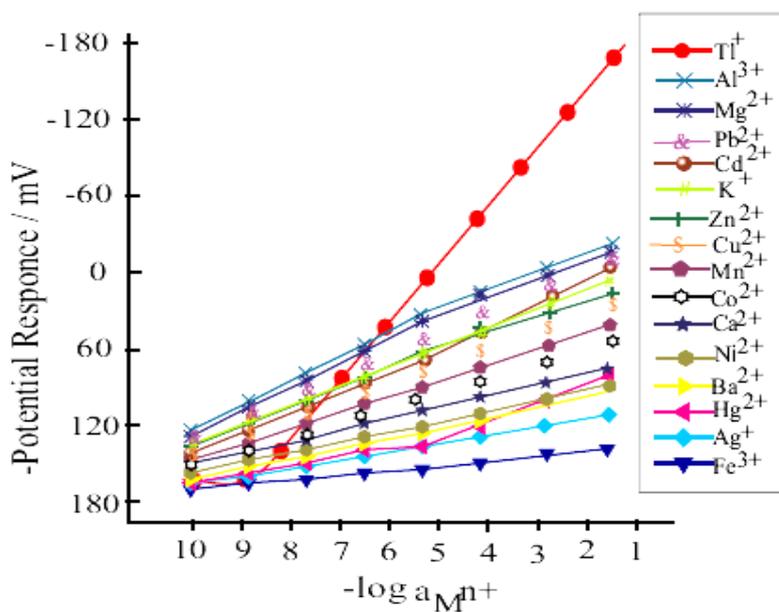| Interfering Ion	Selectivity Coefficient, $\left[K_{Pb^{2+},M^{n+}}^{Pot}\right]$
	Sensor no.1
Al^{3+}	5.3×10^{-5}
Mg^{2+}	5.1×10^{-5}
Pb^{2+}	4.6×10^{-5}
Cd^{2+}	4.3×10^{-6}
K^{+}	4.1×10^{-5}
Zn^{2+}	3.8×10^{-4}
Cu^{2+}	3.5×10^{-5}
Mn^{2+}	2.6×10^{-5}
Co^{2+}	1.7×10^{-5}
Ca^{2+}	2.4×10^{-4}
Ni^{2+}	1.8×10^{-5}
Ba^{2+}	1.4×10^{-5}
Hg^{2+}	1.2×10^{-6}
Ag^{+}	1.7×10^{-5}
Fe^{3}	1.2×10^{-5}

Fig. 4. Calibration curve *vs.* potential for various cations using proposed ionophore

3.7. Comparison study

The performance characteristics of the proposed electrode and those of some reported electrodes [9-13] were compared and it was found that the proposed electrode has wide concentration range, fast response time (5 s), wide pH range (2.5-12) and long life time (7 months). The proposed electrode show lower detection limit with respect to the previously reported sensor (Table 5).

Table 5. Comparison of the reported Tl(I)-selective electrodes with proposed electrode

Sensor no.	Ionophore	Working Conc. range (M)	Slope (mV/decade pH of activity)	pH range	Response time (sec)	Life time	Ref.
1	Calix[6]arene-hexaacetic acid hexaethyl ester	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M	55	2.5-12	<10	4 months	9
2	2′-amino-1,3,5′-trioxospiro[indane-2,4′(5′H)-3′-cyano-indeno(1,2-b)]pyran	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M	-	3.7-8.3	5	3 months	10
3	*N,N*′-dioctylethylenediamine-*N,N*′-disuccinic acid	$6.4 \times 10^{-7} - 1.0 \times 10^{-2}$ M	56±0.2	4.7–9.0	15	3 months	11
4	4'–nitrobenzo –18–crown–6	$5.0 \times 10^{-8} - 1.0 \times 10^{-1}$ M	57.27±0.4	5.0–14	30	10 weeks	12
5	*meso*-tetraspirocyclohexylcalix[4]pyrrole	$1.0 \times 10^{-5.5} - 1.0 \times 10^{-1}$ M	56.0±0.2	2.0-11	<10	4 months	13
6	1,2-bis[2'-(8″-oxyquinoline)ethoxy]-benzene	$2.0 \times 10^{-9} - 1.0 \times 10^{-1}$ M	58.7±0.3	2.5-12	5	7 months	This work

3.8. Analytical applications

3.8.1. Potentiometric titration

The membrane sensor was successfully used in the potentiometric titration of Tl(I) with EDTA. A 40 ml (0.01 M) solution of Tl(I) was titrated with 0.01 M EDTA at pH 8.5 (Fig. 5). The pH of the solution was adjusted by addition of nitric acid and ammonium hydroxide. Upon addition of EDTA, the concentration of Tl(I) ions decreases, which results a decrease in potential of the solution. The break point of the titration curve is sharp and corresponds to the stoichiometry of Tl(I)–EDTA complex. After the end-point, potentials are almost constant

because now the sensor is not responding to small changes in Tl(I) concentration. The curve is of standard sigmoid type indicating the sufficient selectivity of the proposed electrode for Tl(I) ion and sharp inflection point at the titrant volume corresponding to the 1:1 stoichiometry of Tl(I)-EDTA complex. Thus, the electrode assembly can be used for thallium ion determination by potentiometric titration using EDTA.
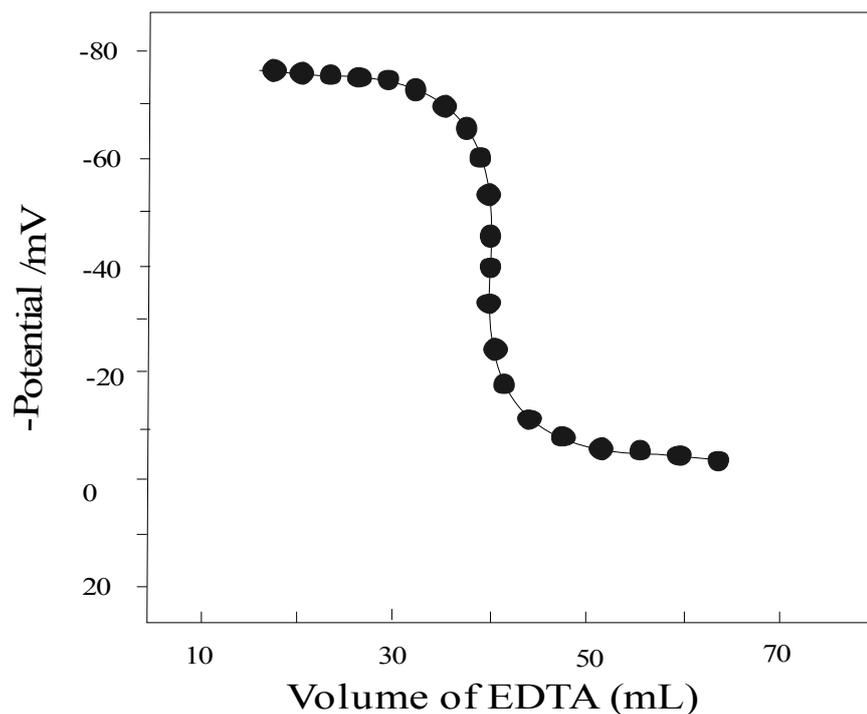

Fig. 5. Potentiometric titration plot of 1.0×10^{-2} M Tl(I) with EDTA(1.0×10^{-2} M)

The propose sensor was also used as an end-point indicator electrode in precipitation titrations of Tl(I) with iodide ion and the titration curves are presented in Fig. 6. As is evident, in this Figure, the titration curve is in standard shape for 10^{-1}-10^{-3} M Tl(I) solutions and, therefore, this electrode could be used for measurement of concentration of Tl(I) cation in solutions. But the curve for 10^{-4} M TlNO$_3$ is less satisfactory due to the relatively high solubility of thallium iodide.
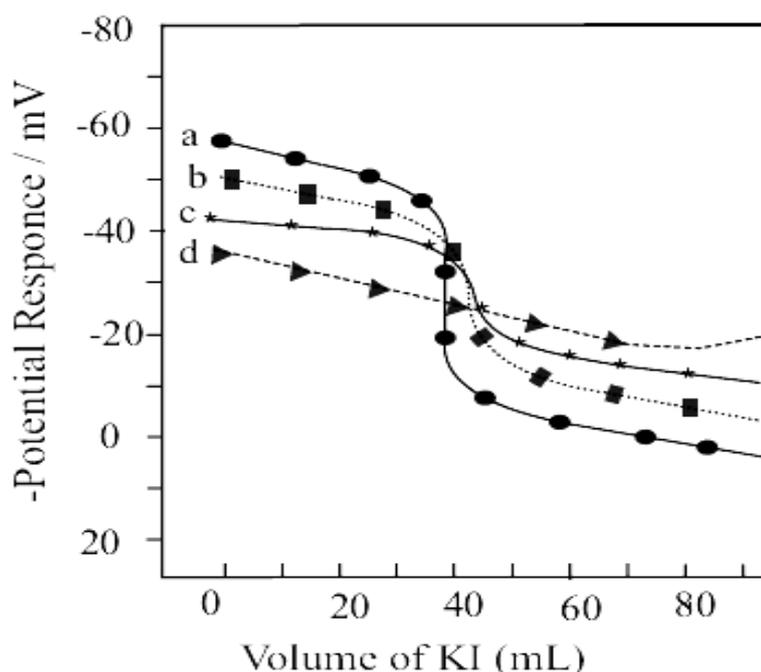
Fig. 6. Potentiometric titration plot (a) 25 mL of 0.10 M TlNO$_3$ with 1.0 M KI; (b) 25 mL of 0.010 M TlNO$_3$ with 0.10 M KI; (c) 25 mL of 0.0010 M TlNO$_3$ with 0.01 M KI; (d) 25 mL of 0.0.0001 M TlNO$_3$ with 0.001 M KI using proposed Tl(I)-selective electrode

3.8.2. Recovery test of Tl(I) from different samples

Thallium is almost always determined as total metal, rather than specific thallium compounds. The proposed sensor was also used for the direct determination of thallium in blood, urine and waste water samples. To prepare test solution 20 mL of these samples (blood, urine and waste water) is dissolve in a 20 mL of 50% nitric acid. 5 mL of this solution was further diluted to 500 mL in a volumetric flask with distilled water. The obtained values are quite comparable to those obtained with AAS and ICP, thereby illustrating the utility of the sensor for determining the Tl(I) in real samples (Table 6).

Table 6. Recovery test of Tl(I) from different samples

Sample	Tl(I)-ISE[a] (μg/L)	AAS (μg/L)	ICP (μg/L)
Blood Sample	2.2	2.0	2.1
Urine Sample	1.2	1.2	1.1
waste water	40.1	40.2	40.0

[a]Average of three replicate measurements

4. CONCLUSION

This work is related with the development of Tl(I)-selective electrode by using 1,2-bis [$2^{'}$-($8^{'}$-oxyquinoline)ethoxy]-benzene as an ionophore. The fast response time (5 s), wide linear range 2×10^{-9}-1.0×10^{-1}), fair selectivity coefficients and long lifetime (7 months) of the response sensor are advantageous over most of the reported Tl(I) ion-selective electrodes. The proposed electrode was successfully used as an indicator electrode for the titration of Tl(I) with 40 mL EDTA solution.

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