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A highly selective thallium(I) electrode based on a thia substituted macrocyclic ionophore

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Abstract

A new highly Tl(I)-selective PVC membrane electrode based on tetrathia macrocycle 6,7: 14,15-dibenzo-5,8,13,16-tetraoxo-1,4,9,12-tetrathiacyclohexadecane [Bz_2O_4(16)aneS_4] (I) as membrane carrier, *o*-nitrophenyloctyl ether (*o*-NPOE) as solvent mediator and potassium tetrakis(*p*-chlorophenyl)borate (KT*p*ClPB) as lipophilic additive has been developed. The best performance was given by the membrane of macrocycle (I) with composition 3:120:1.5:50 (I:*o*-NPOE:KT*p*ClPB:PVC). This electrode exhibits a Nernstian response to Tl(I) ions in the concentration range 1.0×10^{-1}–2.23×10^{-6} M with a slope of 58.2 mV/decade of concentration and a detection limit of 1.58×10^{-6} M. The response time of the sensor is 12 s and can be used over a period of 4 months with good reproducibility. The proposed electrode revealed good selectivity over a wide variety of other cations including alkali, alkaline earth, heavy and transition metals. The electrode works well over a pH range of 3.2–11.5 and in partially non-aqueous medium with up to 30% organic content. The sensor was also used as an indicator electrode in potentiometric titration of Tl(I) ions with KI solution.

Keywords: Tl(I)-selective electrode; Tetrathia macrocycle; PVC-based membrane; Potentiometry

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1. Introduction

The toxicity of thallium compounds especially as a monovalent cation is a well established fact [1]. The distinctive effects of thallium poisoning are loss of hair and damage to peripheral nerves, liver, kidney intestine and testicular tissue [2]. It is a suspected human carcinogen. The major source of its introduction into the environment is the processing of Cu, Pb, Zn and other sulphide ores. Concentration of Tl up to 0.5 mg/100 g of tissue suggests thallium intoxication [3]. Thus, the estimation of thallium ion concentration is important by the environmental as well as biological point of view.

Ion selective electrodes are one of the most convenient and reliable analytical tools for estimating metal-ion concentrations [4]. There have been a few reports concerning thallium(I) liquid membrane electrodes [5–9] that needed improvement with regard to their low selectivity against alkali metals, linearity and pH dependence. Tl(I) ISE's based on crown ethers have also been reported [10–15] but they suffered from significant interference due to their high affinity towards alkali metal ions. Masuda et al. proposed a Tl(I)-ISE based on a polythiamacrocycle [16]. Calix[4]arenes, calix[6]arene and calix[5]arene derivatives have been explored as electroactive material in the preparation of PVC-based Tl(I)-selective electrodes [17,18]. Calix[4]pyrroles and quinoline carbonitrile derivatives have also been used as ionophore in PVC membrane sensor for Tl(I) ions [3,4]. Recently, a tetrathiaoxa macrocycle has been explored as carrier for Tl(I)- and Ag(I)-selective sensor [19]. This paper reports a novel thallium(I) ion selective electrode incorporating the neutral synthetic carrier tetrathia macrocycle which exhibits high selectivity over various interfering ions and can be used in potentiometry.

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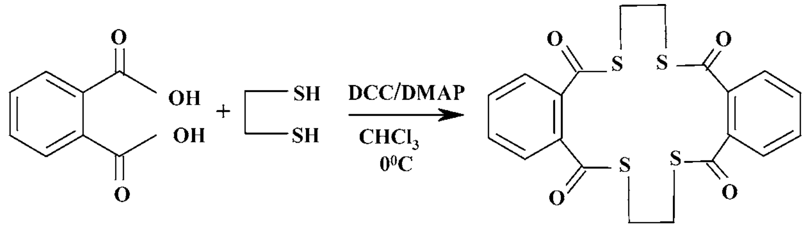
2. Experimental

2.1. Reagents

All the reagents used were of analytical reagent grade. Doubly distilled water was used throughout. The membrane solvent dioctylphthalate (DOP), dibutylphthalate (DBP) and 1-chloro naphthalene (1-CN) were obtained from Aldrich, potassium tetrakis(*p*-chlorophenyl)borate (KT*p*ClPB), oleic acid (OA) and *o*-nitrophenyloctyl ether (*o*-NPOE) were purchased from Fluka. Ethanedithiol, phthalic acid and *N*,*N*′-dicyclohexylcarbidiimide (DCC) from Merck and 4-(dimethylamino)pyridine DMAP from Spectrochem and dichloromethane and THF were obtained from Ranbaxy. The high molecular weight poly (vinyl chloride) (PVC) was used as received from Fluka.

2.2. Synthesis of macrocycle (I)

Catalytic amount of *N*,*N*′-dicyclohexylcarbidiimide, DCC (11.1 mmol) and, 4-(dimethylamino)pyridine DMAP (11.1 mmol) in dichloromethane (50 ml) at 0 °C were stirred. To this solution ethanedithiol (5.1 mmol) and phthalic acid (5.1 mmol) in dichloromethane (50 ml) were added simultaneously. The resultant mixture was stirred for 8 h. The solid product was obtained, filtered off and washed several times with dichloromethane. The white product was recrystallized from methanol and dried in vacuo. Yield 80% (mp 280 °C). ^{1}H NMR of the ligand gave singlets at δ 3.35 ppm attributed to –CH$_2$ (8 H) protons and a multiplet at δ 6.80–7.30 ppm attributed to the aromatic protons (8 H). Found: C, 53.60%; H, 3.72%; S, 28.00%; O, 14.40%; calc.: C, 53.63%; H, 3.58%; S, 28.57%; O, 14.25%. Mass (*m*/*z*): 448. ^{13}C NMR: 61.8, 121.6, 129.4, 130.3 and 166.3. The observed elemental analysis of the compound was consistent with the theoretical data obtained on the basis of the following structure:



(I)

6,7:14,15-dibenzo-5,8,13,16-tetraoxo-1,4,9,12-tetrathiacyclohexadecane [Bz$_2$O$_4$(16)aneS$_4$]

2.3. Electrode preparation

The membrane electrodes in PVC matrix were fabricated by the method as reported [20]. Varying amount of ionophore ($\sim$3.0–10 mg), an appropriate amount of PVC ($\sim$40–100 mg), anion excluder KT*p*ClPB ($\sim$1.0–5.0 mg) and solvent mediators *o*-NPOE, DBP, DOP, 1-CN ($\sim$50–200 mg) were dissolved in $\sim$20 ml THF to get membranes of different compositions. The mixture was poured into polyacrylate rings, placed on a smooth glass plate. The solvent was allowed to evaporate at room temperature, after 24 h, a homogeneous PVC membrane was obtained. The membranes so obtained were detached from glass plate, cut to suitable size, and glued to one end of a “Pyrex” glass tube with araldite.

2.4. Equilbration of membranes and potential measurements

The membranes were equilibrated for 3–5 days in 1.0 M TlNO$_3$ solution. The potentials were measured by varying the concentration of the test solution in the range of 1.0×10^{-7}–1.0×10^{-1} M. Standard TlNO$_3$ solutions were obtained by gradual dilution of 0.1 M TlNO$_3$ solution. The potential measurements were carried out at 25 ± 0.1 °C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

SCE | sample solution || PVC membrane || 0.1 M TlNO$_3$ | SCE

The response time was defined as the time taken to reach a potential of 90% of the potential difference in the two measurements. The detection limit was defined as the intersection of the extrapolated linear regions of the calibration graph [21].

3. Results and discussion

In preliminary experiments, the synthesized tetrathia macrocycle (I) was used as a carrier to prepare PVC membrane electrodes for a wide variety of metal ions including alkali, alkaline earth and transition metal ions. The potential response of the membrane electrodes to various metal ions is shown in Fig. 1. It is seen that the membrane electrode responds to thallium(I) with near-Nernstian slope and a wide concentration range while the response to other metal ions is non-Nernstian. Thus the membrane of (I) gives the best response to Tl^{+}. The existence of four donating sulphur atoms in the macrocycle is expected to show strong complexation behaviour of the carrier for Tl(I) over other metal ions. Thus the membrane electrode was investigated primarily as Tl^{+}-

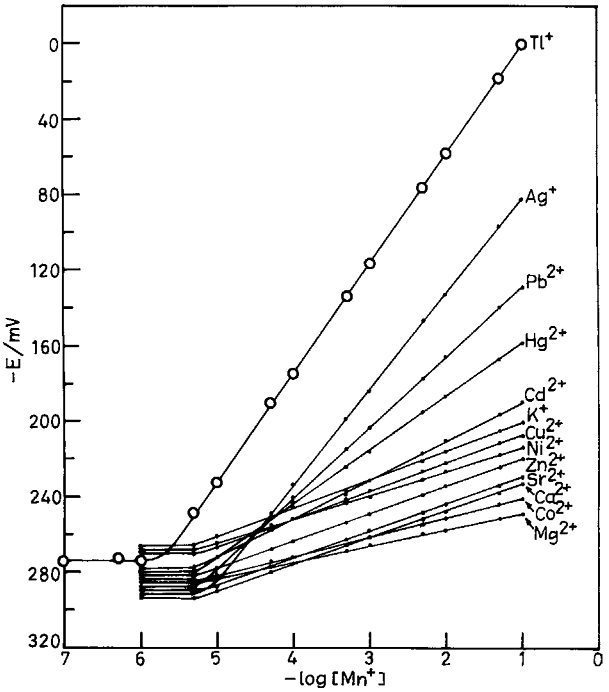


Fig. 1. Potentiometric response of various ion-selective electrodes based on (I).

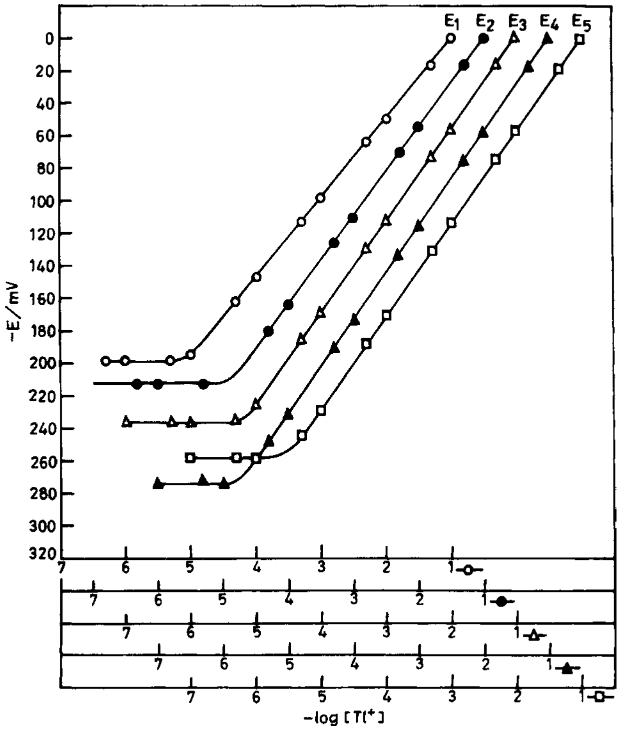


Fig. 2. Plots showing variation of membrane potentials with the concentration of Tl(I) ion based on (I) without plasticizer (E_1) and with plasticizers (E_2–E_5).

selective sensor. The ratio of ionophore (I) to PVC was varied in order to obtain a composition, which gives a membrane of best performance with regard to working concentration range, slope and response time. It was found that the membrane having 3 mg of ionophore and 50 mg PVC gave the best results. Therefore, the ionophore (I) was selected as suitable sensor material for Tl^+-ion in PVC matrix.

Addition of appropriate amount of plasticizer leads to optimum physical properties and ensures high mobility of ions in the membrane. These solvent mediators strongly influence the working concentration range of the sensors. It is well known that plasticizers improve the electrochemical properties of the ion selective electrodes [15,22–25]. Accordingly, the effect of solvent mediators DOP, DBP, CN and *o*-NPOE was investigated. The effect of each solvent mediator on the response function and sensitivity of an electrode system based on carrier (I) are presented in Table 1 and Fig. 2. From these it becomes clear that the use of *o*-NPOE as a membrane solvent yields electrodes with favorable characteristics. *o*-NPOE was concluded to be the best membrane solvent for the proposed PVC membrane electrode system. From Table 1 it can be seen that electrode no. 1 (E_1) having membrane without plasticizer exhibited a range of 1.0×10^{-5}–1.0×10^{-1} M and a slope of 48.0 ± 0.2 mV/decade of activity. However, on addition of plasticizers to the membrane (E_2–E_5) the working concentration range as well as the slope changed. The membranes incorporating solvent mediators 1-CN (E_2), DBP (E_3), *o*-NPOE (E_4), DOP (E_5) exhibited linearity in the concentration ranges of 1.58×10^{-5}–1.0×10^{-1}, 8.41×10^{-6}–1.0×10^{-1}, 2.23×10^{-6}–1.0×10^{-1} and 5.0×10^{-6}–1.0×10^{-1} M with slopes 54.0 ± 0.1, 56.0 ± 0.3, 58.2 ± 0.1 and 51.0 ± 0.5 mV/decade of activity, respectively.

In order to achieve selectivity it is essential that no significant amount of counter ion should enter the membrane phase. Lipophilic salt (NaTPB, OA, KT*p*ClPB) was added to reduce the anionic interference and lower the electrical

Table 1
Optimization of membrane ingredients

S. no.	Composition of membrane (w/w)							Working concentration range (M)	Slope (mV/decade of activity)	Response time (s)	Detection limit (M)
	I	PVC	KT*p*ClPB	1-CN	DBP	*o*-NPOE	DOP				
E_1	3.0	50	1.5	–	–	–	–	1.0×10^{-1}–1.0×10^{-5}	48.0	45	8.90×10^{-6}
E_2	3.0	50	1.5	120	–	–	–	1.0×10^{-1}–1.58×10^{-5}	54.0	29	1.12×10^{-5}
E_3	3.0	50	1.5	–	120	–	–	1.0×10^{-1}–8.41×10^{-6}	56.0	25	6.30×10^{-6}
E_4	3.0	50	1.5	–	–	120	–	1.0×10^{-1}–2.23×10^{-6}	58.2	12	1.58×10^{-6}
E_5	3.0	50	1.5	–	–	–	120	1.0×10^{-1}–5.0×10^{-5}	51.0	20	3.16×10^{-5}

Table 2
Effect of ionic additive on the response of Tl^+-selective electrode

S. no.	Composition of membrane (w/w)						Slope (mV/decade of concentration)
	I	PVC	*o*-NPOE	OA	NaTPB	KT*p*ClPB	
1	0.0	50	120	–	–	1.5	19.3
2	3.0	50	120	1.5	–	–	46.0
3	3.0	50	120	–	1.5	–	51.0
4	3.0	50	120	–	–	1.5	58.2
5	3.0	50	120	–	–	–	22.4

resistance of the membrane. These lipophilic salts also exhibit ion-exchange properties and participate in the selective charge transport process if insufficient amount of ionophore is present. There are several reports on the effect of ionic additives upon the characteristics of ISEs [26–28]. The effect of oleic acid (OA), NaTPB and KT*p*ClPB on the potentiometric response of Tl-selective electrode was examined (Table 2). It can be seen from Table 2, the additives OA and NaTPB do not improve the Nernstian response of the electrode but decrease the slope of the ISE. Therefore, KT*p*ClPB has been used as the best additive for thallium(I) ion. Thus, the membrane electrode E_4 incorporating ionophore I, *o*-NPOE as solvent mediator, KT*p*ClPB as ionic additive and PVC in the ratio (w/w) 3:120:1.5:50 (I:*o*-NPOE:KT*p*ClPB:PVC) gives the best performance with regard to working concentration range and slope and has a detection limit of 1.58×10^{-6} M.

The potentiometric selectivity coefficients of the electrode, ($K^{\mathrm{Pot}}_{\mathrm{Tl^+,B}}$), toward different cationic species were evaluated by separate solution method [21] using 0.1 M solutions of metal nitrate and are given in Table 3. It can be seen from Table 4, that the electrode is characterized by a high selectivity towards Tl^+ ions with respect to alkali metal ions (H^+, Li^+, Na^+, K^+ and Cs^+), alkaline earth metal ions (Mg^{2+}, $Ca^{2+}$and Sr^{2+}), transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+} and Cd^{2+}) and other metal ions (Tl^{3+}, Hg^{2+}, Ag^+, $NH_4{}^+$, $Pb^{2+}$and Al^{3+}).

The dependence of sensor's potential response on the pH has been tested over the range of 1.0–12.0 for 1.0×10^{-2} and 1.0×10^{-3} M Tl(I) ion solution (Fig. 3). The operational range was studied by varying the pH of the test solution with nitric acid or sodium hydroxide solutions. Fig. 3 shows that the potential is independent of pH in the range of 3.5–11.5. Therefore, the same was taken as the working pH range of the sensor assembly. Above pH 11.5 the measured potential decreases due to the effect of the hydroxyl ions and the observed drift below pH 3.5 may be due to effect of hydrogen ions.

Table 3
Selectivity coefficients $\log(K^{\mathrm{Pot}}_{\mathrm{Tl^+,B}})$ of various interfering ions using E_4 at 1.0×10^{-2} M

Interfering ion	$\log(K^{\mathrm{Pot}}_{\mathrm{Tl^+,B}})$	Interfering ion	$\log(K^{\mathrm{Pot}}_{\mathrm{Tl^+,B}})$
H^+	−3.01	Zn^{2+}	−3.65
Li^+	−2.21	Cd^{2+}	−4.16
Na^+	−3.24	Ag^+	−1.50
K^+	−2.06	Hg^{2+}	−3.26
Mg^{2+}	−3.48	$NH_4{}^+$	−2.15
Ca^{2+}	−3.50	Pb^{2+}	−3.10
Sr^{2+}	−3.63	Al^{3+}	−4.72
Co^{2+}	−4.41	Tl^{3+}	−3.25
Ni^{2+}	−4.25	Cr^{3+}	−4.01
Cu^{2+}	−3.29		

Table 4
Performance of E_4 in partially non-aqueous media

Non-aqueous content (%, v/v)	Working concentration range (M)	Slope (mV/decade activity)
0	1.0×10^{-1}–2.23×10^{-6}	58.2
Methanol		
10	1.0×10^{-1}–2.23×10^{-6}	58.2
20	1.0×10^{-1}–2.23×10^{-6}	58.2
30	1.0×10^{-1}–2.64×10^{-6}	56.4
35	1.0×10^{-1}–8.61×10^{-6}	48.0
Ethanol		
10	1.0×10^{-1}–2.23×10^{-6}	58.2
20	1.0×10^{-1}–2.23×10^{-6}	58.2
30	1.0×10^{-1}–2.23×10^{-6}	55.9
35	1.0×10^{-1}–2.23×10^{-6}	46.0
Acetone		
10	1.0×10^{-1}–2.23×10^{-6}	58.2
20	1.0×10^{-1}–2.23×10^{-6}	58.2
30	1.0×10^{-1}–3.21×10^{-6}	57.2
35	1.0×10^{-1}–1.0×10^{-5}	49.0

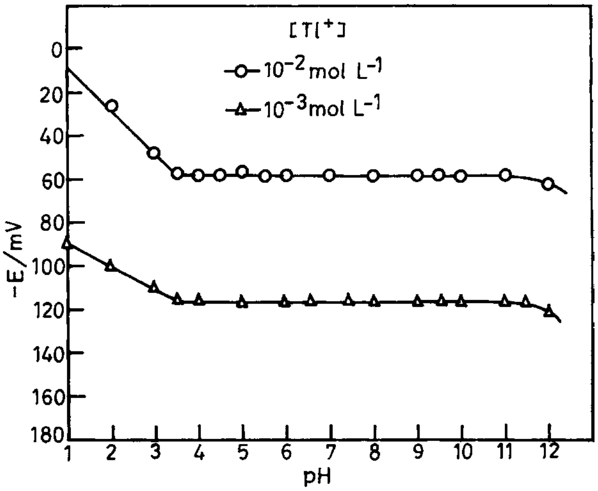


Fig. 3. Effect of pH at 1.0×10^{-2} and 1.0×10^{-3} M Tl^+ solutions on the potential response of Tl^+ ISE (E_4).

Table 5
Comparison of the proposed Tl^+-selective electrode with the reported electrode

Sensor	Working concentration range (M)	Slope (mV/decade of activity)	pH range	Response time (s)	Lifetime (weeks)	Reference
1	10^{-5}–10^{-1}	55.5	>3	NM	NM	[13]
2	10^{-5}–10^{-1}	55	NM	30	4–6	[4]
3	3×10^{-6}–10^{-1}	58	NM	NM	NM	[17]
4	$10^{-5.5}$–10^{-1}	56.0	2–11	30	2	[3]
5	10^{-6}–10^{-2}	55.0	2.5–12.0	10	NM	[18]
6	10^{-5}–10^{-1}	Near-Nernstian	4.0–11.0	10	12	[15]
7	1.58×10^{-6}–10^{-1}	58.2	3.2–11.5	12	16	Proposed electrode

The time of contact and concentration of equilibration solution were optimized so that the electrode generates stable and reproducible potentials at relatively short response time. It was found that an equilibration solution of 1.0 M and contact time of 3 days was appropriate for smooth functioning of the electrode. The response time was determined for all the membranes. It can be seen from Table 2, that the electrode E_1 (without plasticizer) exhibits a response time of 45 s while those incorporating solvent mediators 1-CN, DBP, *o*-NPOE, DOP (E_2–E_5) exhibit faster response times of 29, 25, 12 and 20 s, respectively. The best response time is given by E_4 with *o*-NPOE as solvent mediator and it also has a lifetime of more than 4 months, during which it could be used without any measurable divergence in potentials. Membranes were stored in 0.1 M $TlNO_3$ solutions when not in use. The response time of the electrode E_4 is 12 s as compared to other electrodes (E_1–E_3 and E_5) that have larger response times. Hence, electrode (E_4) has been selected for subsequent studies.

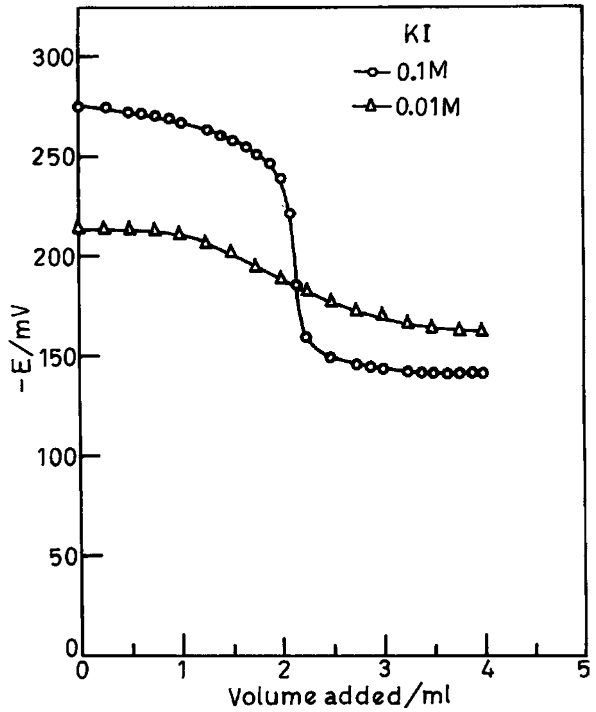


Fig. 4. Titration of 10^{-2} and 10^{-3} M Tl^+ with 0.1 and 0.01 M KI, respectively, using E_4.

The functioning of the membrane electrode E_4 was also investigated in partially non-aqueous media using methanol–water, ethanol–water and acetone–water mixtures (Table 4). It is observed that the sensor could tolerate up to 30% (v/v) non-aqueous content; in these mixtures, the working concentration range and slope remains unaltered. However, above 30% non-aqueous content the slope decreases appreciably and reliable measurements could not be obtained. Also, the membranes decompose due to leaching of the ionophore from PVC matrix.

The proposed Tl^+-selective electrode was found to work well under laboratory conditions. The electrode was used as an indicator electrode for the potentiometric titration of Tl(I) with KI solution. During this titration no pH or ionic strength adjustments were made. The titration curves are presented in Fig. 4. A sigmoid curve was obtained for 10^{-2} M Tl(I) ions with 10^{-1} M KI solution but the curve for 10^{-3} M $TlNO_3$ with 10^{-2} M KI solution is not sigmoid due to relatively high solubility of thallium iodide.

4. Conclusion

A new PVC membrane electrode for Tl(I) ions based on $[Bz_2O_4(16)aneS_4]$ (I) as ionophore was investigated. The selectivity may be due to the soft–soft interaction of the cation with sulphur atoms of the ionophore. In comparison to the reported Tl^+-selective electrodes [3–18] the present studies have helped in developing a better sensor in terms of working concentration range, pH range, selectivity, response time and lifetime (Table 5). The proposed electrode can be used successfully as an indicator electrode in potentiometric titrations, at least, in the moderate concentration range.

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