

Novel Thallium(I)-Selective Membrane Electrode Based on a Podal Ligand

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A PVC-based membrane electrode for thallium(I) ions based on 1,21,23,25-tetramethyl-2,20: 3,19-dimetheno-[H, 2] H, 23H, 25H-bis-[1,3] dioxocino[5,4-i:5',4'-i] benzo [1,2-d: 5,4-d'] bis [1,3] benzodioxocin(II) has been prepared. The electrode displays a linear dynamic range of 1.0×10^{-1} - 1.0×10^{-5} M, with a Nernstian slope of 59.8 ± 0.2 mV dec⁻¹, and a detection limit 5.0×10^{-6} M. It has a very fast response time of <10 s and can be used for at least ten weeks without a considerable divergence in potentials. This electrode revealed comparatively good selectivity with respect to alkali, alkaline earth, and some transition and heavy metal ions and was effective in a pH range of 2.0-10.0. It was used as an indicator electrode in potentiometric titration of thallium ion with sulfide ion.

Key Words : Podal ligand, Thallium(I) selective membrane, Potentiometry, PVC

Introduction

Thallium is toxic, especially as its monovalent cation. From the environmental and biological viewpoints, soluble univalent thallium compounds, *e.g.*, thallium(I) sulfate, acetate and carbonate are very toxic because they are easily absorbed into the human body by skin contact or ingestion.¹ Thallium poisoning in the human body has to be checked quickly by analyzing urine and blood samples. Atomic absorption spectroscopy and polarography have already been recommended for the thallium(I) assay. A more compact instrumentation for the thallium(I) assay in human body fluids is the thallium(I)-selective membrane electrode.

Ion-selective electrodes based on ionophores are well established for many inorganic cations and anions. During the last two decades, a large number of ionophores, especially a wide variety of neutral macrocyclic polyethers, has been developed and found widespread applications in potentiometric and optical sensors for the determination of respective ions in real samples.² The design and function of synthetic ionophores for ion-selective electrodes are based on such diverse parameters as the structure and cavity size of the ligand, the stability and selectivity of its metal ion complex, its solubility and the ability to extract the metal ion into membrane phase.

Crown ether and calix[4]aren derivatives have been tested as thallium(I)-neutral carriers for ion-selective electrodes,³⁻¹² and the resulting thallium(I)-selective electrodes gave good results. However, since crown ethers and calix[4]arens generally have a high affinity for alkali-metal ions and in some cases silver, these thallium(I) electrodes suffer from severe interference by Na⁺, K⁺, Cs⁺ and Ag⁺. In the present study, we wish to introduce a novel thallium(I) electrode by

incorporation of a podal ligand as a suitable neutral ionophore for fast monitoring of thallium ion.

Experimental Section

Reagents. Reagent grade benzyl acetate (BA), dibutyl phthalate (DBP), dioctyl phthalate (DOP), potassium tetrakis (p-chlorophenyl)borate (KTPCIPB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF), and high relative molecular weight PVC (all from Merck) were used as received. The nitrate and chloride salts of all cations used (all from Merck) were of the highest purity available and were used without any further purification except for vacuum drying over P₂O₅. Doubly distilled de-ionized water was used throughout the experiment.

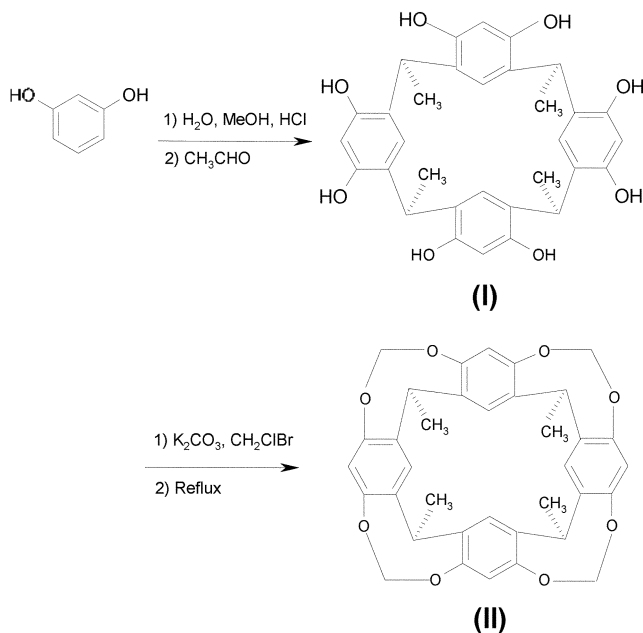
Synthesis of podal ligand. The podal ligand was synthesized in two steps as follow; **Step 1.** Synthesis of 2,8,14,20-tetramethylpentacyclo[19.3.1.1_{3,7}.1_{9,13}.1_{15,19}] octacosane, 1(25), 3, 5, 7 (28), 9, 11, 13 (27), 15, 17, 19 (26), 21, 23-dodecaen 4, 6, 10, 12, 16, 18, 22, 24-octol (I). Resorcinol (342 g, 3.11 mol) was dissolved in 620 mL of ethanol and 310 mL of 37% aqueous HCl. To this stirred solution was added slowly 137.1 g of CH₃CHO. Immediately after the addition was complete, the reaction was cooled in a water bath to control the exotherm. The reaction mixture was then maintained at 80 °C for 16 h, and the yellow needles that separated were collected and washed with cold 1 : 1 ethanol-water until the washing was light yellow to give material dried at 80 °C at 10⁻¹ Torr for 30 h (310 g, 73%). The physical properties of this compound corresponded to those reported, and the material was suitable for use in subsequent reactions.

Step 2. Synthesis of 1,21,23,25-tetramethyl-2,20: 3,19-dimetheno-1H, 21H, 23H, 25H-bis[1,3] dioxocino[5,4-i:5', 4'-i] benzo [1,2-d: 5,4-d'] bis [1,3] benzodioxocin (II). To a mixture, stirred at 30 °C under Ar, of 3.5 L of dry DMSO and 307 g (2.38 mol) of finely ground dry K₂CO₃ were

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added over 4 days by syring pump 109 g (0.2 mol) of dried compound I and 100 mL (1.1 mol) of CH_2ClBr dissolved in 300 mL of dry DMF. The mixture was stirred for an additional day at 30 °C under Ar and poured into 6 L of 2 M aqueous NaCl solution. The mixture was agitated for 1 h, and the fine precipitate that separated was filtered and washed with water. This material was suspended in 2 L of CH_2Cl_2 , stirred for 5 h, and filtered. The residue was suspended in 1L of 10% acetone in CH_2Cl_2 and then filtered. The combined organic layers were washed with 300 mL of aqueous 2 N NaOH and water and dried (MgSO_4). The solvent was evaporated under reduced pressure. The residue was washed through a 40×3 cm column of 10-60 μm , silica gel with CH_2Cl_2 . If the eluates were still brown, the product was again chromatographed at medium pressure through silica gel. The eluates were evaporated to a volume of 200 mL and diluted with 300 mL of EtOH. The product that crystallized at 0 °C was collected, washed with cold CH_2Cl_2 and dried at 70 °C and 10^{-1} Torr to give, after drying, 28.0 g (23%) of II- CH_2Cl_2 . The CH_2Cl_2 was removed by repeated evaporation of solution containing II- CH_2Cl_2 to give II, mp > 360 °C: TLC R_f 0.15 (SiO_2 - CH_2Cl_2); ^1H NMR (CDCl_3) δ 1.77 (d, 12H, CH_3CH , $J = 7.4$ Hz), 4.44 (d, 4H, inner of CH_2 , $J = 7.2$ Hz), 4.96 (q, 4H, CH_3CH , $J = 7.4$ Hz), 5.75 (d, 4H, outer of CH_2 , $J = 7.2$ Hz), 6.47 (s, 4H, 2-Ar H), 7.25 (s, 4H, 5-Ar H); MS (70 eV), m/z 592 (M^+), Anal. Calcd. for $\text{C}_{30}\text{H}_{32}\text{O}_8$; C, 72.86; H, 5.44, Found: C, 72.72; H, 5.36. Anal. Calcd. for $\text{C}_{36}\text{H}_{32}\text{O}_8 \cdot \text{CH}_2\text{Cl}_2$; C, 65.58; H, 5.05. Found: C, 65.49; H, 4.92.

Electrode preparation. The general procedure to prepare the PVC membrane was to mix thoroughly 30.0 mg of



powdered PVC, 58.0 mg of plasticizer DBP, 4.0 mg of additive KTpCIPB, and 8.0 mg of ionophore II in a glass dish of 2 cm diameter. The mixture was then completely dissolved in 5 mL of THF. The solvent was evaporated

slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s. to allow a nontransparent membrane of 0.3 mm thickness to form. The tube was then pulled out of the mixture and kept at room temperature for 24 h. The tube was filled with internal filling solution (1.0×10^{-3} M TlCl). The electrode was finally conditioned for 12 h in a 1.0×10^{-2} M solution of TlCl.

EMF measurements. All emf measurements were carried out with the following assembly:

Ag-AgCl | 3 M KCl internal solution (1.0×10^{-3} M TlCl) | PVC membrane | test solution | Hg-Hg₂Cl₂, KCl (saturated).

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution.

Results and Discussion

At first, II was used as a neutral carrier to prepare PVC-based membrane electrodes for a variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The potential responses of various ion-selective electrodes based on II are shown in Figure 1 (a and b). As seen, among different cations tested, thallium(I) with the most sensitive response seems to be suitably determined with the PVC

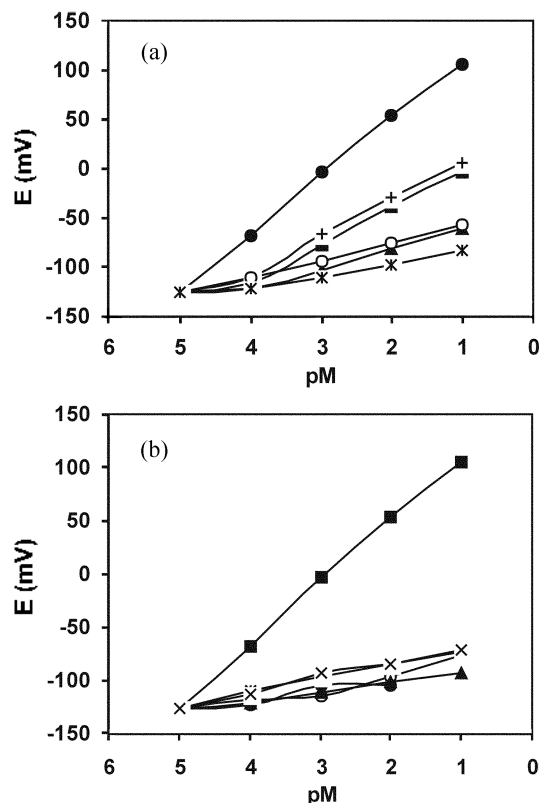


Figure 1. Potential response of various ion-selective electrodes based on the II. (a) (●) Tl^+ (■) Ag^+ (+) Cs^+ (▲) Na^+ (○) K^+ (×) Cu^{2+} , (b) (■) Tl^+ (○) Ni^{2+} (▲) Mg^{2+} (●) Zn^{2+} (×) Pb^{2+}

membrane based on II. This is probably due to both the selective behavior of the ionophore against thallium(I) in comparison with other metal ions and the rapid exchange kinetics of the resulting II-Tl(I) complex.

Some important features of the PVC membranes, such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore, and especially the nature and amount of the additives used, are reported to significantly influence the sensitivity and selectivity of the ion-selective electrodes.¹³⁻²¹

Thus, several membranes of various plasticizer/PVC/II/additive ratios were tested and the results are summarized in Table 1.

As observed, a plasticizer/PVC ratio of about 2.0 together with 8% of the ionophore II resulted in satisfactory potential responses (membrane no. 8). A study of the influence of the nature of plasticizer on the potentiometric response characteristics was conducted by using BA, DBP and DOP and the results are given in Table 1 and Figure 2. As is obvious, the sensitivity of the membrane electrode is strongly affected by the nature of plasticizer, this is due to the influence of plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligand.¹⁴⁻¹⁶ Among three different plasticizers employed, the use of DBP resulted in the Nernstian behavior of the

Table 1. Optimization of membrane ingredients

Membrane Number	Composition [%]				Slope* (mV/decade)
	PVC	Plasticizer	Ionophore	Additive	
1	30	DBP:66	4	—	27.7 ± 0.5
2	30	DBP:64	6	—	30.7 ± 0.1
3	30	DBP:62	8	—	35.5 ± 0.4
4	30	DBP:60	10	—	33.2 ± 0.1
5	30	DBP:60	8	NaTPB.2	51.1 ± 0.2
6	30	DBP:59	8	NaTPB.3	52.7 ± 0.4
7	30	DBP:59	8	KTpCIPB.3	55.9 ± 0.3
8	30	DBP:58	8	KTpCIPB.4	59.8 ± 0.2
9	30	DOP:58	8	KTpCIPB.4	41.1 ± 0.5
10	30	BA:58	8	KTpCIPB.4	50.1 ± 0.4

*Results are based on triplicate measurements.

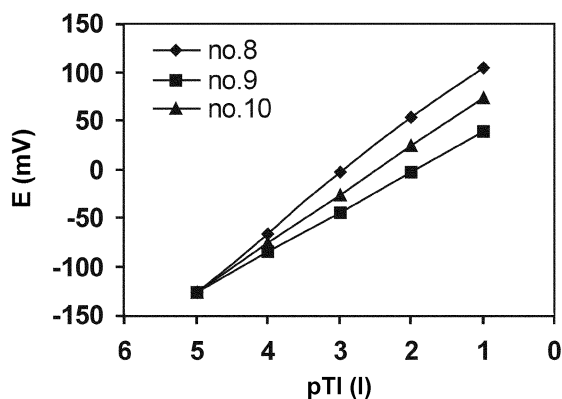


Figure 2. Influence of the nature of plasticizer on the potential response of the electrode for membrane number 8, 9 and 10.

electrode over a wide concentration range.

It is well known that the incorporation of lipophilic additives can significantly influence the performance characteristics of membrane electrodes.¹⁷⁻¹⁹ The presence of additives not only improves the response behavior and selectivity, but also may catalyze the exchange kinetics at sample-membrane interface.^{20,21} In the present study, we examined NaTPB and KTpCIPB as suitable lipophilic additives in conjunction with ionophore II in the preparation of thallium(I) ion-selective electrode. As is obvious from Table 1, the use of 4% KTpCIB significantly improves the sensitivity of the membrane electrode. As it is obvious from Table 1, the membrane obtained with the PVC/DBP/II/KTpCIPB ratio of 30%/58%/8%/4% (membrane 8) displays a nice Nernstian slope of 59 mV decade⁻¹ over a wide thallium(I) concentration range.

The influence of the concentration of the internal solution on the potential response of the membrane electrode was also checked. The TlCl concentration was changed from 1.0×10^{-2} to 1.0×10^{-1} M, and the emf vs. $-\log [Tl]$ plot was obtained. It was found that the concentration of internal filling solution has a negligible effect on the potential response of the electrode, except for an expected change in the intercept of the resulting plot. A 1.0×10^{-3} M concentration of the reference solution was found quite appropriate for a smooth Nernstian function of the electrode.

The static response time of the electrode, tested by measuring the time required to achieve a steady potential (within ± 1 mV), was about 10 s and was sustained for at least 5 min over the entire concentration range. The detection system was very stable, and the calibration slope did not change over a period of two weeks. The standard deviation of 10 identical measurements with 10 electrodes at several concentrations of thallium ion was found to be in the range of ≤ 0.8 mV.

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the thallium ion concentration in solution over a concentration range 1.0×10^{-1} – 1.0×10^{-5} M.

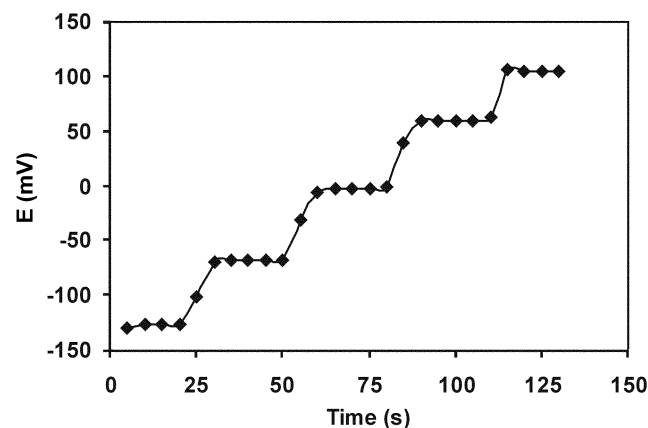


Figure 3. Dynamic response of the II-based membrane electrode for step changes in concentration of Tl^+ : A) 1.0×10^{-5} M, B) 1.0×10^{-4} M, C) 1.0×10^{-3} M, D) 1.0×10^{-2} M, E) 1.0×10^{-1} M.

The actual potential versus time trace is shown in Figure 3. As can be seen, across the concentration range, the electrode reaches its equilibrium response in a very short time (10 s). This is most probably due to the fast exchange kinetics of the complexation-decomplexation of thallium ion at the test solution-membrane interface.

The EMF response of the proposed thallium ion electrode (prepared under optimal membrane ingredients) indicates a rectilinear range from 1.0×10^{-1} to 1.0×10^{-5} M (Fig. 4). The slope of the calibration curves was $59.8 = 0.2$ mV/decade of thallium ion concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.0×10^{-6} M. The standard deviation of ten replicate measurements (10^{-3} M of thallium ion) was 0.6 mV.

The pH dependence of the membrane electrode was tested over a pH range 2.0-10.0 at a 1.0×10^{-1} M of thallium ion concentration. The potential was found to stay fairly constant in the pH range 2.0-10.0. Beyond this range, a gradual change in potential was detected. The observed decreased potential drift at higher pH values could be due to the formation of some hydroxy complexes of thallium ion in solution (Fig. 5).

Perhaps the most important characteristic of an ion-selective membrane electrode is its relative proclivity to respond to the primary ion over other ions present in

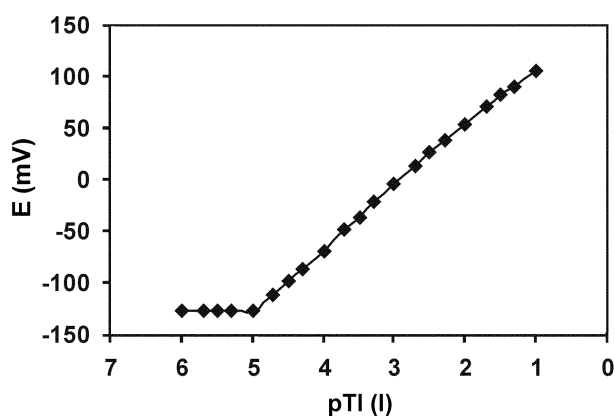


Figure 4. Calibration curve for thallium(I) electrode based on II.

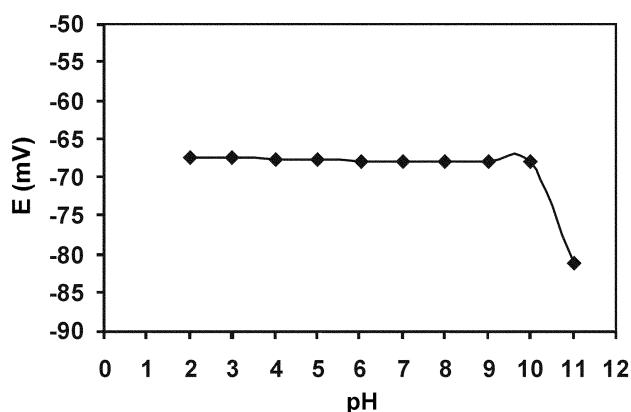


Figure 5. Effect of the pH of the test solution on the potential response of the thallium ion-selective electrode (1.0×10^{-3} M).

solution, which is usually expressed in terms of the potentiometric selectivity coefficient (K_{Sel}). In this study, the matched potential method²² was used to determine selectivity coefficients. According to this method, a specific activity (concentration) of primary ions ($A=1.0 \times 10^{-3}$ M of thallium ion) is added to a reference solution (5.0×10^{-6} M of thallium ion) and the potential is measured. In a separate experiment, interfering ions ($B=1.0 \times 10^{-1}$ - 1.0×10^{-1} M) were added to an identical reference solution, until the measured potential matched the one obtained by adding primary ions. The matched potential method selectivity coefficient, K_{MPM} , is given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{A,B} = a_A/a_B$. The resulting values are listed in Table 2. From the data given in Table 2, it is immediately obvious that the proposed thallium ion electrode is highly selective with respect to the other cations.

In Table 3, the major interfering ions of the proposed electrode are compared (a gross relative comparison) with the best of the reported thallium ion selective membrane

Table 2. Selectivity coefficients of various interfering ions

K_{Sel}		K_{Sel}	
Cs ⁺	1.0×10^{-2}	Cu ²⁺	3.3×10^{-3}
K ⁺	3.5×10^{-1}	Co ²⁺	3.6×10^{-4}
Na ⁺	1.4×10^{-1}	Ni ²⁺	3.5×10^{-4}
Li ⁺	5.5×10^{-1}	Zn ²⁺	3.0×10^{-4}
Ag ⁺	9.3×10^{-1}	Mg ²⁺	3.0×10^{-4}
Pb ²⁺	1.0×10^{-1}	Ca ²⁺	2.9×10^{-4}
Cd ²⁺	5.1×10^{-1}	Hg ²⁺	9.0×10^{-4}

Table 3. Comparison of major interfering ions for various thallium(I) ion-selective electrodes

Major interfering ions	
Ref. (7)	Ag ⁺
Ref. (8)	Ag ⁺
Ref. (9)	K ⁺ , Rb ⁺ , Cs ⁺
Ref. (10)	Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺

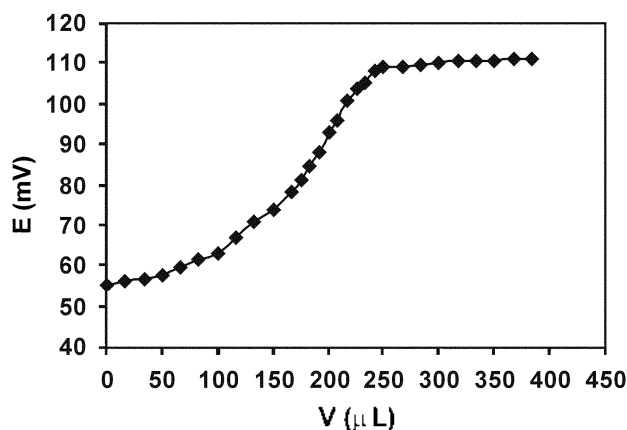


Figure 6. Potentiometric titration curve of 40.0 mL of 1.0×10^{-4} M thallium ion with 1.0×10^{-2} M S^{2-} , using the proposed membrane electrode as an indicator electrode.

electrodes. As can be seen, the proposed electrode in terms of selectivity coefficient is superior to all of the thallium ion-selective electrodes reported in the literature.⁷⁻¹⁰

The proposed thallium ion-selective electrode was found to work well under laboratory conditions. This electrode was used as an indicator electrode in the titration of thallium(I) with K_2S , and the resulting titration curve is shown in Figure 6. As seen, the amount of thallium(I) ions in solution can be determined with this electrode.

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