Thallium (I) ion Selective Membrane Electrode based on Dibenzopyridino-18-crown-6

JAVED ZOLGHARNEIN*, GHULAM AZIMI, AND MORTEZA HABIBI
Department of Chemistry, Arak University, Arak, Iran.

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Summary: A new PVC membrane electrode for determination of thallium (I) ion based on dibenzopyridino-18-crown-6 as membrane carrier was designed. The electrode exhibits a near Nerstian response (54.4 ± 0.2 mV/ decade) for Tl^+ over a wide concentration range (2.70×10^{-2} to 8.9×10^{-7}M). It has very short response time and can be used for three months without observing any divergence. The proposed electrode revealed good selectivity for Tl^+ over a wide variety of other metal ions except for Ag^+ and could be used in a pH range of 2.5 - 10. This electrode has been used as an indicator electrode in potentiometric titration of thallium (I) ion and in direct determination of it in spiked water samples.

Introduction

Due to the advantages of selective solvent polymeric membrane electrodes in determination of various species in biochemical, clinical, environmental and other areas in analytical chemistry [1-3], stimulation on designing of these sensors has been increased in recent years[4,5]. The advantages of the membrane electrodes: sensitivity, simplicity, versatility and low cost characterize it from the other analytical techniques. After recognition of selective behavior of macrocyclic polyethers (crown ethers) with alkaline and alkaline earth [6, 7], and further with other metal ions [8, 9], attempts to use crown ethers as ionophore has increased [10-12] Designing of membrane electrode for determination of heavy metal ions because of their importance in environmental pollution and biochemical determi-nation and other effects, have been of interest in recent years [3, 4, 13-15]. Among the heavy metals, thallium univalent compounds are soluble and very toxic because Tl^+ ions are easily absorbed into human body and skin contact or ingestion [16]. Thus, from the environmental and biological viewpoint determination of thallium (I) ion is of special interest. The direct determination of Tl^+ in blood and urine with Tl^+-selective membrane electrodes is the most convenient and reliable analytical tools for Tl^+ assay [5, 17-24]. Currently, our group has interested the chemistry of dibenzopyridino-18-crown-6 in several areas and when a pyridyl unit introduced into dibenzo-18-crown-6 ring, it changes drastically the behavior of this crown ether [25-29]. In this work, we have reported a new PVC membrane based on dibenzopyridino-18-crown-6 (DBPY18C6), as depicted in Fig. 1, which exhibits significantly selective potentiometric response toward Tl^+ ion over alkali, alkaline earth and several transition metal ions.

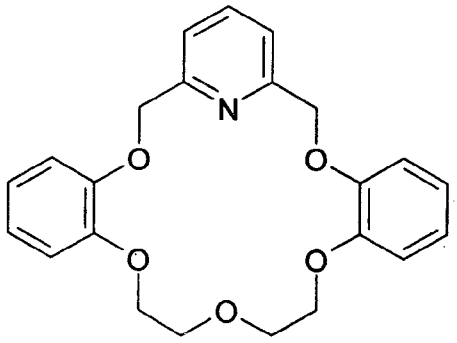

Fig. 1: The structure of dibenzopyridino-18-crown-6 (DBPY18C6).

Results and Discussion

In the previous study regarding of complexation of dibenzopyridino –18-crown-6 with some transition and heavy metal ions, showed that this crown ether could selectivity behave toward thallium (I) ion [26]. The stability constant of Tl^+- DBPY18C6 has a quantitative value, which is a suitable condition for selective membrane preparation. Such stability of the Tl^+ complex could be partly due to the stronger interaction of the pyridino nitrogen of this crown as a soft base with the Tl^+ ion as a soft acid [26]. According to this result, we were stimulated to designing a new membrane electrode for thallium (I) ion activity measurements based on DBPY18C6.

*To whom all correspondence should be addressed.

Thus in preliminary experiments, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. It is thus obvious that the Tl^+ ions are more easily attracted to the PVC-DBPY18C6 membrane that results in a near- Nerstian potential- concentration response over a wide range.

The Nature of Plasticizer and Additive:

The sensitivity and selectivity of ion-selective electrodes are known to be depended not only on the nature of ionophore but also on the composition of the membrane ingredients [31-33]. Thus, the effects of the membrane composition, nature and amount of plasticizer and additive on the potential response of the Tl^+ sensor were investigated, and the results are summarized in Table-1. Since the nature of plasticizer influences the dielectric constants and the state of ligands [4,5], it is expected to play an important role in determining the ion-selective electrode characteristics. As it is shown in Table-1, among the two plasticizers examined, NOPE results in a better sensitivity, as well as a faster response time (15s). It is seen that, the use of 1.8 % KTpClPB , 4.2 % ionophore, 31 % PVC, and 63.2 % NPOE results in the best sensitivity, with a near- Nerstian slope of 54.4 mV/ decade.

The Effect of Concentration of Internal Solution:

The influence of the concentration of internal solution on potential response of the Tl^+ ion-selective electrode was studied. The Tl NO_3 concentration was varied from 1.0×10^{-4} M to 1.0×10^{-2} M and the potential response was obtained. It was found that the variation of concentration of the internal solution does not cause any difference in the potential response. A 1.0×10^{-3} M concentration of the reference $TlNO_3$ solution is quite appropriate for smooth functioning of the electrode system.

Calibration and Detection Limit:

The PVC – based membrane of DBPY18C6 generates stable potentials when placed in contact with Tl^+ solutions. The critical response characteristics of the Tl^+ selective electrode were assessed according to IUPAC recommendations [34]. The potentiometric response of the membrane at varying activity of Tl^+ Fig 2 indicates a rectilinear range from 2.70×10^{-2} to 8.9×10^{-7} M. The slopes of the calibration curves were 54.4 ± 0.2 mV per decade of thallium

Table-1: The optimization of the membrane ingredients.

	Composition, %					
No	PVC	Plasticizer		Iono-phore	Additive	Slope
1	30.1	59.5	DBP	2.3	8.1 OA	40
2	38.9	52.1	DBP	2.6	6.4 OA	38
3	32.7	57	DBP	2.4	7.9 OA	43
4	36.7	59	DEP	3.1	3.8 OA	44
5	32.8	59	DEP	3.7	4.5 OA	48
6	32.4	58.5	DEP	4	5.2 OA	49
7	31.9	59.7	DEP	3.9	4.5 OA	46
8	33.1	59.1	DES	2.1	5.4 OA	41
9	32.4	57.9	DES	3.2	6.8 OA	44.6
10	32.8	58.4	DES	2	6.8 NaTPB	47
11	32	62	O-NPOE	6	-	40
12	32	64	O-NPOE	4	-	44
13	39	56.6	O-NPOE	4	2.6 NaTPB	46
14	32	57	O-NPOE	4	7 NaTPB	40
15	34.5	59.1	O-NPOE	2.9	3.4 OA	44.9
16	31.9	57.9	O-NPOE	3.7	7.1 OA	46
17	31	63.2	O-NPOE	4.2	1.8 KTpClPB	54.4
18	34	60.7	O-NPOE	1.9	3.4 KTpClPB	43
19	32	63.5	O-NPOE	1.1	3.3 KTpClPB	45.5

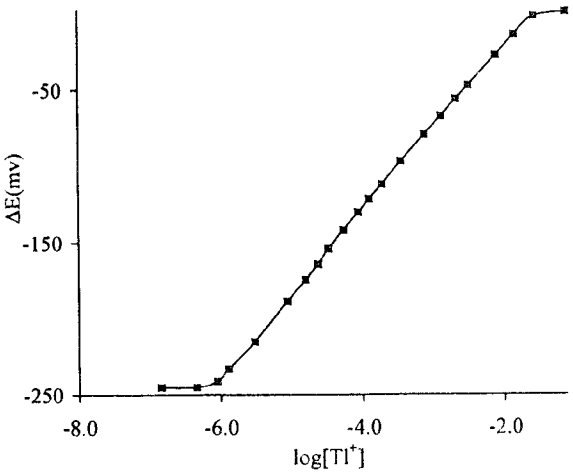

Fig. 2. Calibration plot for Tl^+ selective electrode based on DBPY18C6.

ion concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration plot, was 7.5×10^{-7} M [5].

The Response Time:

The average time required for the Tl^+ selective electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of thallium (I) ion solutions, each having 10-fold difference in concentration was measured. The static response time thus obtained was 15s for

concentration $\leq 5 \times 10^{-3}$ M, and potentials stayed constant for more than 10 min, after that only a very slow divergence was recorded. The standard deviation of ten replicate measurements was ± 0.2 mV. The sensing behavior of the membrane remained unchanged when the potentials recorded either from low to high concentration or vice versa. The ion-selective membranes prepared could be used for at least 3 months without any measurable divergence.

The pH Effect:

The pH dependence of the membrane electrode was examined by adjusting the pH of measured solution(Tl^+ concentration of 1.0×10^{-4} M) with 1 M nitric acid and sodium hydroxide.. The response remained constant from pH 4 to 10, but the response was reduced at pH below 4 Fig 3. At lower pH, the decrease of complexing ability due to the porotonation of the ionophore cause the lower response electrode, while increasing the pH has no influences on membrane response exception at higher pH (> 10) beginning of precipitation of Tl^+ disturb the potential behavior.

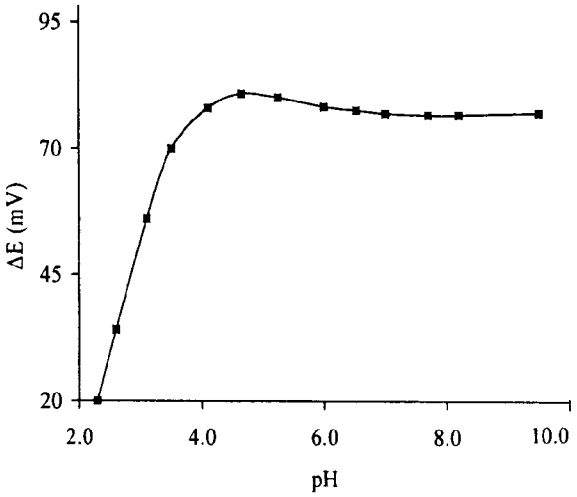

Fig. 3: The effect of pH of 1.0×10^{-4} M solution of Tl^+ on the potential response of the Tl^+ ion-selective electrode. The pH adjusted with 1.0 M nitric acid and sodium hydroxide solution.

The Selectivity:

The selectivity behavior is obviously the most important characteristics of an ion-selective electrode, determining whether a reliable measure-ment of the target sample is possible. In order to investigate the selectivity of proposed Tl^+ selective electrode, its response was examined in the presence of various foreign ions. The potentiometric selectivity coefficients (K_{Tl}^{pot}) were evaluated graphically by the mixed solution method [35,36] from potential measurements on solutions containing a fixed amount of Tl^+ (1.50×10^{-4} M) and varying amounts of the interfering ions (Mn^+) according to the equation:

$$K_{Tl}^{pot} a_M^{1/n} = a_{Tl} \{\exp[(E_2-E_1)F/RT]\} - a_{Tl} \quad (1)$$

Where E_1 and E_2 are the electrode potentials for the solution of Tl^+ alone and for the solution containing interfering ions (M^{n+}) and Tl^+ ions. According to Eq. (1), the K_{Tl}^{pot} values for diverse ions can be evaluated from the slope of the plot of

$$a_{Tl} \{\exp[(E_2-E_1) F/RT]\} - a_{Tl+} \text{ versus } a_M^{1/n}$$

The resulting K_{Tl}^{pot} values thus obtained for the proposed Tl^+ ion-selective electrode are summarized in Table-2. As can be seen, the alkali, alkaline earth and transition metal ions used as interfering ions did not disturb the functioning of the Tl^+ ion-selective membrane electrode significantly. The Na^+ and K^+ ions do not seem to interfere unless they are present at high concentrations. The only serious interfering ion is Ag^+ which interacts with DBPY18C better than Tl^+ [26].

Table 2. Selectivity coefficients of various interfering ions

	(K_{Tl}^{pot}) of diverse ions		
Ion	K_{Tl}^{pot}	Ion	K_{Tl}^{pot}
Ag^+ (4.7×10^{-5})	3.14	Li^+ (4.1×10^{-2})	3.6×10^{-4}
K^+ (1.1×10^{-1})	1.3×10^{-2}	Pb^{+2} (4.4×10^{-2})	3.6×10^{-4}
Ba^{+2} (7.5×10^{-3})	2.0×10^{-2}	Ca^{+2} (4.3×10^{-2})	3.5×10^{-4}
NH_4^+ (1.5×10^{-1})	7.6×10^{-3}	Cd^{+2} (4.5×10^{-2})	3.3×10^{-4}
Na^+ (3.2×10^{-2})	4.6×10^{-4}	Cu^{+2} (9.3×10^{-2})	1.6×10^{-4}
Zn^{+2} (3.9×10^{-2})	3.8×10^{-4}	Ni^{+2} (5.5×10^{-2})	2.4×10^{-4}

The values in parenthesis are concentration (Molar) of ion being studied.

Table-3: Thallium concentration (ppm) in spiked sample of water as determined by proposed membrane sensor and AAS.

Taken	Found	
Spiked Sample(ppm)	AAS	proposed elecrode
20	20 ± 0.1	21.8 ± 0.1
30	30 ± 0.1	29.5 ± 0.1
40	40 ± 0.1	38.1 ± 0.1

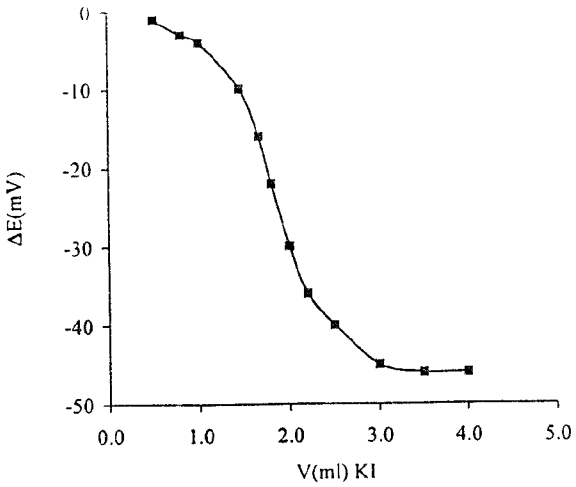

Fig. 4: Potentiometric titration curve for 20.0 mL of 0.010 M $TlNO_3$ with 0.1 M KI,by using the Tl^+ - ISE .

Application:

The proposed Tl^+ membrane electrode was successfully applied to the titration of a Tl^+ solution with KI, and the resulting titration curve is shown in Fig 4. As seen, the amount of Tl^+ in solution can be accurately determined with this electrode. The electrode was also applied to the direct determination thallium (I) content of spiked water samples. The results obtained comparing with that atomic absorption spectrometric (AAS), are summarized in Table-3. These results are in agreement with those obtained by AAS. A statistical treatment shows no significant difference between two techniques at 95 % confidence level.

Experimental

Reagents and Chemicals

Reagent grade nitrophenyl octylether (NPOE) from Fluka, dibuthyl phthalate (DBP), acetophenon (AP), tetrahydrofuran (THF), Oleic acid (OA), high relative molecular weight PVC, and dibenzopyridino-18-crown-6 (DBPY18C6), were purchased from Merck, Germany company and used as received. All the cations studied as interfering ion were nitrate salts, sodium tetraphenyl borate (NaTPB, all from Merck) and potassium tetrakis(p-chlophenyl) borate (KTpClPB, from Fluka) were of the guarantee reagents and used without any further purification except for vacuum drying over P_2O_5. Triply distilled deionized water prepared by an Aquatron system and used throughout.

Procedure

The Tl^+ sensitive PVC membrane was prepared by mixing 31 mg of powdered PVC, 63.2 mg of plasticizer NPOE, 1.8 mg KTpClPB and 4.2 mg ionophore (DBPY18C6) in 5 ml of dry freshly distilled THF. The resulting mixture was evaporated slowly until an oily membrane casting concentrated mixture was obtained. A Pyrex tube (3 -5 mm O.D.) was dipped into the mixture for about 10s, so that a membrane of about 0.3 mm thickness was formed, the tube was then pulled out from the mixture and kept at room temperature for about 1 hour. The tube was filled with internal filling solution (1×10^{-3} M $TlNO_3$). The electrode was finally conditioned for 18 h by soaking in a 1.0×10^{-3} M of Thallium (I) nitrate. A silver /silver chloride coated wire was used as an internal reference electrode.

Apparatus

A Metrohm ion analyzer pH/ mV meter (model 691) was used for the measuring the potential and pH at 25 ± 1 ° C. The used cell has the following assembly:

Ag | $AgCl_{sat}$, $TlNO_3$ (1.0×10^{-3} M) | PVC Tl^+ sensitive membrane | test solution | Hg/Hg_2Cl_2, KCl_{sat}. The e.m.f. measurements were made relative to a double-junction saturated calomel electrode (Metrohm), with the chamber filled with an ammonium nitrate solution. The activities were calculated according to the Debye-Huckel procedure [30].

A Perkin Elmer 3280 atomic absorption spectrophotometer was used for determination of Tl^+ in real sample determination, for comparison with the developed Tl^+ sensor.

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