

Thallium(I)-Selective Membrane Potentiometric Sensor Based on Dibenzyldiaza-18-Crown-6

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A new thallium(I) selective electrode based on dibenzyldiaza-18-crown-6 as membrane carrier was successfully prepared. The electrode exhibits a near-Nernstian response for Tl^+ ions over a wide concentration range from 1.0×10^{-5} - 1.0×10^{-1} M at 25 °C, and was found to be selective, precise and useable within the pH range 4.0-11.0. The electrode was successfully used as an indicator electrode in potentiometric titration of thallium ions.

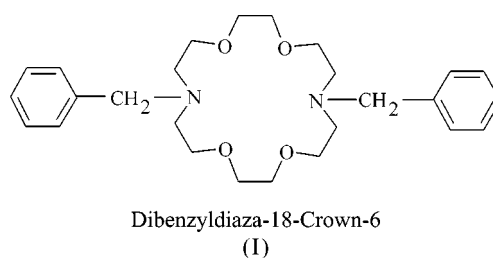
Key Words : Thallium ion-selective electrode, PVC membrane, Potentiometry

Introduction

From the environmental and biological viewpoint, thallium poisoning is still a problem.¹ Thallium(I) is especially toxic in its bivalent compounds, *e.g.* sulfate (Tl_2SO_4), acetate (CH_3COOTl), and carbonate (Tl_2CO_3). Moreover Tl^+ may substitute for K^+ in activation of some important enzymes, such as ATPase² and pyruvate kinase.³ The lethal dose of thallium(I) and its compounds are very low (level as low as 0.5 mg/100 g of tissue suggests thallium intoxication).⁴ Thus, the direct determination of Tl^+ in biological materials, such as blood and urine are of special interest.

Ion-selective electrode (ISE) is one of the most convenient and reliable analytical tools for estimating metal ion-concentrations.⁵ There have been only a few reports concerning thallium(I) liquid-membrane electrodes.⁶⁻⁹ They need to be improved with regard to their low selectivities against alkali metal ions, linearity and pH-dependence.⁵ The thallium(I) selective electrodes based on bis(crown ether)s containing the benzo-15-crown-5 moiety were described.¹⁰ These crown ether-based ISEs exhibited good slope of calibration plots and the electrode response was stable over a wide pH range. However, the Tl^+ selectivity against K^+ for one of the bis(15-crown-5)s was fairly poor ($\log K_{Tl,K}^{pot} = -0.52$).¹⁰ Yamashoji *et al.*¹¹ found that Tl^+ -selective PVC membrane electrodes based on dibenzo-20-crown-6 and dibenzo-22-crown-6 show higher selectivities to Tl^+ than that of symmetrical dibenzo-18-crown-6. The electrode based on DB18C6, DB20C6 or DB22C6 showed a linear response to the Tl^+ activity over a range of 3.2×10^{-5} - 1.0×10^{-1} M $TlNO_3$ with a slope of 59 mV decade⁻¹. The $\log K_{Tl,K}^{pot}$ values for the electrodes based on DB18C6, DB20C6 and DB22C6 are 0.15, -1.26 and -1.73, respectively.

Recently, calix[4]pyrroles and quinoline-carbonitriles have been proposed as Tl^+ -PVC based ISEs.^{4,5} In this paper, we report the use of dibenzyldiaza-18-crown-6 (DBzDA18C6, I) as an excellent neutral carrier ion in the construction of a thallium(I)-PVC membrane electrode.



Experimental Section

Materials. Reagent grade dibutyl phthalate (DBP), *o*-nitrophenyl octyl ether (*o*-NPOE), dimethyl sebacate (DMS), benzyl acetate (BA), tetrahydrofuran (THF) and high relative molecular weight PVC (all from Merck) were used as received. Dibenzyldiaza-18-crown-6 (DBzDA18C6) and sodium tetra phenyl borate (NaTPB) (all from Fluka) were used as received. The nitrate salts of the cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Doubly distilled deionized water was used throughout. The pH adjustments were made by the addition of 1.0 M HNO_3 and NaOH solutions.

Apparatus. All potentiometric measurements were carried out with the following assembly:

Ag | AgCl | KCl(sat.) | internal solution (1.0×10^{-1} M $TlNO_3$) | PVC membrane | test solution | KCl(sat.) | AgCl | Ag

A Metrohm ion analyzer Model 632 pH/mV meter was used for the potential and the pH measurements at 25.0 ± 0.1 °C.

Preparation of Membrane and Electrodes. The general procedure to prepare the PVC membrane was to mix thoroughly 3.0 mg of ionophore DBzDA18C6, 60 mg of plasticizer *o*-NPOE, 30 mg of powdered PVC and 7.5×10^{-2} mg of NaTPB in 3 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A pyrex tube (8-10 mm o.d.) was dipped into the mixture for about 5 s so that a nontransparent membrane

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of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 12 h. The tube was then filled with internal filling solution (0.1 M TlNO_3). The electrode was finally conditioned by soaking in 0.1 M TlNO_3 solution for 24 h. A silver/silver chloride wire was used as an internal reference electrode.

Results and Discussion

In preliminary experiments, the potential responses of four different ion selective electrodes based on DBzDA18C6 are illustrated in Figure 1. As can be seen, The sensitivity of the potential responses decreases in the order $\text{Tl}^+ > \text{K}^+ > \text{Cs}^+ > \text{Na}^+$. Actually the Tl^+ ion-selective electrode exhibits a linear response to the activity of thallium ions within the concentration range of about 1.0×10^{-1} M to 1.0×10^{-5} M with a near Nernstian slope of 56.9 mV per decade.

Interestingly, the observed trend in the sensitivity of the ion-selective electrodes tried seem to follow the order of decreased stability of the resulting 1 : 1 complexes with the macrocyclic ionophore. Although the ionic radius's of K^+ (1.33 Å)¹² and Tl^+ (1.5 Å) are suited to fit inside the cavity of DBzDA18C6 (with a radius of about 1.3-1.6 Å),¹³ the stronger soft-soft interaction of the latter cation with the nitrogen groups of the ring is expected to cause a higher stability of Tl^+ -DBzDA18C6 in comparison with K^+ -DBzDA18C6¹⁴⁻¹⁷ (The stability constants for Tl^+ -DBzDA18C6 and K^+ -DBzDA18C6 are 3.51 ± 0.03 ¹⁵ and 2.84 ± 0.14 ¹⁷ in dimethylformamide solvent at 25 °C). The stability order of other cations with smaller and larger sizes (*i.e.* 0.98 Å for Na^+ , 1.67 Å for Cs^+ ions) than the cavity of the macrocyclic ligand are too loose in the DBzDA18C6 cavity, resulting in weaker complexes.¹⁸ Thus, DBzDA18C6 seems suitable for use as a metal ion carrier in the Tl^+ -PVC membrane electrode for thallium ion, but not for other cations used.

It is well known that the sensitivity and selectivity of the

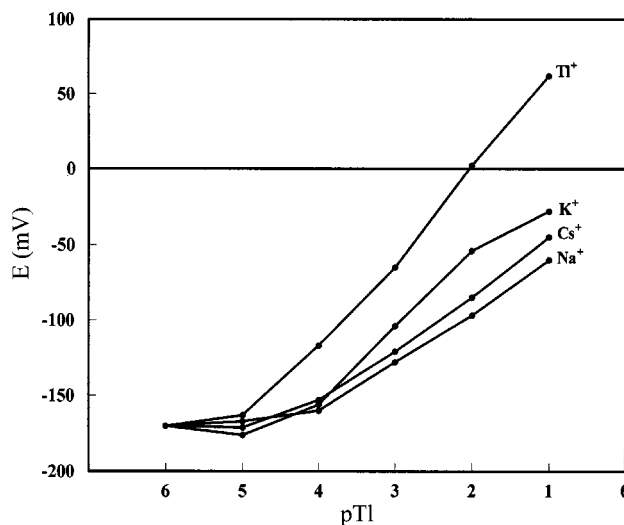


Figure 1. Potential response of various metal ion-selective electrodes based on DBzDA18C6.

ion-selective sensors not only depend on the nature of ionophore used, but also significantly on the membrane composition and the properties of plasticizers and additives used.¹⁸⁻²³ Thus, the influences of the membrane composition, the nature and amount of plasticizer and amount of NaTPB as a suitable lipophilic additive on the potential response of the Tl^+ sensor were investigated; the results are summarized in Table 1.

Several plasticizers including DBP, *o*-NPOE, DMS and BA, which are often used with PVC membrane electrodes, were evaluated. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands,^{3,19,24} it is expected to play an important role in determining the ion-selective characteristics. As it is seen from Table 1, among different plasticizers examined, *o*-NPOE results in the best sensitivity.

Table 1. Optimization of the membrane ingredients

Number	Composition (mg)							Slope (mV/decade)
	DBzDA18C6	PVC	<i>o</i> -NPOE	BA	DMS	DBP	Additive	
1	0.0	30	60	–	–	–	0.75	25.3
2	1.0	30	60	–	–	–	0.75	49.7
3	1.5	30	60	–	–	–	0.75	52.8
4	3.0	30	60	–	–	–	0.75	56.9
5	4.0	30	60	–	–	–	0.75	34.0
6	3.0	30	30	–	–	–	0.75	21.7
7	3.0	30	90	–	–	–	0.75	30.1
8	3.0	30	–	60	–	–	0.75	13.5
9	3.0	30	–	–	60	–	0.75	24.5
10	3.0	30	–	–	–	60	0.75	47.2
11	1.5	30	–	60	–	–	0.75	11.2
12	1.5	30	–	–	60	–	0.75	23.9
13	1.5	30	–	–	–	60	0.75	46.3
14	3.0	30	60	–	–	–	0.0	21.8
15	3.0	30	60	–	–	–	1.5	41.9

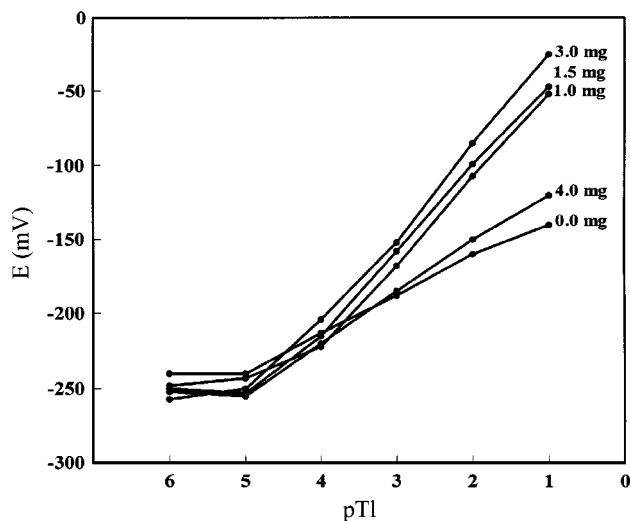


Figure 2. Effect of the content of DBzDA18C6 on the responses of thallium ion-selective electrodes.

The dependence of the electrode response (slope and detection limit) on the amount of carrier was also examined and is shown in Figure 2. In the case of the carrier-type ion-selective electrodes, the mechanism of the electrode response depends mainly on the extraction equilibrium in the vicinity of the interface between the membrane and aqueous layer.^{5,25} In spite of these considerations, a carrier content of 3.0 mg was chosen as the optimum condition (No. 4, Table 1), because the surface condition of the PVC membrane deteriorated as a result of decreasing and increasing the carrier content (1.0 and 4.0 mg, respectively).

The plasticizer/PVC ratio of 1.0-3.0 were examined. The membranes prepared with a plasticizer/PVC ratio of about 2.0 were found to have the best sensitivity, with a slope of 56.9 mV per decade over a wide concentration range (Figure 3). It is well known that the presence of lipophilic additives in ISEs not only diminishes the ohmic resistance^{26,27} and enhances the response behavior and selectivity,^{22,28} but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes.²⁹ Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface.³⁰

The influence of the concentration of internal solution on the potential response of the Tl^+ ion-selective electrode was studied. The $TlNO_3$ concentration was changed from 1.0×10^{-3} to 1.0×10^{-1} M and the emf-pTl plot was obtained. It was found that the variation of the concentration of internal solution does not any significant difference in the electrode's potential response, except for an expected change in the intercept of the resulting near-Nernstian plots. A 0.1 M concentration of the reference solution is quite appropriate for smooth functioning of the system.

Optimum conditioning time for the membrane sensor in a 0.1 M $TlNO_3$ solution is 24 h. It then generate stable potentials when placed in contact with Tl^+ solutions. The response time ($t_{95\%}$) measured was less than 10 s for Tl^+ concentrations 1.0×10^{-2} M. It is noteworthy that the equi-

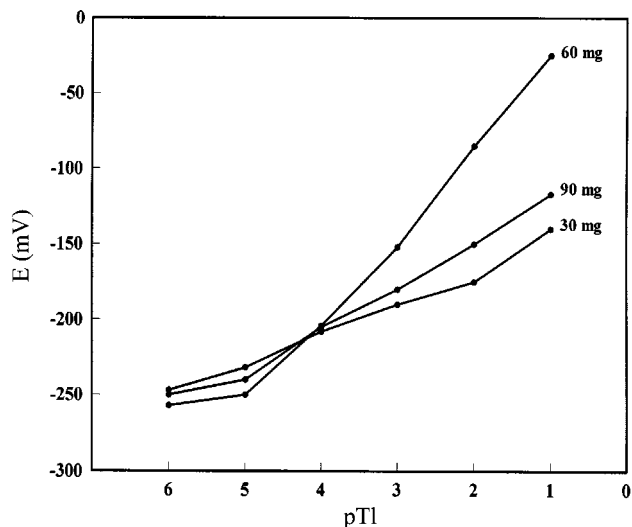


Figure 3. Effect of the content of membrane solvent (*o*-NPOE) on the responses of thallium ion-selective electrodes.

rium potentials essentially remained constant for more than 5 min, after which only a very small divergence within the resolution of the pH meter was recorded the membrane sensor prepared could be used for at least 3 months without any measurable divergence.

The emf response of the proposed Tl^+ sensor (prepared under optimal membrane ingredients) indicate a rectilinear range from 1.0×10^{-5} – 1.0×10^{-1} M. The slopes of the calibration curves were 56.9 ± 0.5 mV decade⁻¹. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.6×10^{-6} M.

The pH dependence of the electrode was studied for the pH range 2-12. The results indicate the working range of the electrode to be between pH 4 and 11 (see Figure 4). Above pH 11 the measured potential decreased, due to the effect of the hydroxyl ion. Moreover, the observed sharp change in

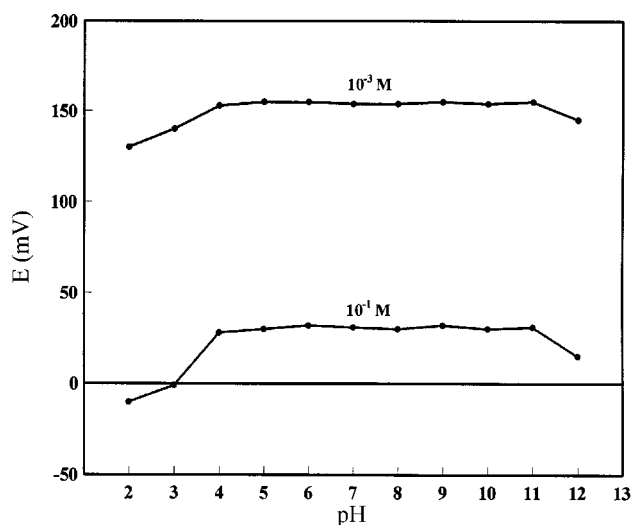


Figure 4. Effect of pH on the potential response of thallium ion-selective electrodes based on DBzDA18C6.

Table 2. Selectivity coefficients ($\log K_{\text{TI,J}}^{\text{pot}}$) of various interfering ions

Interfering ion	$\log K_{\text{TI,J}}^{\text{pot}}$	Interfering ion	$\log K_{\text{TI,J}}^{\text{pot}}$
H ⁺	-2.12	Ba ²⁺	-2.66
Li ⁺	-2.08	Fe ²⁺	-2.37
Na ⁺	-3.10	Co ²⁺	-1.11
K ⁺	-1.31	Ni ²⁺	-2.54
Cs ⁺	-2.20	Cu ²⁺	-2.57
Ag ⁺	-1.36	Zn ²⁺	-1.55
NH ₄ ⁺	-1.10	Cd ²⁺	-0.92
Mg ²⁺	-2.50	Hg ²⁺	-0.08
Ca ²⁺	-2.82	Pb ²⁺	-3.34
Si ²⁺	-2.10		

Table 3. Solubility products for some insoluble thallium(I) salts at 25 °C in this work

Salt	TlCl	TlBr	TlI	Tl ₂ CrO ₄
pK _{SP}	3.80	5.39	7.10	12.15

the metal nitrate are given in Table 2. It can be seen from these values that the electrode is characterized by a high selectivity towards thallium ions with respect to alkali, alkaline earth, transition and heavy metal ions.^{5,10,11,31}

Analytical Application

The proposed thallium membrane electrode was found to work well under laboratory conditions. It was successfully applied to the titration of a Tl⁺ ion solution with sodium chloride, sodium iodide, potassium bromide and potassium chromate. During the titration no pH or ionic strength adjustments were made. All titration were performed with 50 mL of sample solutions. A typical titration curve is shown in Figure 5 (a, b). The other titrants led to similar titration curves, the steepness of the potential jump being inversely dependent on the solubility product, as usual. As shown, the amount of Tl⁺ ions in solution can be accurately determined with the electrode.

On the other hand, solubility products were calculated with a previously described method,⁵ and the resulting data were summarized in Table 3. As can be seen, there is good agreement between the results obtained by the proposed electrode and those obtained by the previously reported methods.^{5,9,32-36}

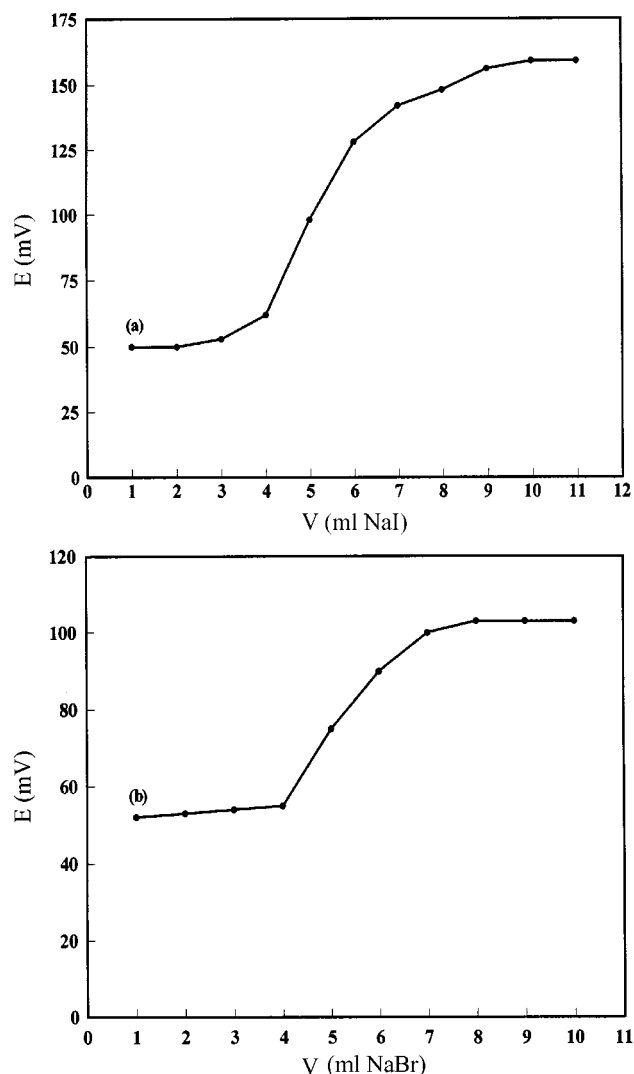
Conclusion

A new PVC-membrane electrode for Tl⁺ ions based on DBzDA18C6 as ionophore, was investigated. The optimized formulation of the membrane (*i.e.* 3.0 mg DBzDA18C6, 30 mg PVC, 60 mg *o*-NPOE, 0.75 mg NaTPB) resulted in a linear concentration range of 1.0×10^{-5} – 1.0×10^{-1} M with a slope of 56.9 mV/decade and a limit of detection of 5.6×10^{-6} M.

The fast response time, wide linear range, fair selectivity coefficients and long lifetime of the proposed sensor are advantageous over most of the reported Tl⁺ ion-selective electrodes.⁴⁻¹¹ The proposed electrode can be used successfully as a sensor in potentiometric titrations.

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**Figure 5.** Titration of Tl⁺ (0.01 M) in 50 mL of aqueous solution with (a) 0.1 M NaI and (b) 0.1 M NaBr using a thallium ion-selective electrode.

potential response below pH 4 may be due to the protonation of the crown, causing its diminished tendency for complex formation with Tl⁺ under acidic conditions.

The values obtained for selectivity coefficients by the separate solutions method using aqueous 0.1 M solutions of

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