

## Lead(II)-selective Polymeric Electrode Using a Schiff Base Complex of *N,N'*-Bis-thiophene-2-ylmethylene-ethane-1,2-diamine as an Ion Carrier

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We prepared lead ion-selective PVC membranes that were based on *N,N'*-bis-thiophene-2-ylmethylene-ethane-1,2-diamine as a membrane carrier. The membrane electrode has a linear dynamic range between  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-1}$  M with a Nernstian slope of 29.79 mV per decade, and its detection limit was  $2.04 \times 10^{-6}$  M at room temperature. The potentiometric response is independent of the pH of the solution in the pH range of 5–7. The proposed electrode revealed good selectivity and response for  $\text{Pb}^{2+}$  over a wide variety of other metal ions in pH 5.0 buffer solutions, and there was good reproducibility of the base line on the subsequent measurements. The membrane electrode has a relatively fast response time, satisfactory reproducibility and a relatively long life time.

**Key Words :** Polymeric membrane, Lead ion, Ion-selective electrode, *N,N'*-Bis-thiophene-2-ylmethylene-ethane-1,2-diamine, Schiff base

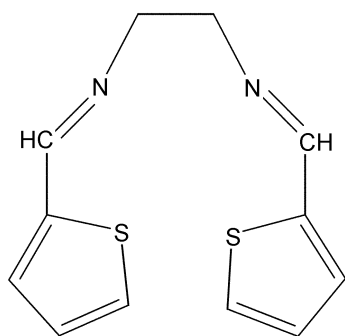
### Introduction

The ion-selective electrode (ISE) dynamic response is generated by the selective complexation of the target ion by the ion carrier that is dispersed in a poly(vinyl chloride) (PVC) matrix. The ISEs that are based on polymeric membranes incorporated with ionophores are well known to be very useful tools for clinical, chemical and environmental analysis. Until now, large numbers of ionophores with high selectivity for specific metal ions have been developed as potentiometric sensors for the determination of the respective metal ions. The ISEs for determining the lead ion have received much interest, and many ligands have been studied for their use as sensing ionophores.<sup>1–4</sup> Piroxicam, quinaldic acid, capric acid, diaza-crown, dibenzyl phosphate, benzyl sulfide, acyclic diamide, anthraquinone, calix-azo, calix-phosphine oxides, thiocrown 5,5'-dithiobis-2-nitrobenzoic acid, crown-ethers and porphyrins as ionophores have been used for lead-ISEs.<sup>5–20</sup> The potentiometric sensors that use Schiff Base (SB) as an ion carrier have been reported to exhibit excellent selectivity for specific metal ions. The SBs are known to form very stable complexes with the transition metal ions, and they act as ion carriers in the polymeric membrane. Almost all metals form 1 : 1 complexes with SBs. The feature of SBs allow geometric and cavity control of the host-guest complexation and modulation of its lipophilicity, and this produces remarkable selectivity, sensitivity and stability for a specific ion. The resulting SB complexes have attracted increasing attention in the field of ionic binding due to their unique properties and reactivity. Many studies were reported about their complex formation equilibria in solution,<sup>21,22</sup> and studies have also reported about the use of SBs as cation carriers in ion-selective electrodes (ISEs) for determining such cations as copper(II), aluminium(III), mercury(II), nickel(II), silver(I), gadolinium

(III), cobalt(II) and yttrium(III).<sup>23–40</sup> It was reported that lead(II) forms a strong complex with *N,N'*-bis(5-methyl salicylidene)-*p*-diphenylene methane diamine and bis(acetylacetonate)-*p*-phenylenediamine.<sup>41,42</sup> We have also recently reported on a lead(II)-selective membrane based on a Schiff Base Complex of *N,N'*-bis(salicylidene)-2,6-pyridinediamine.<sup>43</sup> These ligands formed a selective complex with lead(II) ions rather than with other metal ions. In order to improve the selectivity for the lead ion compared with the other ions, we used a new SB ionophore. Therefore in the present study, we describe the preparation and characterization of new ISEs that are based on *N,N'*-Bis-thiophene-2-ylmethylene-ethane-1,2-diamine as a SB ionophore. The coordinating effect for the selective response of the lead ion was investigated by using PVC membranes. Polymeric ISEs provide one of the most powerful sensing methods because it is possible to select various sensory elements according to the shape and size of the target ion. The ISE based on *N,N'*-bis-thiophene-2-ylmethylene-ethane-1,2-diamine exhibits good sensitivity and selectivity towards the lead ion.

### Experimental Section

The *N,N'*-bis-thiophene-2-ylmethylene-ethane-1,2-diamine that was tested as a lead(II) ionophore is shown in Figure 1. The ionophore was synthesized by condensing ethylenediamine with thiophenecarboxaldehyde with using a previously reported method.<sup>44,46</sup> High molecular weight PVC, 2-nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS), potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB) and tetrahydrofuran (THF) were all obtained from Fluka, and these substances were used to prepare the PVC membranes. The nitrate salts of the cations we used (all from Merck) were of the highest purity available and they were used without any



**Figure 1.** *N,N'*-bis-thiophene-2-ylmethylene-ethane-1,2-diamine as the lead ionophore used in this study.

further purification except for vacuum drying over  $P_2O_5$ . Doubly distilled water in a quartz apparatus was used to prepare all the aqueous electrolyte solutions.

Table 1 summarizes the compositions of the lead-selective membranes employed in this study. The typical composition of the PVC-based lead(II)-selective electrodes was 33 mg PVC, 66 mg plasticizer, 1 mg ionophore and 100 mol% additive. The ionophore, plasticizer, additive and PVC were dissolved in the appropriate volume of THF and this was mechanically stirred. All the membrane cocktails were cast in glass rings placed on glass plates for creating the conventional ion-selective electrodes. The solvent from the PVC membrane was allowed to evaporate for at least 24 hours at room temperature. The thickness of the resulting membrane, as measured by a micrometer, was about 0.3 mm.

The electrochemical properties of the lead(II)-selective electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and these were mounted in Philips electrode bodies (IS-561). For all the electrodes, 0.1 M KCl were used as an internal filling solution. The electrode was finally conditioned for 24 h by soaking it in a buffer solution of 10 mM lead nitrate. A silver/silver chloride coated wire was used as an internal reference electrode. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-20) with two chambers. This reference electrode had two different filling solutions: the inner chamber filling solution was a green colored solution

saturated with AgCl, and the outer chamber filling solution consisted of 10%  $KNO_3$ . The potential measurements were carried out at  $25 \pm 1$  °C with a Kosentech 16-channel potentiometer (KST101-1) that was coupled to a computer by setting up the following cell assembly: Ag/AgCl/0.1 M KCl/PVC membrane/test solution/Ag/AgCl. All the potential measurements were carried out with the following assembly: Ag/AgCl/0.1 M KCl/PVC membrane/test solution/Ag/AgCl. The electrochemical potential was measured by using a 16-channel potentiometer coupled to a computer. The electrochemical measurements were conducted within a 1 mV variance of the open circuit potential with 5 minutes. The dynamic response curves were produced by adding standard solutions of the cations to a magnetically stirred, pH 5.0 buffer solution (0.1 M Tris-HCl). The use of buffer solution was necessary to prevent pH deviation and the pH 5.0 solution of 0.1 M Tris-HCl among all the tested pHs was most proper for this system. The selectivity coefficients ( $\log K_{Pb^{2+},j}^{pot}$ ) were determined by the separate solution method (SSM) with using nitrate salts of the involved cations. The detection limits were estimated at the intersection of two linear lines; the one line was extrapolated from a high concentration range and the other line parallel to the x-axis was drawn through the mean potential value of the lowest metal ion concentration that was used in the plot of the potential change and the concentration of  $Pb^{2+}$ . At least three-time measurements were performed, and the data were determined from the plot.

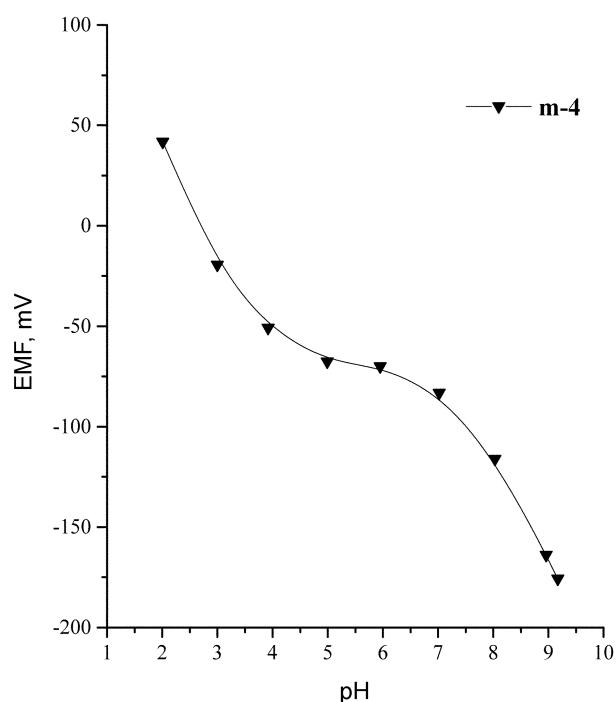
## Results and Discussion

**Potentiometric response.** Schiff bases as ligands seem to have potential to serve as ionophores for soft heavy metal ions in the PVC membrane electrodes because of their excellent metal-binding properties, their water insoluble and their rapid exchange kinetics. The Schiff base of *N,N'*-Bis-thiophen-2-ylmethylene-ethane-1,2-diamine was used as an ionophore for preparing the PVC membrane ion-selective electrodes for a wide variety of metal ions. Table 1 shows the compositions of the ionophore, the plasticizer, the additive and the PVC. Figure 2 shows the pH dependence for the potentiometric response of the novel membrane electrode (m-4) in a variety of pH solutions that were

**Table 1.** The compositions of the membranes and their potentiometric characteristics of the lead-selective electrodes in pH 5.0 buffer solution

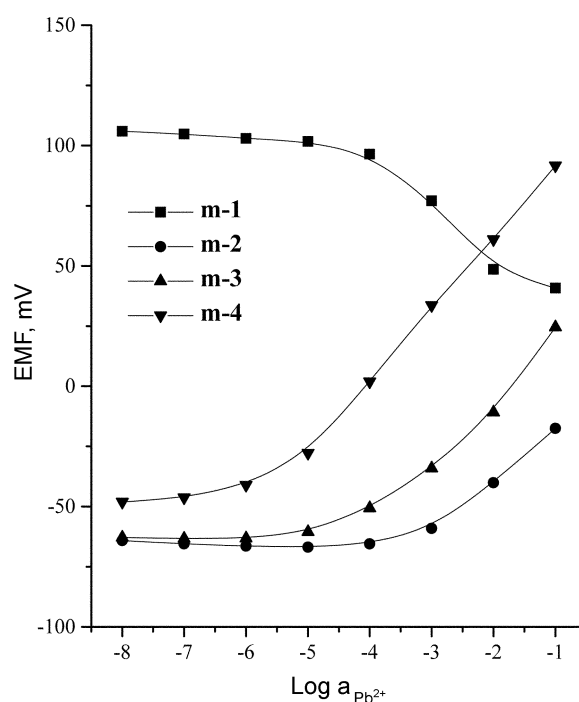
Membrane	Ionophore <sup>a</sup>	PVC <sup>a</sup>	<i>o</i> -NPOE <sup>a</sup>	DOP <sup>a</sup>	DOA <sup>a</sup>	DOS <sup>a</sup>	KTpCIPB <sup>b</sup>	LOD	Slope (mV)
m-1	1	33	66				0	–	–
m-2	1	33	66				20	–5.15	24.31
m-3	1	33	66				50	–5.52	26.96
m-4	1	33	66				100	–5.69	29.79
m-5	1	33		66			100	–5.20	17.91
m-6	1	33			66		100	–3.65	9.70
m-7	1	33				66	100	–3.59	18.90
m-8	0	33	66				100	–2.52	9.80

<sup>a</sup>In mg. <sup>b</sup>mol% relative to the ionophore.



**Figure 2.** Effect of the pH of the test solution on the potential response of the  $\text{Pb}^{2+}$  ISE (m-4).

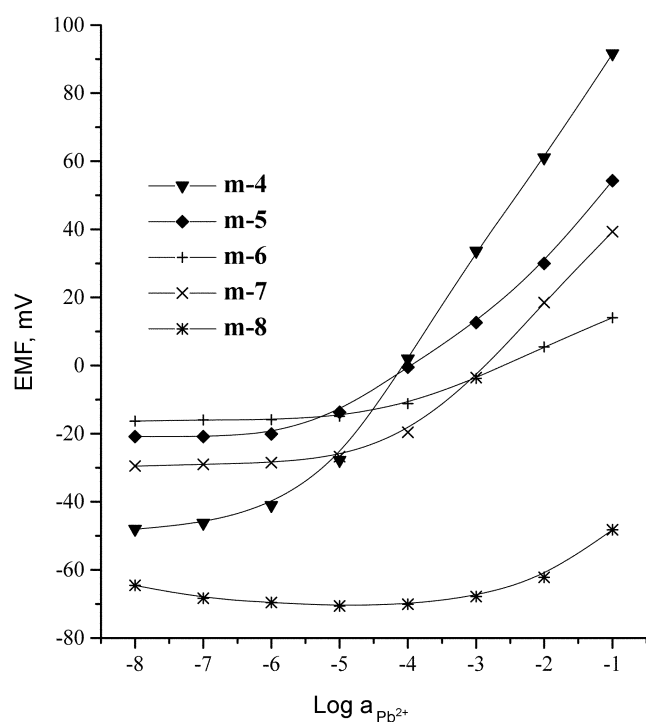
without any lead ions, and the potentiometric response for the potential obtained from the m-4 electrode shows a similar value between pH 5 and pH 7. Therefore, the potentiometric response of the PVC polymeric  $\text{Pb}^{2+}$ -ISEs that were based on the Schiff base was examined for many metal ions in the pH 5.0 buffer solutions. The  $\text{Pb}^{2+}$ -ISE membrane compositions were optimized to obtain the best sensitivity and selectivity towards the lead ion because the sensitivity and selectivity of the ion-selective electrodes were dependent upon the nature of ionophore used, as well as being significantly dependent on the membrane composition and the additives that were used. The optimization was carried out by varying the ratio of the PVC membrane components such as the PVC, the plasticizer, the ionophore and the additive (KTpCIPB). The potentiometric response of the membranes without the additive ion-exchanger (KTpCIPB) showed worse sensitivity and selectivity than those with the KTpCIPB, and in this study, most of the membrane electrodes were prepared with KTpCIPB. The potentiometric response of the membranes was evaluated as to the slope and the detection limit towards the lead ion. The slope and detection limit for the membranes were determined in accordance with IUPAC recommendations.<sup>47</sup> The effect of the ionophore that was used was investigated in a PVC polymeric membrane (m-8) with no ionophore, 100 mol% KTpCIPB, 33 mg PVC and 66 mg plasticizer. When the membrane (m-4) was compared with m-8, the slope and the detection limit were highly increased. This result indicated that the ionophore had good sensing ability toward the lead-ion. Figure 3 illustrates the typical response curves for the lead ion, and the curves were obtained in pH 5.0



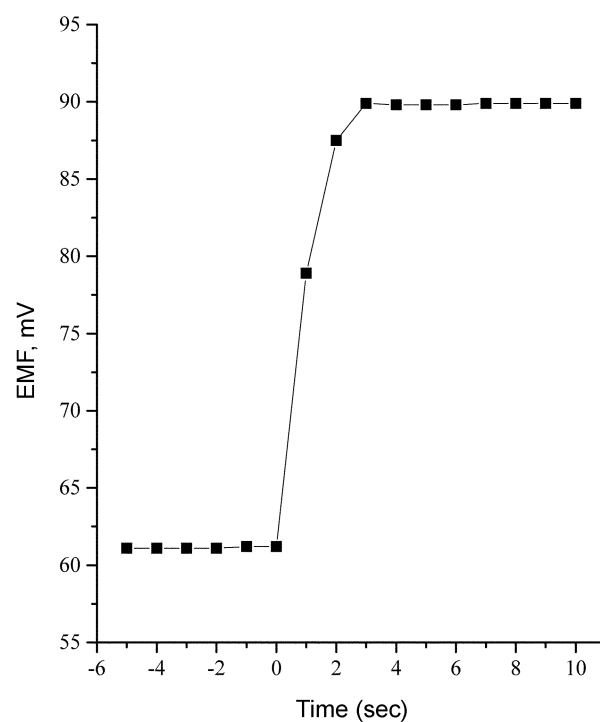
**Figure 3.** Potentiometric responses of the  $\text{Pb}^{2+}$  ion-selective electrodes based on different mol% of the additive: m-1; no response, m-2; 20 mol%, m-3; 50 mol%, and m-4; 100 mol%.

buffer solutions with membranes (m-1, m-2, m-3 and m-4) containing different amount of the additive (KTpCIPB) in order to measure the effect of the additive capacity under the same amount of the ionophore. The results showed that the membrane electrode (m-4) containing the 100 mol% additive ionophore gave the best sensitivity towards the lead ion. The effects of the membrane composition, the nature of plasticizers, the ionophores and the lipophilic additive on the potentiometric response of the  $\text{Pb}^{2+}$ -ISE were investigated and the results are summarized in Table 1. A membrane (m-4) prepared with *o*-NPOE as a plasticizer and 100 mol% of the additive displays a good Nernstian response to  $\text{Pb}^{2+}$  over a wide range. The slope of the calibration curve was 29.79 mV/decade of the  $\text{Pb}^{2+}$  concentration at room temperature, and the limit of detection (LOD) of the log a (M) was equal to  $-5.69$ .

The effect of the plasticizer on the  $\text{Pb}^{2+}$ -ISE membrane electrodes based on the Schiff base is shown in Figure 4. According to Figure 4 and Table 1, it is clear that *o*-NPOE is a more effective solvent mediator than the others in preparing the  $\text{Pb}^{2+}$  ISEs. It is noteworthy that the lipophilicity of the plasticizer influences both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex because the dielectric constant of the membranes controls the mobility of metal ions. The prepared electrodes were also examined for their effect on the inner reference solution. It was found that the concentration and composition of the internal solution insignificantly affected on the potentiometric response. Thus, the 0.1 M KCl as a reference solution is quite appropriate for the



**Figure 4.** The lead-ion responses of the membranes prepared by using different plasticizers with the ionophore: m-4; *o*-NPOE, m-5; DOP, m-6; DOA, m-7; DOS and m-8; *o*-NPOE (no ionophore).



**Figure 5.** Response-time profile of the  $Pb^{2+}$  ion-selective electrodes m-4 based on the ionophore.

smooth functioning of the electrode system. The optimum equilibration time for the membrane electrode is 24 h. After that time, it generates stable potentials when placed in contact with the  $Pb^{2+}$  solutions. A potential-time plot for the electrode is shown in Figure 5. The static response time of the membrane electrode thus obtained was  $< 5$  s for the addition of  $1.0 \times 10^{-2}$  M  $Pb^{2+}$  to the  $1.0 \times 10^{-1}$  M lead ion solution. The response-time profile of the  $Pb^{2+}$  ion-selective electrodes based on the ionophore shows that the steady potential can reach very quickly in the pH 5.0 buffer solution. Thus, all the membranes responded rapidly, within 5s, to changes in the lead concentration. The rate of response was only limited by the speed of stirring and the injection technique. The membranes are stored in 0.1 M Tris-HCl pH 5.0 buffer solution when they are not in use. The degradation of the sensitivity in the polymeric membrane may be dependent upon the lipophilicity and chemical stability of an ionophore, and this can result in the ionophore bleeding from the membrane. Since Schiff bases as ionophores are compounds having high lipophilicity, the membranes containing them should provide very slow bleeding of the ionophore.

**Selectivity.** The selectivity coefficients of the new membranes are very important for determining their characteristics as ISEs. The selectivity coefficients represent their response to the ion species that are to be measured over the other ions that are present in solution. They were evaluated by the separate solution method. The selectivity coefficients towards  $Pb^{2+}$  were determined against the interfering cations,  $Ba^{2+}$ ,  $Rb^{+}$ ,  $Cs^{+}$ ,  $Na^{+}$ ,  $K^{+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Ag^{+}$ ,

$Zn^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Mg^{2+}$ . The Schiff base as the employed ionophore was selective towards the lead ion against all the interfering ions that were tested. Among all the tested membranes, the best results were gained from the m-4 membrane. The selectivity coefficients ( $\log K_{Pb^{2+},j}^{pot}$ ) for the m-4 with respect to the corresponding nitrate of the interfering ions that were tested are given in Table 2. As can be seen, with the exception of  $Ba^{2+}$  and  $Rb^{+}$  for all ions that were used, the selectivity coefficients are on the order of  $10^{-3}$  or smaller, indicating they would not significantly disturb the functioning of the  $Pb^{2+}$  selective electrode. Moreover,  $Ba^{2+}$  and  $Rb^{+}$  with the selectivity coefficients on the order of  $10^{-2}$  revealed very low interfering effects. In Table 2, the selectivity coefficients of the different lead ion-selective electrodes that have been previously reported on are compared with those obtained in the present work. As shown in Table 2, the selectivity coefficients of  $Pb^{2+}$  against  $Na^{+}$ ,  $K^{+}$ ,  $Ag^{+}$  and  $Cu^{2+}$  were improved when compared with the other electrodes in Table 2. Thus, it is clear that the membrane electrode has good selectivity over the mono-valent and divalent cations. Meanwhile, the effect of counter anions was investigated with using the lead salts of chloride and nitrate, and no significant changes in the working concentration range and the slope were observed. Moreover, the lead salt of chloride is easily precipitated at higher concentrations. Examination of the selectivity data for the electrodes employed in this study indicates that the extent of the complex formation between the ionophore and the metal ion, the geometrical structure and the rigidity of the ionophores are the major factors that determine the

**Table 2.** Selectivity coefficients ( $\log K_{pb^{2+},j}^{pot}$ ) for the various different lead ion selective electrodes

Electrode	Cu <sup>2+</sup>	Ba <sup>2+</sup>	Cd <sup>2+</sup>	Sr <sup>2+</sup>	Zn <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Ag <sup>+</sup>
Capric acid <sup>a</sup>	2.3	2.3	2.6	–	2.7	–	–	1.2	1.1	–	–	–
Piroxicam <sup>b</sup>	1.9	2.2	2.3	2.3	2.9	4.0	2.4	1.4	2.2	–	–	0.5
Dibenzyl phosphate <sup>c</sup>	4.5	–	3.2	–	5.2	2.3	–	3.5	2.8	–	–	0.1
Calix phosphine oxide <sup>d</sup>	4.3	–	5.3	4.2	4.5	2.3	–	0.8	2.5	–	–	0.2
Schiff base BSPD <sup>e</sup>	2.7	3.1	3.6	3.8	4.1	4.1	4.9	2.5	2.2	2.5	2.6	2.2
Schiff base BTEA <sup>f</sup>	3.3	2.6	3.4	4.1	3.7	4.0	4.6	3.2	3.1	2.9	3.1	3.5

<sup>a</sup>ref [10], <sup>b</sup>ref [12], <sup>c</sup>ref [17], <sup>d</sup>ref [18], <sup>e</sup>ref [43], <sup>f</sup>this work (by SSM)

selectivity, and the other factor that determines it is the kind of plasticizer that is used in the PVC membrane electrodes. The result indicates that the geometry and ligating cavity of the Schiff base should be a significant factor for determining the selectivity coefficients towards Pb<sup>2+</sup>. Based on the data for the m-4 in Tables 1 and 2, the good sensitivity and highest selectivity towards the lead ion can be attributed to the strong complexation of the lead ion to the Schiff base, which geometrically has the proper cavity to coordinate to the ligand. The electrode was applied to the direct measurement of Pb<sup>2+</sup> in the prepared solutions. The potential was measured by direct potentiometry in pH 5.0 buffer solution.

### Conclusions

The membrane electrode incorporating *N,N*-Bis-thiophen-2-ylmethylene-ethane-1,2-diamine as an ion carrier can be used for the development of a lead ion-selective electrode. Among the membranes we tested, the polymeric membrane m-4 that is based on the Schiff base with *o*-NPOE and lipophilic additive displays a good Nernstian response (29.79 mV/decade) to Pb<sup>2+</sup> over the linear range of  $1.0 \times 10^{-5}$  M– $1.0 \times 10^{-1}$  M. Most of the metal ions would not seriously affect the selectivity of the lead electrode. It can be concluded that the membrane electrode has a rapid potential response and excellent selectivity towards the lead ion over the other interfering metal ions.

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