

Polymeric Lead(II)-selective Electrode Based on N,N'-Bis-thiophen-2-ylmethylene-pyridine-2,6-diamine as an Ion Carrier

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Received October 18, 2006

Polymeric electrodes for lead ion based on N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine as an ion carrier were prepared. The membrane electrode (m-3) containing *o*-NPOE as a plasticizer and 50 mol% additive of ionophore gives an excellent Nernstian response (29.59 mV/decade) and the limit of detection of $-\log a(\text{M}) = 5.74$ to Pb^{2+} in $\text{Pb}(\text{NO}_3)_2$ solution at room temperature. The prepared electrode provided good sensitivity and outstanding selectivity and response for Pb^{2+} over a wide variety of other metal ions in pH 7.0 buffer solutions. The good sensitivity and selectivity towards lead ion are attributed to the strong complexation of lead ion to N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine which has geometrically the proper cavity to coordinate to the ligand.

Key Words : Lead ion, Ion-selective electrode, Polymeric membrane electrode, Schiff base, N,N'-Bis-thiophen-2-ylmethylene-pyridine-2,6-diamine

Introduction

The ion-selective electrode (ISE) based on polymeric membranes incorporated with ionophores is well known as very essential device for chemical, environmental and clinical analysis. Potentiometric sensors containing Schiff base as an ion carrier have been reported to exhibit excellent selectivity for specific metal ions. Schiff base is known to form very stable complexes with transition metal ions, and it acts as ion carrier in the polymeric membrane electrode. Almost most of metals make 1:1 metal complexes with Schiff base. The characteristic of Schiff base gives geometric configuration and cavity control of host-guest complexation and modulation of its lipophilicity, and provides remarkable selectivity, sensitivity and stability for a specific metal ion. The resulting Schiff base complexes have attracted increasing attention in the area of ionic binding and selectivity due to their unique properties and reactivity. Recently, many works were reported about their complex formation equilibria in solution^{1,2} and also about the use of Schiff base as an ion carrier in ISEs for determining metal ions such as aluminium(III),³ chromium(III),⁴ cobalt(II),⁵ copper(II),⁶⁻¹² gadolinium(III),¹³ lead(II),¹⁴⁻²⁰ mercury(II),^{21,22} nickel(II),²³ silver(I),²⁴⁻²⁶ yttrium(III).²⁷ Many ionophores with high selectivity for specific metal ions have been developed for the potentiometric sensors for the determination of the target metal ions. The ISEs for determining lead ion have received much interest, and many ligands have been investigated as sensing ionophores. Acyclic diamide, piroxicam, quinaldic acid, diaza-crown, benzyl sulfide, anthraquinone, calix-azo, thiacycrown 5,5'-dithiobis-2-nitrobenzoic acid, porphyrin as ion carriers were used for lead-ISEs.²⁸⁻⁴¹ In this work, we describe the fabrication and characterization of new ISE based on N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine as an ion carrier. The coordinating effect for the selective response of

lead ion was studied by using PVC membrane electrode. Polymeric ISE provides one of the most powerful sensing tools because it is possible to select various sensory elements according to the shape of the ion carrier and the size of the target metal ion. The ISE based on N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine exhibits good sensitivity and selectivity towards lead ion.

Experimental

Reagents. N,N'-Bis-thiophen-2-ylmethylene-pyridine-2,6-diamine (BTPD) as a Schiff base for using as an ion carrier was synthesized according to the similar procedure described previously.⁴¹ A solution of 5 mmol 2,6-pyridinediamine was slowly added to 10 mmol 2-thiophenecarboxaldehyde in ethanol under nitrogen atmosphere. After 1 day at room temperature, the precipitate was collected by filtration. The product was recrystallized from ethanol and dried under reduced pressure at 50 °C, 97% yield. ¹H NMR (DMSO-*d*₆): 9.26 (br s, CH=N). BTPD is shown in Figure 1. High molecular weight PVC, 2-nitrophenyl octyl ether (*o*-NPOE), di-

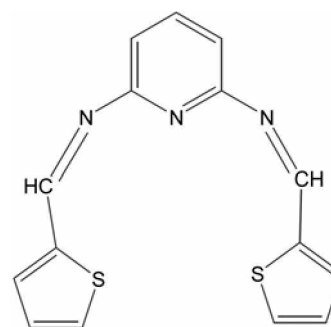


Figure 1. N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine (BTPD) as a lead ionophore used in this work.

Table 1. The compositions of membranes and their potentiometric characteristics of the lead-selective electrodes in pH 7.0 buffer solutions

Membrane No	Ionophore ^a	PVC ^a	<i>o</i> -NPOE ^a	DOP ^a	DOA ^a	DOS ^a	DBS ^a	KTpCIPB ^b	LOD	Slope (mV)
m-1	0	33	66					50	-4.27	39.68
m-2	0.5	33	66					50	-4.35	36.69
m-3	1	33	66					50	-5.74	29.59
m-4	2	33	66					50	-3.97	38.39
m-5	1	33	66					0	-4.13	40.30
m-6	1	33	66					20	-5.87	20.76
m-7	1	33	66					100	-3.98	46.00
m-8	1	33		66				50	-5.31	21.92
m-9	1	33			66			50	-5.26	17.22
m-10	1	33				66		50	-5.83	22.75
m-11	1	33					66	50	-4.76	19.47

^aIn milligrams. ^bMole percent relative to the ionophore.

octyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS), dibutyl sebacate (DBS), potassium tetrakis-(*p*-chlorophenyl)borate (KTpCIPB) and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare the PVC membranes. The nitrate salts of cations used (all from Merck) were used without any further purification except for vacuum drying over P₂O₅. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions.

Preparation of polymeric ion-selective electrodes. The representative composition of PVC-based lead-selective electrodes was 33 mg PVC, 66 mg plasticiser, 1 mg ionophore, 50 mol% additive. Table 1 summarizes the compositions of the lead-selective membranes tested in this work. The ionophore, plasticizer, additive, and PVC were dissolved in the appropriate volume of THF and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates for conventional ion-selective electrodes. Solvent from PVC membrane was allowed to evaporate for at least 24 hours at room temperature.

Potentiometric measurements. The electrochemical properties of lead-selective electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M KCl was used as an internal filling solution. The electrode was finally conditioned for 24 h by soaking 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. The potential measurements were carried out at room temperature with Kosentech 16-channel potentiometer (KST101-1) coupled to a computer by setting up the following cell assembly: Ag/AgCl/0.1 M KCl/PVC membrane//test solution//Ag/AgCl. The electrochemical measurements were conducted after within 1 mV variance of open circuit potential. The dynamic response curves were produced by adding standard solutions of cations to magnetically stirred pH 7.0 buffer solution (0.1M Tris-HCl). The use of buffer solution is necessary to prevent pH deviation and pH 7.0 solution of 0.1M Tris-HCl

among tested pHs is most proper in this system. The selectivity coefficients ($\log K_{Pb^{2+}, J}^{pot}$) were determined by the separate solution method (SSM) using nitrate salts of the cations involved. Detection limits were estimated at the intersection of two linear lines, the one extrapolated from a high concentration range and the other parallel to the x-axis drawn through the mean potential value of the lowest metal ion concentration used in the plot of the potential change and the concentration of Pb²⁺. At least five-time measurements were performed, and the data were determined from the plot.

Results and Discussion

Potentiometric response. Schiff base as a ligand seems to be a potential ionophore for soft heavy metal ions in the PVC membrane electrodes due to its excellent metal-binding properties, quick exchange kinetics, and good lipophilicity. N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine was used as an ionophore for preparing PVC membrane ion-selective electrodes for a variety of metal ions. Table 1 gives the compositions of ionophore, plasticizer, additive and PVC. The pH dependence on the potentiometric response of the novel membrane electrode (m-3) is studied in a variety of pH solutions, and shown in Figure 2. The result shows

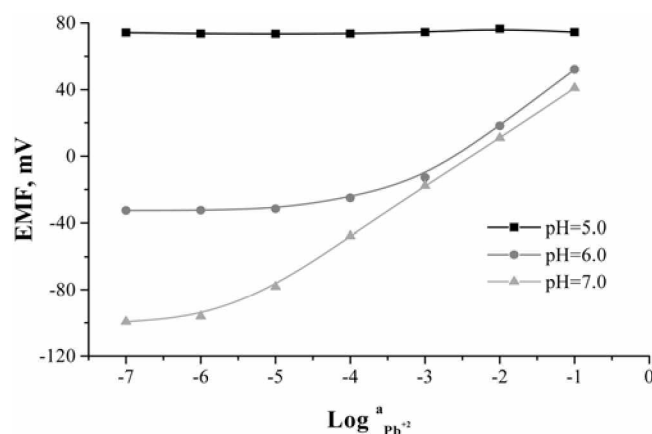


Figure 2. Potentiometric responses of Pb²⁺ ion-selective electrodes at the typical membrane (m-3) according to the solution pHs.

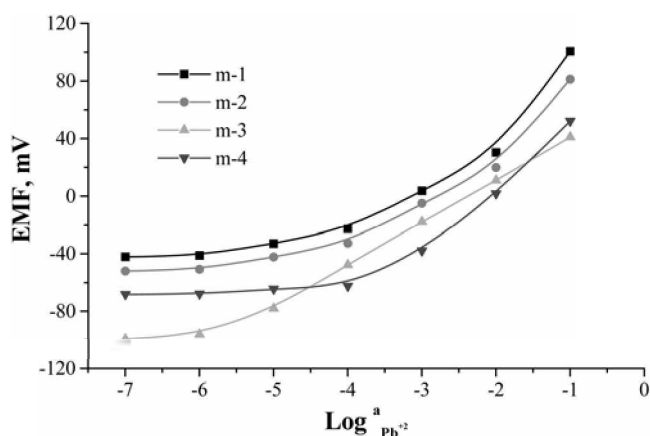


Figure 3. Potentiometric responses of Pb^{2+} ion-selective electrodes based on different amount of ionophore in the solution pH 7.0. (m-1) No, (m-2) 0.5 mg, (m-3) 1 mg, and (m-4) 2 mg.

that the potentiometric response towards lead ion of m-3 membrane depends on the solution pHs used, and gives good sensitivity in pH 7. Therefore, the potentiometric response of PVC polymeric Pb^{2+} -ISEs based on BTPD was examined for many metal ions in pH 7.0 buffer solutions. The Pb^{2+} -ISE membrane compositions were optimized to produce the best sensitivity and selectivity towards lead ion, because the sensitivity and selectivity of the ion-selective electrodes depend on the character of ionophore used as well as significantly on the membrane compositions. The optimization was carried out with varying of the ratio in PVC membrane components such as PVC, plasticizer, ionophore, additive (KTpCIPB). The polymeric membranes are investigated to measure the ability of the ionophore to act as an ion carrier in the absence and presence of the ion exchanger. The response of the membranes without additive ion-exchanger (KTpCIPB) gave the worse sensitivity and selectivity than those with KTpCIPB. Most of membrane electrodes were prepared with KTpCIPB in this work. The potentiometric response of the membranes was evaluated as to the slope and detection limit towards lead ion. The slope and detection limit for membranes were determined in accordance with IUPAC recommendations. Figure 3 illustrates representative response curves for lead ion, measured in pH 7.0 buffer solutions by membranes (m-1, m-2, m-3, and m-4) containing different amount of ionophore BTPD, respectively. The result shows that the membrane electrode prepared with 1 mg ionophore gives best sensitivity towards lead ion, and about 1% ionophore in the PVC membrane is suitable for high quality electrode. Meanwhile, Figure 4 illustrates representative response curves for lead ion, measured in pH 7.0 buffer solutions by membranes (m-3, m-5, m-6, and m-7) containing different amount of additive (KTpCIPB), respectively. It shows that the membrane electrode prepared with 50 mol% additive at same amount (1 mg) of ionophore gives best sensitivity towards lead ion, and also the proper additive should be needed to get good character. The effects of the membrane composition, the nature of plasticizers, ionophores, and lipophilic additive on the potentiometric

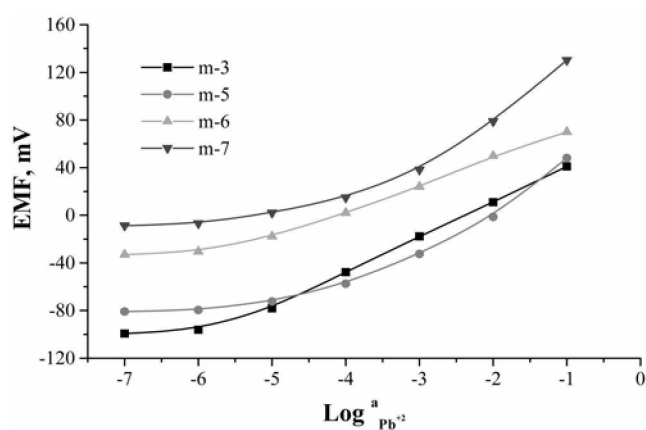


Figure 4. Potentiometric responses of Pb^{2+} ion-selective electrodes based on different mol % of additive in the solution pH 7.0. (m-5) No, (m-6) 20 mol%, (m-3) 50 mol%, and (m-7) 100 mol%.

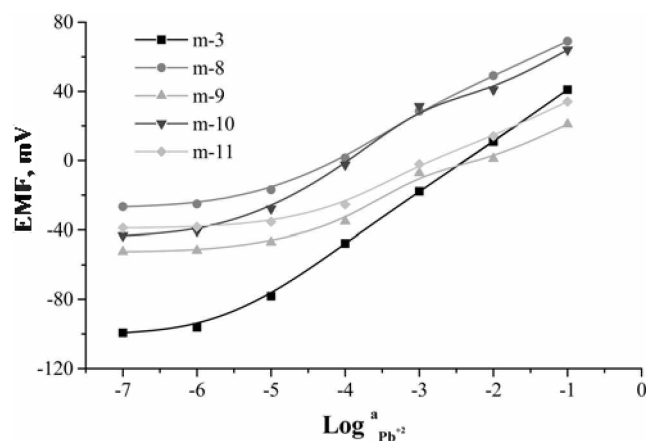


Figure 5. Pb^{2+} -ion potentiometric responses of membranes prepared by different plasticizers with ionophore BTPD. (m-3) *o*-NPOE, (m-8) DOP, (m-9) DOA, (m-10) DOS, and (m-11) DBS.

response of the Pb^{2+} -ISE were investigated and summarized in Table 1. A membrane (m-3) prepared by *o*-NPOE as a plasticizer and 50 mol% of additive with about 1% ionophore displays a good Nernstian response to Pb^{2+} ion over the wide range. The slope of the calibration curve was 29.59 ± 0.5 mV/decade of Pb^{2+} concentration at room temperature, and the limit of detection (LOD) of $-\log a$ (M) = 5.74 ± 0.1 . In Figure 4, the potentiometric response for the electrodes prepared from the other amount of additive is also included for comparison. As seen, the m-5 prepared without additive resulted in a diminished slope (40.30 mV/decade) and a higher LOD ($-\log a$ = 4.13). The above result demonstrates that BTPD behaves as an effective ionophore with an appropriate amount of additive about 50 mol% vs ionophore. It should be noted that the presence of lipophilic anions in cation-selective membrane electrodes provides the decrease of the ohmic resistance as well as the improvement of their sensitivity and selectivity.

The effect of plasticizer on Pb^{2+} -ISE membrane electrodes based on BSPD is shown in Figure 5. According to Figure 5 and Table 1, it is clear that *o*-NPOE is a more effective

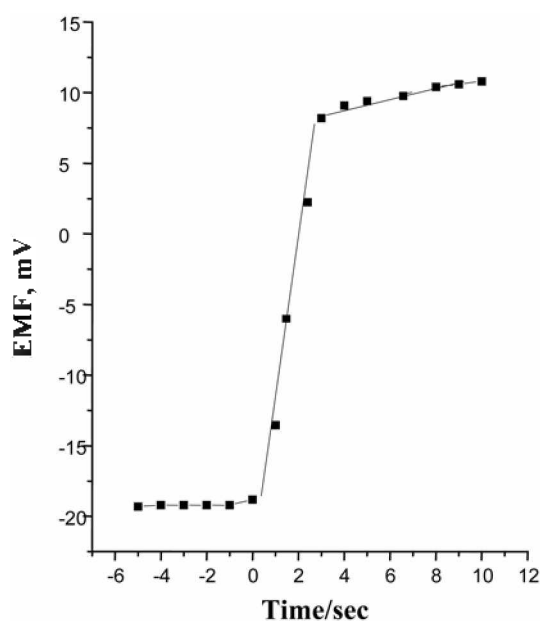


Figure 6. Response-time profile of Pb^{2+} ion-selective electrode based on ionophore **BTPD**.

solvent mediator than others in preparing the Pb^{2+} ISEs. It is noteworthy that the character of plasticizer influences both the dielectric constant of the polymeric membranes and the mobility of an ionophore and its metal complex. The prepared membranes were also examined on the effect of inner reference solution. It was found that the concentration and composition of the internal solution affected on the potentiometric response insignificantly. Thus, 0.1 M KCl as a reference solution is proper for smooth functioning of the membrane system. The optimum equilibration time for the membrane electrode is 24 h, and it generates stable potentials when placed in Pb^{2+} solutions. A potential-time plot in the potentiometric response for the membrane electrode towards lead ion is shown in Figure 6. The static response time of the membrane electrode was less than 5 s for the addition of 9.0×10^{-3} M Pb^{2+} to 1.0×10^{-3} M lead ion solution, indicating that the equilibrium can reach very rapidly. Therefore, the rate of response was only limited by the speed of stirring and the injection technique. Figure 7 shows a titration curve for the response to 100 mL volume of 1.0×10^{-3} M lead concentration by the successive addition of 0.01 M Na_2SO_4 solution. The response time of the electrode was within a few seconds, indicating that the amount of lead ions in

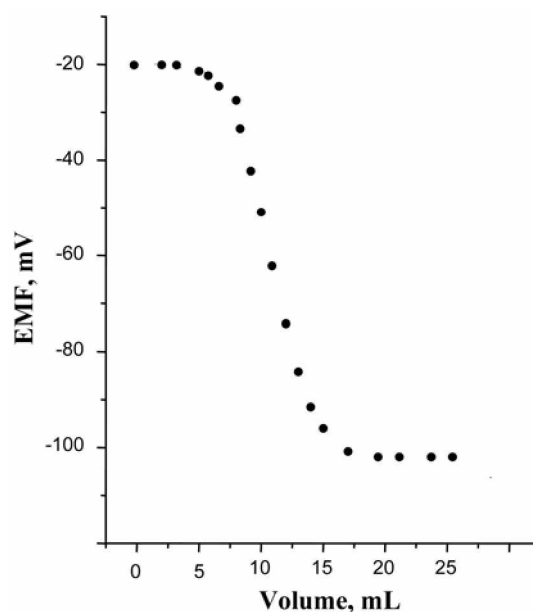


Figure 7. The titration curve for the response to 100 mL volume of 1.0×10^{-3} M lead concentration by the successive addition of 0.01 M Na_2SO_4 solution.

solution can be accurately determined from the resulting neat titration curve providing a good end point. The stability of membrane electrodes was measured as a function of time. The membranes are stored in 0.1 M Tris-HCl pH 7.0 buffer solutions when not in use. The degradation of the sensitivity in the polymeric membrane may be dependent upon the lipophilicity and chemical stability of an ionophore, which 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 ionophore. The stability of these membranes was evidenced in both the slopes of the calibration curve and the detection limits.

Selectivity. The selectivity coefficients of the new membranes are very significant for determining their nature as ISEs. It is well known that the selectivity coefficients represent their response to the species to be measured over other ions present in solution. The selectivity coefficients were evaluated by the separate solution method. The selectivity coefficients towards Pb^{2+} were determined against the interfering cations. The selectivity coefficients ($\log K_{\text{Pb}^{2+},j}^{\text{pot}}$) with respect to the corresponding nitrate of the interfering ion tested are shown in Table 2. From this it can be considered

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

Electrode	Ba^{2+}	Ca^{2+}	Cd^{2+}	Cu^{2+}	Sr^{2+}	Zn^{2+}	Ag^+	Na^+	K^+
Calixphosphine oxide ^a		2.3	5.3	4.3	4.2	4.5	0.2	0.8	2.5
Dibenzyl phosphate ^b		2.3	3.2	4.5		5.2	0.1	3.5	2.8
Piroxicam ^c	2.2	4.0	2.3	1.9	2.3	2.9	0.5	1.4	2.2
Schiff base BSPD ^d	3.1	4.1	3.6	2.7	3.8	4.1	2.2	2.5	2.2
Schiff base BTPD ^e	3.0	4.0	3.5	3.1	3.6	3.8	2.6	3.0	3.0

^aref [40], ^bref [39], ^cref [34], ^dref [19], ^ethis work (by SSM)

that N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine as an ionophore employed is selective towards lead ion against all interfering ions tested. Among membranes tested, the best response was obtained from m-3 membrane. As can be seen, the selectivity coefficients are in the order of 10^{-2} or smaller for all diverse ions tested, indicating they would not significantly disturb the functioning of the Pb^{2+} selective electrode. It should be noted that Cu^{2+} provides negligible interference with $[log K_{Pb^{2+}, Cu^{2+}}^{pot} = -3.1]$ for the determination of lead ion. Thus, it is clear that the membrane electrode has good selectivity over monovalent and divalent cations tested. Meanwhile, the effect of counter anions was investigated using the lead salts of chloride and nitrate, indicating that no significant changes in the working concentration range and slope were observed. Examination of the selectivity data for the membranes used in this work gives that the complex formation constant between ionophore and metal ion, the three-dimensional structure, and the lipophilicity of ionophores are the major aspects determining the selectivity, and the other aspect determining it is also the composition of the membrane electrodes. In this work, the geometrical structure and cavity size of N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine as an ion carrier, and the formation constant of BTPD with lead ion seem to be typical aspects for determining a selectivity of lead ion relative to others. Based on the data of m-3 in Table 1 and 2, the good sensitivity and selectivity towards lead ion are attributed to the strong complexation of lead ion to N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine which has geometrically the proper cavity to coordinate to the ligand.

Conclusions

The membrane electrode incorporating N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine as an ion carrier can be used in the development of a lead ion-selective electrode. Among membranes tested, polymeric membrane m-3 based on BTPD with *o*-NPOE and lipophilic additive of 50 mol% displays a good Nernstian response (29.59 mV/decade) to Pb^{2+} and the limit of detection of $-\log a(M) = 5.74$. Most of metal ions would not disturb the selectivity of the lead electrode severely. It can be concluded that the PVC membrane electrode has a rapid and good sensitivity, and outstanding selectivity towards lead ion over other interfering metal ions.

Acknowledgments. This work was supported by Korea Research Foundation Grant (KRF-2002-070-C00066).

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