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A lead(II)-selective PVC membrane based on a Schiff base complex of *N*,*N*'-bis(salicylidene)-2,6-pyridinediamine

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Abstract

PVC membrane electrodes for lead ion based on *N*,*N*'-bis(salicylidene)-2,6-pyridinediamine as membrane carrier were prepared. Among their membranes, a membrane electrode (m-3) containing *o*-NPOE as a plasticizer and 50 mol% additive displays an excellent Nernstian response (29.4 mV/decade) and the limit of detection of $-\log a$ (M) = 6.04 to Pb^{2+} in $Pb(NO_3)_2$ solutions at room temperature. It has a rapid response time within 10 s over the entire concentration range. The proposed electrode revealed good selectivity and response for Pb^{2+} over a wide variety of other metal ions in a pH 5.0 buffer solutions, and good reproducibility of base line in subsequent measurements.

Keywords: Polymeric membrane; Lead ion; Ion-selective electrode; *N*,*N*'-Bis(salicylidene)-2,6-pyridinediamine; Schiff base

1. Introduction

The ion-selective electrode(ISE) dynamic response is generated by selective complexation of the target ion by ion carrier dispersed in a poly(vinyl chloride) (PVC) matrix. The ISEs based on polymeric membranes incorporated with ionophores are well-known as very useful tools for clinical, chemical and environmental analysis. Until now, a large number of ionophores with high selectivity for specific metal ions have been developed for the potentiometric sensors for the determination of the respective metal ions. The ISEs for determining lead ion have received much interest, and many ligands have been studied as sensing ionophores [1–4]. Piroxicam, quinaldic acid, capric acid, diaza-crown, dibenzyl phosphate, benzyl sulfide, acyclic diamide, anthraquinone, calix-azo, calix-phosphine oxides, thiacrown5,5′-dithiobis-2-nitrobenzoic acid, crown-ethers, porphyrin as ionophores were used for lead-ISEs [5–20]. Potentiometric sensors comprising 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 transition metal ions, and they act as ion carriers in the polymeric membrane. Almost all metals form 1:1 metal complexes with SBs. The feature of SBs give geometric and cavity control of host–guest complexation and modulation of its lipophilicity, and produce remarkable selectivity, sensitivity and stability for a specific ion. The resulting SB complexes have attracted increasing attention in the area of ionic binding due to their unique properties and reactivity. Recently, a few studies were reported about their complex formation equilibria in solution [21,22] and also about the use of SBs as cation carriers in ion-selective electrodes (ISEs) for determining cations such as copper(II) [23–31], aluminium(III) [32], mercury(II) [33], nickel(II) [34], silver(I) [35–37], gadolinium(III) [38], cobalt(II) [39], yttrium(III) [40]. It was also reported that lead(II) forms a strong complex with *N*,*N*'-bis(5-methyl salicylidene)-*p*-diphenylene methane diamine and bis(acetylacetone)-*p*-phenylenediamine[41,42]. These ligands formed selective complex with lead(II) ions than another metal ions. In the present study, we describe the fabrication and characterization of new ISEs based on *N*,*N*'-bis(salicylidene)-2,6-pyridinediamine as SB ionophore. The coordinating effect for the selective response of lead ion was

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investigated by using PVC membrane. 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(salicylidene)-2,6-pyridinediamine exhibits good sensitivity and selectivity towards lead ion.

2. Experimental

2.1. Reagents

N,*N*’-Bis(salicylidene)-2,6-pyridinediamine (BSPD) tested as a carrier of lead ion was synthesized according to the similar procedure described previously [43]. A solution of 0.1 mol 2,6-pyridinediamine was slowly added to 0.2 mol salicylaldehyde in ethanol under nitrogen atmosphere. After 3 h 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, ^{1}H NMR($CDCl_3$): 6.8–7.4 (ArH), 8.6 (CH=N), 13.0 (C–OH). BSPD is shown in Fig. 1. High molecular weight PVC, 2-nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS), potassium tetrakis(*p*-chlorophenyl)borate (KT*p*ClPB) 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 P_2O_5. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions.

2.2. Preparation of polymeric ion-selective electrodes

The typical composition of PVC-based lead-selective electrodes was 33 mg PVC, 66 mg plasticizer, 1 mg ionophore, 50 mol% additive. Table 1 summarizes the compositions of the lead-selective membranes tested in this study. 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 h at room temperature.

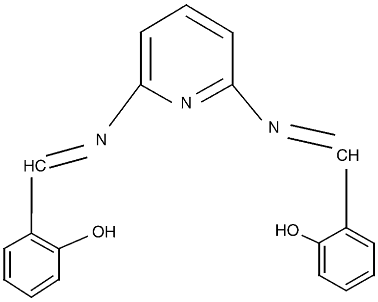

Fig. 1. *N*,*N*’-Bis(salicylidene)-2,6-pyridinediamine (BSPD) as lead ionophore used in this study.

2.3. 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 were used as an internal filling solution. The electrode was finally conditioned for 48 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 25 ± 1 °C 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 5.0 buffer solution (0.1 M Tris–HCl). The use of buffer solution is necessary to prevent pH deviation and pH 5.0 solution of 0.1M Tris–HCl among tested pHs is most proper in this system. The selectivity coefficients ($\log K^{\text{pot}}_{\text{Pb}^{2+},j}$) were determined by the matched potential method (MPM) 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 Pb^{2+}. At least five-time measurements were performed, and the data were determined from the plot.

3. Results and discussion

3.1. Potentiometric response

Schiff bases as ligands seem to be a potential ionophore for soft heavy metal ions in the PVC membrane electrodes, because of its excellent metal-binding properties, rapid exchange kinetics, and water insoluble[26–28]. *N*,*N*’-Bis(salicylidene)-2,6-pyridinediamine was used as an ionophore for preparing PVC membrane ion-selective electrodes for a wide variety of metal ions. Table 1 shows the compositions of ionophore, plasticizer, additive and PVC. The pH dependence on the potentiometric response of the novel membrane electrodes (m-1 and m-3) is studied in a variety of pH solutions, and shown in Fig. 2. The results indicate that the potentiometric response for m-1 electrode depends on the solution pHs employed, but the potential obtained from