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A Lead (II)-selective PVC membrane electrode based on Chloro (bis(salicyliclenimine-phenyl)disulphide)(CSPDS)

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ABSTRACT

A PVC based membrane electrode for lead ion based on Chloro(bis(salicyliclenimine-phenyl)disulphide) (CSPDS) as a membrane carrier was prepared. The influence of membrane composition, pH of the test solution and foreign ion on the electrode performance were investigated. The electrode show the Nernestian response of 29,4 over a concentration range of 1×10^{-8} to1×10^{-2} and was found to be very selective ,précis e and usable within pH range of 4-6.The electrode was successfully used as an indicator in potentiometric titration of lead ions and its direct determination in water samples.

Key words: Lead ion selective electrode, CSPDS, Potentiometry, PVC based membrane.

1. INTRODUCTION

Over the years, the importance of controlling the level of environmental pollutants in natural waterways and potable water has generated increased interest in the development of noval sensors for the detection of heavy metals. Lead is one of the heavy elements, which is almost present in the different industrial waste effluents. Many industries such as lead glasses [1] and optical sensors [2] use lead salts as main components. It is also considered as one of the radionuclides that present in the radioactive waste solution.

This work is decided to introduce an ion selective electrode (ISE) for accurate and precise quantitative analysis of lead ions and many ligands have been investigated as a sensing agent in electrode based on ionophore – doped poly(vinyl chloride) (PVC) membrane. A lead ISE finds applications to the electroplating industry [3], the environmental monitoring and waste water analysis [4] and to the detection of some anion like amide, sulphide [5] etc. The use of complexing agents offers the possibility of designing ligands with a wide range of functional groups and, consequently, different abilities to form complexes. Several neutral compounds with oxygen, nitrogen and sulphur donor atoms have been examined as ionophores for lead selective electrodes [6-8]. Acyclic amide and oxamides have also been investigated as potential ionophore for lead [9-10]. Sheen and Shih [11] have reported the use of crown ethers as lead selective agents. Kamata and Onoyama [12-13] used acyclic dithiocarbamate as ionophore as lead ISE's.

In this paper, we use Chloro (bis(salicyliclenimine-phenyl)disulphide)(CSPDS) as an excellent neutral carrier in the construction of a lead PVC membrane electrode. It exhibits significantly high sensitivity, stability, and selectivity for Pb^{2+} over many common metal ions and was successfully applied to the direct determination of lead in real samples. Also, it was used for the potentiometric determination of lead ions in solution.

2. EXPERIMENTAL

2.1. Reagents

The chemicals used are of analytical grade and used without any further purification. Triply distilled water was used throughout. High molecular weight polyvinyl chloride powder (PVC) was purchased from Sigma Aldrich. Reagents like 2- nitrophenyl octyl ether (o-NPOE) and sodium tetraphenyl borate (NaTPB) were also brought from merck and dibutyl phthalate ,dioctyl phthalate was from Reidel (India). Glyoxal was obtained from CDH.

2.2. Synthesis of electroactive material

The ligand was formed by adding 0.02mole of salicyladehyde to a methanol solution containing 0.02 mole of 2,2'diaminodiphenyldisulphide. The solution was heated to boiling point and it was filtered while hot. Finally on cooling the filtrate produced a colorless solid which was separated from the solution by filtration [14].

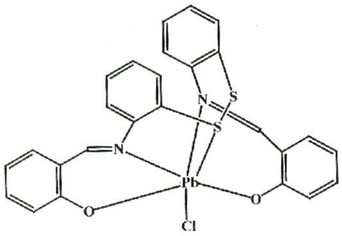

Figure – 1: Structure of Chloro (bis(salicyliclenimine-phenyl)disulphide)lead (II).

2.3. Electrode preparation

The solution of PVC membrane was prepared by thorough mixing of ionophore (Schiff base ligand) (0.5 %.), NPOE (66%) and PVC (33.5%) and STPB (5%) in THF. The resulting solution was poured into a glass mould and THF was allowed to evaporate off at room temperature for 24 h. A flexible membrane of the thickness of 0.2-0.4 mm was obtained. The disc of 6 mm diameter was cut and pasted onto the glass tube with PVC glue and conditioned with AgNO3 solution of 0.01M for 2-3 days. The ratio of member constituents, time of contact and concentration of equilibrating solution were properly adjusted to obtain the best potential response [15].

2.4. Potential measurements

The membrane was equilibrated with a 1×10^{-3}M $Pb(NO_3)_2$ solution for 3 days and the potential across the membrane was measured by setting up the following cell assembly.

External 1 × 10-3 mol/L $Pb(NO_3)_2$/ PVC/ Test Internal SCE Membrane Solution.

All the potential measurements were made by using a digital pH meter, potentiometer in conjunction with SCE as reference electrode.

2.5. Determination of lead in soil sample

0.1g of soil sample was digested with a mixture of 100ml of conc. HCl and 10ml of conc. HNO_3.The residue was evaporated with 50ml of conc, HCl to dryness. Then 20ml of 0.1N HCl was added and centrifuged. The aqueous layer was transferred into 100ml of volumetric flask and dilute with 0.1N HCl to the mark [16].

3. RESULT AND DISCUSSION

Macrocyclic ligands seem to be a potential ionophore for soft heavy metal ions in PVC membrane electrode because of its excellent metal binding properties and water insoluble nature [17-19]. Chloro (bis(salicyliclenimine-phenyl)disulphide) (CSPDS) is used as an ionophore for preparing PVC based electrode. The potential response of various ion selective electrode based on CSPDS as ionophore (in conc.range of 1×10^{-8} to 1×10^{-2}M) is depicted in fig 2.

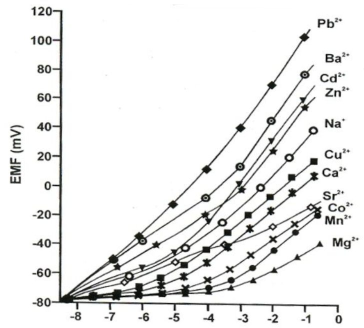

Figure – 2: Potential response of various metal ISE based on CSPDS as ionophore.

It is well known that the sensitivity and selectivity of the ion selective members not only depend upon nature of ionophore used, but also on membrane composition and properties of plasticizer and additive used [20-25]. Several membranes of different compositions were prepared. The ratios of PVC, ionophore and plasticizers were varied18. Some of the results of this study are summarized in table 1. The membrane composition which is suitable with regard to Nernstian's slope (29.4) was found to contain 33mg PVC, 1mg CSPDS as ionophore, 66% NPOE as plasticizer and 50mol% of additive NaTPB .The limit of detection is -6.04.

Table - 1: The potentiometric characteristic of the lead selective electrode in ph 5.0 buffer solution

Membrane	Ionophore	PVC	o-NPOE	DOP	DBP	NaTBP	LOD	Slope
a	1	33	66			0	-384	22.8
b	1	33	66			20	-5.81	29.3
c	1	33	66			50	-6.04	29.4
d	1	33	66			100	-5.80	13.3
e	1	33		66		50	-5.22	28.8
f	1	33			66	50	-4.06	28.0
g	1	33				50	-4.17	31.7

The effect of plasticizer on Pb^{2+} ISE membrane electrode based on CSPDS is shown in Fig 3. From Table 1 and Fig 3 it is predicted that *o*-NPOE is a better solvent mediator than other in preparing the Pb^{2+} -ISE. Lipophilicity of plasticizer influences both the dielectric constant of the polymer membrane and mobility of the ionophore and its metal complexes.

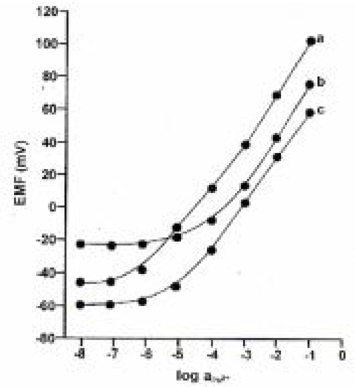

Figure - 3: Lead ion response of the membrane prepared by the different plasticizer with CSPDS : (a)o-NPOE (b)DOP (c) DBP

The pH dependence of the potential of the electrode for 1.0×10^{-3}M (b) and 1.0×10^{-4}M (c) was tested over the pH range 2-10 and result are depicted in fig 4. The potential response for both the concentration remain almost constant over the pH range 4-6,beyond which a gradual change in pH was observed. The observed drift at higher pH value was due to formation of some hydroxyl ions (such as $Pb(OH)^+$ or $Pb(OH)_2$)in Pb^{2+} ion in solution [26]. Therefore, the PVC polymeric Pb^{2+} -ISE's based on CSPDS was considered best for solution at pH 5.0 and utilized for further investigation.

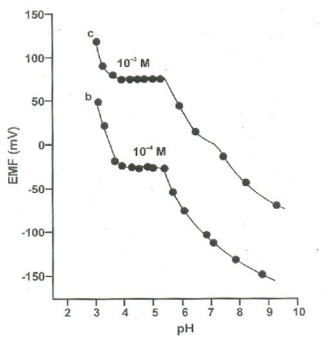

Figure – 4: Effect of pH on potentiometric response of two lead membrane electrodes (b & c).

The potential response of Pb^{2+} was obtained when membrane was stored in 0.1 M $Pb(NO_3)$ solution at a pH 5.0 by adding dilute HNO_3 or standard buffer solution. Membrane containing microcyclic compounds with high lypophilicity, such as, CSPDS, provides slow bleeding of ionophore. After 12 weeks, electrode with membrane 'c' was responding with the limit of 95%of initial response. This is shown in Fig 4. Membrane work satisfactorily in partial non aqueous medium upto maximum 15% contents of methanol or ethanol. Sensor become less sensitive to Pb^{2+} ion if the conc. It's increased beyond 15%.

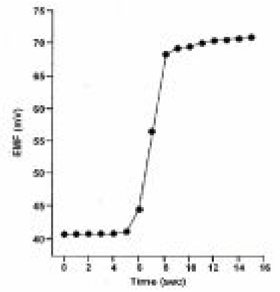

Figure – 5: Response of Pb2+ ion selective c-PVC Membrane Electrode at different time interval.

Table – 2: Selectivity coefficient values of Pb^{2+} Selective (CSPDS)-PVC Membrane electrode at different cations.

METAL IONS	SELECTIVITY COEFFICIENT VALUE(Kij)
Ca^{2+}	8.3×10^{-3}
Mg^{2+}	8.3×10^{-3}
Sr^{2+}	1.3×10^{-3}
Ba^{2+}	5.0×10^{-2}
Co^{2+}	2.7×10^{-3}
Cu^{2+}	28.4×10^{-3}
Cd^{2+}	50.0×10^{-3}
Zn^{2+}	38.0×10^{-3}
Na^{+}	16.3×10^{-3}
Mn^{2+}	$2.78 \times 10^{2-}$

The most important characteristic of membrane sensor is its response for the primary ion in presence of the other ion. This is determined by selectivity coefficient which is evaluated by match potential method [27-29]. Table 2 shows the different selectivity coefficient values for the various foreign ions .since all the selectivity coefficients are in 10^{-3} range, this indicates that foreign ions would not significantly disturb the functioning of lead selective electrode. Examination of data indicates that the extent of complex formation between the ionophore and metal ion, the geometrical structure and rigidity of ionophore are the major factor for determining the selectivity. The resuts also show that other factor for selectivity is geometry and ligating cavity of CSPDS. Good sensitivity and high selectivity is due to geometrically proper cavity of CSPDS to coordinate with the ligand Pb^{2+}.

Proposed sensors were also used as an indicator electrode in titration with Pb^{2+} with 1×10^{-2} M EDTA. Analytical applications of Pb^{2+} were sound to work well under laboratory conditions. The electrode was successfully applied to lead samples from lead acid bath, taken from many lead electroplating factories. Lead contents in samples, estimated by this proposed ISE was in close agreement with the AAS data.

4. CONCLUSION

According to the obtained results in the present work, the proposed electrode is easy to be prepared and used. It has good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range). This electrode can be used for determination of lead ion concentration in potentiometric titrations and real samples.

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