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Fabrication and Characterization of Phthalic acid Sensor for Detection of Lead(II) ion

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Abstract

Lead(II) ion sensor has been fabricated by using phthalic acid as ionophore and acetophenone as plasticizer. The functional parameters (slope and selectivity) of the sensor membrane with composition: (Ionophore:PVC:Plasticizer) in different ratio was investigated in liquid contact mode. Sensor was characterized by direct potentiometry, pH effect, potentiometric titration and selectivity coefficient. Selectivity coefficient was studied by matched potential method(MPM). Thus prepared sensor membrane showed Nernstian behavior with slope 30.05 mV per decade in the concentration range 10^{-1} to 10^{-4}M and response time was 35 second.

Keywords:*ISE, liquid contact, MPM, phthalic acid, sensor*

Introduction

Heavy metals are found in the earth's crust and expose in environment as a consequence of human activities. Heavy metals can be dangerous leading to a damage of human health, because they are non-biodegradable and can be accumulated in living tissues. Therefore, determination of trace levels of heavy metals is very critical for environmental protection, food and agricultural chemistry[1,2]. Lead (Pb), is a non-physiological metal which is expose to most of the general human population and cause clinical effects of toxicity. It has been demonstrated that it is accumulated in bone and in some soft tissues, such as liver, kidney and brain[3-6]. Though there are various methods for determination of heavy metals but the quick determination of minute quantities of ionic species by simple methods has a great importance in analytical chemistry[7-12].

Potentiometric detection based on ion selective electrodes is the simplest method. Simple design and operation, reasonable selectivity, fast response, applicability to colored and turbid solution and low cost are some of the advantages of this method. Due to such advantages this work is based for fabrication of lead ion sensor membrane. An ion selective electrode of a cell is an electrode in which the potential depends in the activity of a particular ionic species which it is desired to quantify. According to Nernst equation(1)

$$E_{cell} = E_0 \pm (RT/nF) \ln a_x \quad .....(1)$$

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Where, a_x is the activity of the determinant ion X, E_0 is the standard potential of the cell, and n is the number of charges on X. The sign in equation (1) is positive when X is a cation and negative when it is an anion[13-15].

Experimental Methods

Fabrication of membrane:

The sensor membrane was fabricated in laboratory by using phthalic acid as ionophore. For preparing the sensor membrane, a glass tube of 39 and 42 mm inner and outer diameter and height 58 mm was taken and was fixed on a flat glass surface with epoxy resin. The homogeneous mixture of phthalic acid as ionophore, PVC and acetophenone as a plasticizer in THF was poured inside the hollow glass tube. Mixture was solidified in controlled evaporation for 24 hours. Solidified form of thin film is known as sensor membrane.

Working electrode preparation and response study

All sample solutions were prepared by using chemical of research grade. Ag/AgCl electrode was prepared which and connected with liquid junction with sensor membrane(working electrode).Working electrode was now dipped in test solutions of different concentrations.With the help of calomel as reference electrode, potential of that solution was measured. Similar process was repeated for all solutions. In the similar way potentiometric titration, interference study, dynamic response and the effect of pH was also studied.

Results and Discussion

Direct potentiometric study:

Direct potentiometry was studied for this seonsor electrode. It is reported that addition of $NaNO_3$ in determinant solution has positive effect for solid state ion selective electrode[2]. In ionophore based on ion selective electrode addition of sodium nitrate does not have any effect but addition of ascorbic acid gives significant effect. Ascorbic acid controls the oxidation of metal ion and helps to detect the metal ion easily. The detection limit for membrane electrode is 10^{-4}M with Nernstian slope 30.05 mV per decade. The slope is too good but the detection limit is not improved. This shows electrode can detect metal ions up to 10^{-4}M concentration and below than this limit it cannot be used.

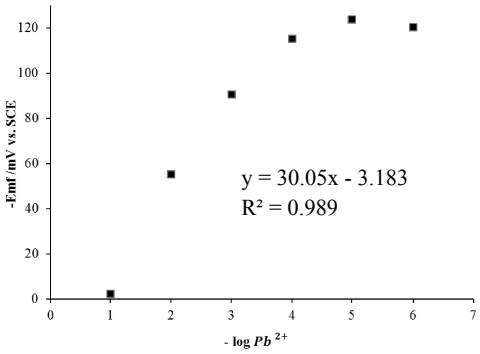

Figure 1: *Emf measurement of working electrode in mixture of $Pb(NO_3)_2$ and ascorbic acid.*

Effect of pH on Sensor Membrane

Calibration of the pH meter was done by using the buffer solutions of the pH 4, 7 & 9.2. After the calibration of the pH meter it was ready to use and then solution was tested. To study the effect of pH in the potential, solutions of different pH were used. pH of the solution was varied by using solutions of acid and base. The potential of two solutions (strengths of 10^{-2}M and 10^{-4}M) was measured from pH 1 to 11.

The potential response of sensor membrane is independent in pH range 3.0 to 8.0, and potential changes considerably in other pH. The increased potential in acidic medium indicates that there is effect of proton in membrane. The observed decrease in potential at basic medium could be due to the formation of insoluble $Pb(OH)_2$ on the membrane surface. This protonation and formation precipitation on solution, limits the use of this electrode in certain range of pH.

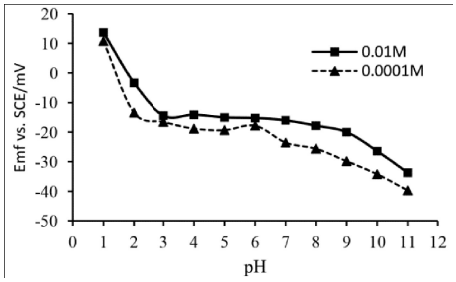

Figure 2: *Potential vs. pH for working electrode electrode.*

Dynamic Response

For the study of dynamic response of the sensor electrode, the potential of standard $Pb(NO_3)_2$ solution of 10^{-4}M concentration was measured for 2.30 min in each 5/5 sec of time interval. Similarly, potential of concentrated solution was measured. For working electrode dynamic response was studied by taking 10^{-4}M and 10^{-2}M lead nitrate solutions and potential stability with respect to time was observed. This electrode attained equilibrium potential within 35 sec from immersion time. The rapid response of the electrode is due to preconditioning of the sensor membrane in 1mM lead nitrate solution.

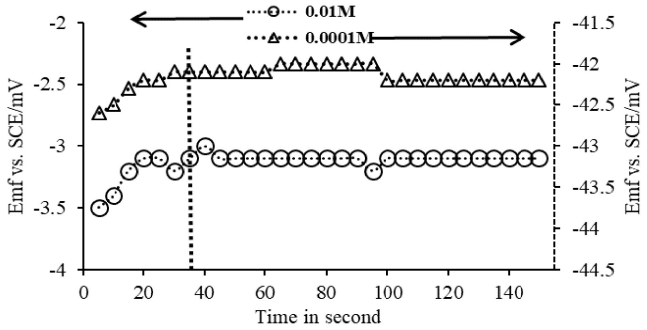

Figure 3: *Dynamic response of working electrode in two different solutions of 10^{-2}M and 10^{-4}M lead nitrate.*

Potentiometric Titration

Potentiometric titration of the test solution was carried out by using ISE as indictor electrode. Potential was recorded on each addition of 0.5 mL EDTA solution from burette to test solution. On addition of EDTA solution, the lead ion forms complex with EDTA and the concentration of lead ion decreases resulting the decrease in Emf of the solution. At equivalence point the Emf is changed drastically/significantly due to change of all lead ions in lead-EDTA complex. Further addition of EDTA doesn't changes potential as the ISE is not selective towards EDTA.

This shows that at equivalence point the Emf of the solution is changed significantly on addition of 4.5 mL of EDTA solution in 10^{-3}M lead nitrate.

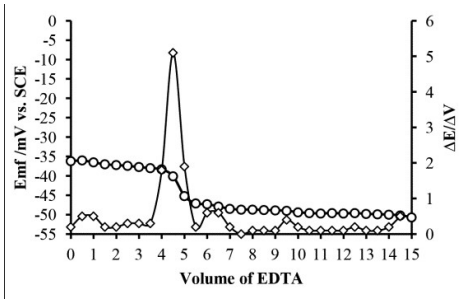

Figure 4: *Potentiometric titration of 10^{-3}M lead nitrate with EDTA solution.*

Selectivity Coefficient

There are number of methods for the measurement of potentiometric selectivity coefficients of ion selective electrodes. Among all, MPM is more convenient and reliable[16-18]; and this method is followed in this work.

For this method the selectivity coefficient is related as,

$$K^{pot}_{A,B} = \Delta A/B$$

Where, ΔA is change in potential between two solutions of different concentration. B is the concentration of interference ion.

This effect is studied for working electrode in interfering ions like Cd^{++}, Cu^{++}, Ni^{++}, Ag^{+}, NH_4^{+}, Co^{++} etc by using their respective salts like $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $AgNO_3$, NH_4NO_3, $Co(NO_3)_2$ in the form of solution(table 1). For interference study, 0.001M solutions of the nitrate salts of the mentioned cations are taken and added in 10^{-4}M lead nitrate solution and the change in potential as well as the added volume of solution containing interfering ion is noted for calculation.

Table 1: Selectivity coefficient for working electrode.

Interfering ions	$\log K^{pot}_{A,B} = \log(\Delta A/B)$
Ni^{2+}	3.07
Cd^{2+}	2.50
Cu^{2+}	2.44
Ag^{+}	2.18
Co^{2+}	2.08
NH_4^{+}	2.00

Though the result shows interference by other ions but these results are not overly surprising, since similar findings are reported earlier in cadmium ion selective electrode[19] and lead ion selective electrode[20] by E. Bakker.

Conclusions

Lead ion sensor is fabricated in laboratory in this research by simple method using PVC plasticizing membrane and phthalic acid. The liquid contact in the working electrode is made by using 0.1M lead nitrate solution. This electrode fabricated in laboratory is found to be well behaved and the selectivity coefficients for the electrode is found to be as expected.

The working electrode gives Nernstian slope of 30.05 mV with detection limit 10^{-4}M. Thus, constructed lead ion sensor in our laboratory performs Nernstian behavior, fast respond and of expected selectivity. This is applicable for the detection of lead ion in water as well soil samples, due to its applicable detection limit.

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