Pb(II) sensor based on the membrane of 3,4,4a,5-tetrahydro-3-methylpyrimido-[1,6-a] benzimidazole-1 (2H) thione in PVC matrix

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3,4,4a,5-Tetrahydro-3-methylpyrimido [1,6-a] benzimidazole-1 (2H) thione (TMPB) has been synthesized and investigated as electroactive phase of membranes for use as Pb2+ selective electrode. PVC based membranes of TMPB have been prepared without plasticizer and with a number of plasticizers and investigated. Of the various plasticizers used, tris (2-ethylhexyl)phosphate (TEP) has been found to improve the performance of the membrane significantly. The membrane having the composition of TMPB:PVC:TEP as 1:40:10 has been found to perform best. The electrode having such a membrane responds linearly to Pb2+ over a wide concentration range, 1.9×10−5–1.0×10−1 M, with a slope of 28.5 mV/decade of concentration and small response time of 20 s. The electrode can work over a pH range of 2 to 5.7 and also in partially non-aqueous media. Selectivity coefficient values revealed that the electrode is sufficiently selective over a large number of mono, bi- and trivalent metal cations. It is found to have a life time of one month and could also be used as indicator electrode in the potentiometric titration of Pb2+ with EDTA.

Lead is one of the most toxic metals and causes brain damage, nephropathy, sluggishness, hyperirritability, restlessness, loss of skin colour and appetite. In spite of these harmful effects of lead, it is used in various industries such as storage batteries, gasoline, cable manufacture, paint industry and ammunition which leads to its widespread occurrence in the environment. In view of the toxicity of the metal, its determination is important. Some of the methods used for lead determination are spectrophotometry12, fluorimetry13, polarography14, atomic absorption spectrometry5 and HPLC6. These methods give accurate results but are not very convenient for large scale monitoring and require good infrastructure back up. For such monitoring, as is the case for environmental analysis, ion selective electrodes if available, are being increasingly used as they permit quick, convenient and low cost procedure. Thus, during the last three decades intensive efforts have been made to develop good electrodes systems for Pb (II) determination. A number of heterogeneous Pb2+ ion selective electrodes based on PbS-Ag2S-CuS, PbSe-Ag2S and PbS-Ag2S79 as electro active phase have been reported but not found very satisfactory as transition metals such as Cu2+, Cd2+, Ag+ and Hg2+ cause significant interference. Later on, attempts have been made to prepare improved electrodes having organic compounds as electroactive phase and the electrodes based on the membranes of polyhydroxamic acid10, piroxicam11, crown compounds12-14, derivatives of 9,10-anthraquinone15 and quinaldic acid16, perform better as compared to sulphide electrodes in respect of selectivity, working concentration range and response time. However, even these electrodes show interferences to a number of metal ions and determine Pb2+ in a limited pH range. Efforts are still continuing to have a much better Pb2+ selective electrode. We have, therefore, attempted to explore a PVC based membrane of a derivative of pyrimidobenzimidazole as Pb2+ ion sensor and the results obtained are presented in this communication.

Materials and Methods

All reagents were of analytical grade and used without further purification. High molecular weight poly vinyl chloride (PVC), Aldrich; dibutyl phthalate (DBP), Reidel and dioctyl phthalate (DOP), GSC India; dibutyl butyl phoshonate (DBBP), Mobile, USA; 1-chloro naphthalene (1-CN), tris-n-butyl phosphate (TBP), tris (2-ethylhexyl)phosphate (TEP) from Merck (Germany) were used. Metal salt solutions of their respective nitrates were prepared in double distilled water. Solutions of different
concentration were made by diluting 0.1 mol/l stock solution.

Preparation of membrane electrodes
The PVC based membranes of TMPB were prepared by the method of Craggs et al. Varying amounts of the ion active phase (TMPB) and an appropriate amount of PVC were dissolved in 20 ml THF. Plasticizers DBP, I-CN, DBBP, TEP, DOP were added in order to improve the response of the membranes. The solution thus obtained, after complete dissolution of the various components, was poured into acrylic rings placed on a smooth glass plate and allowed to evaporate at room temperature. After 24 h, transparent membranes of 0.5 mm thickness were obtained. From these membrane, circular pieces of 5.0 mm diameter were cut out and glued to one end of the ‘Pyrex’ glass tube with Araldite. Membranes of different compositions were prepared and studied. The composition of the membranes was optimized and the only membranes producing reproducible and stable potentials were selected. The composition of such membranes is indicated in Table 1.

Membrane potential measurements
The membranes attached to the Pyrex tubes were equilibrated in 0.5 M Pb²⁺ solution for 3 days. To investigate the potential response of the membrane electrode, the following cell was set up and its potential determined.

<table>
<thead>
<tr>
<th>Internal Reference Electrode (SCE)</th>
<th>Internal solution 0.1 M Pb(NO₃)₂</th>
<th>Membrane</th>
<th>Test solution External reference electrode (SCE)</th>
</tr>
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Results and Discussion
Working concentration range and slope
The potential response of the cell set up with different membrane electrodes was studied in the concentration range 1.0 x 10⁻⁶-1.0 x 10⁻¹ M of Pb²⁺ and the results obtained are shown in Fig.1 and Table 1. It is seen that for membrane electrode 1, the linear response of potential is obtained in the concentration range 4.0 x 10⁻⁵-1.0 x 10⁻¹ M. This linear response range is normally called working concentration range of the electrode. This electrode has a slope of 24.0 mV/decade of concentration and response time of 40 sec. The electrodes having membranes with plasticizers show response different from electrode 1 having membrane without plasticizer. For example the effect of addition of I-CN, DBBP and DBP to the membrane (electrode nos. 2-4) is to decrease the working concentration range to 3.2 x 10⁻⁵-1.0 x 10⁻¹ M, 4.5 x 10⁻⁵-1.0 x 10⁻¹ M and 1.6 x 10⁻⁵-1.0 x 10⁻¹ M respectively. The slope of electrodes 2 and 4 remains non-Nernstian but of electrode no. 3 is Nernstian and the response time is slightly increased compared to electrode 1. On the
other hand the working concentration range is increased to $2.6 \times 10^{-2}$-1.0x10$^3 M$ and $1.9 \times 10^{-3}$-1.0x10$^3 M$ with the addition of DOP and TEP (electrodes 5 and 6), respectively. Thus these two electrodes can determine Pb$^{2+}$ over a wider concentration range compared to electrode 1 and are, therefore, considered better. Of these two electrodes, the electrode no.6 with membrane having TEP as plasticizer is considered best because it has wider concentration range $1.9 \times 10^{-3}$-1.0x10$^3 M$, Nernstian slope (28.5mV/decade of concentration) and smallest response time. This electrode generates stable and reproducible potential with standard deviation of 0.2mV. The electrode could be used over a period of one month without any significant drift in potential. However, when not in use, it was stored in 0.1M Pb$^{2+}$ solution. In view of better performance of electrode no 6, all further studies were done with this system only.

**Effect of pH and non-aqueous medium**

The performance of the electrode has been tested over pH range 2.0 to 7.0 at 1.0x10$^3 M$. The potential response is shown in Fig. 2. It is seen that potential remains constant over a pH range of 2.0 to 5.7 and therefore it can be taken as useful working pH range of the electrode. The deviation in potential at lower pH can be ascribed to H$^+$ co-exfluxing and at pH values above 5.7 to hydrolysis of Pb$^{2+}$. The functioning of the electrode was also investigated in partially non-aqueous media using methanol-water, ethanol-water and acetone-water mixture and the results are presented in Table 2. It is seen from Table 2 that up to 15% non-aqueous content of methanol, ethanol and 10% acetone in water mixture, the slope and the working concentration range are only slightly decreased. Therefore the electrode can be used for the determination of Pb$^{2+}$ in these mixtures having 15% methanol, ethanol and up to 10% acetone. The higher non-aqueous content reduces the slope and working concentration range significantly which affects the utility of the electrode.

**Potentiometric selectivity**

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of foreign ions. It is discussed in terms of selectivity coefficient values which are determined by various methods$^{22}$. The potentiometric selectivity coefficients of the electrode were determined by IUPAC recommended Fixed Interference Method$^{23}$ at 1x10$^2 M$ concentration of the interfering ions and are given in Table 3. A value of 1.0 of selectivity coefficient shows equal response to primary as well as interfering ion whereas the value less than 1.0 indicates that the electrode is more selective to primary ion as compared to interfering. It is seen from Table 3 that the selectivity coefficients are smaller than 1.0 and therefore sensor prepared is selective to Pb$^{2+}$ over all these ions listed in Table 3. Thus this electrode can be used to determine Pb$^{2+}$ in presence of
Table 3—Selectivity coefficients for Pb²⁺ selective electrode (No.6) for various Interfering ions using fixed interference method

<table>
<thead>
<tr>
<th>Interfering Ion B</th>
<th>Selectivity coefficient (K_{\text{Pb}^+}^B)</th>
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<tbody>
<tr>
<td>K⁺</td>
<td>7.1×10⁻²</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>2.5×10⁻²</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1.8×10⁻²</td>
</tr>
<tr>
<td>Na⁺</td>
<td>3.2×10⁻²</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.6×10⁻²</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>6.3×10⁻²</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>3.2×10⁻²</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>3.1×10⁻²</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>1.7×10⁻²</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>2.2×10⁻²</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>1.9×10⁻¹</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>4.5×10⁻²</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>1.3×10⁻²</td>
</tr>
<tr>
<td>Bi³⁺</td>
<td>3.9×10⁻²</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>6.3×10⁻²</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>2.8×10⁻²</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>2.5×10⁻²</td>
</tr>
</tbody>
</table>

these interfering ion in concentration lesser or comparable. However, these ions may start interfering at concentrations much higher than Pb²⁺. In order to assess the concentration level which may cause interference, mixed run studies²⁴,²⁵ were carried out. This was done in case of Cu²⁺ because it has the highest selectivity coefficient and so likely to interfere most at higher concentration levels. The mixed run studies with different concentration of Cu²⁺ were carried out and results are plotted in Fig. 3. These results show that when the concentration of Cu²⁺ is equal or less than 1×10⁻⁵ M, there is no effect on the working concentration of the electrode. Therefore Cu²⁺ in amounts equal or less than 1×10⁻⁵ M can be tolerated over the entire working concentration range. However, at concentrations of Cu²⁺, 1×10⁻⁴ M and 1×10⁻³ M, the potential response shows deviation from that obtained for pure Cu²⁺ solution. This indicates that working concentration range has been reduced due to some interference of Cu²⁺ at these concentration levels. It can be worked out from these mixed run plots that 1×10⁻³ M Cu²⁺ can be tolerated for Pb²⁺ estimation over a reduced concentration range 7.9×10⁻⁷–1.0×10⁻⁴ M and 1×10⁻³ M Cu²⁺ over 4×10⁻⁸–1.0×10⁻⁴ M. The tolerance level of the electrode towards other interfering ion would be better than Cu²⁺ because selectivity coefficients for them are smaller than that for Cu²⁺.

Analytical application

The membrane sensor was also used as indicator electrode for titrating Pb²⁺ with EDTA potentiometrically. 10 ml of 1.0×10⁻⁢M Pb²⁺ solution was titrated with 1.0×10⁻⁶ M EDTA solution. The potentiometric plot obtained was not of conventional type. This may be due to the interference caused by Na⁺ ions and such a behaviour has been observed earlier as well¹⁰. However, the break point of the titration plot is sharp and corresponds to Pb(II)-EDTA complex stoichiometry. Therefore, it can be taken as the end point of the titration and can be used for Pb²⁺ estimation.

This electrode is comparable to the reported electrodes with regard to response time, slope and working concentration range. However, it is superior to them in terms of selectivity. The present electrode is sufficiently selective over a large number of metal ions studied whereas the reported electrodes exhibit serious interference specially to Hg²⁺, Cd²⁺, Fe³⁺, Ni²⁺, K⁺, Ag⁺, Ti³⁺, NH₄⁺ (Refs 10,12,13) and to low pH values¹⁰,12,13,15. Thus the electrode reported shows improved performance in terms of selectivity and in pH range and can be used for Pb²⁺ estimation by direct potentiometry or by potentiometric titration.
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References