Chapter 4

Preparation and Characterization of Poly-o-toluidine Zr(IV) phosphate Composite Cation-Exchanger Based Ion-Selective Membrane Electrode
4.1. INTRODUCTION

Precipitate based ion-selective membrane electrodes are well known as they are successfully employed for the determination of several anions and cations [1]. There are some homogeneous as well as heterogeneous hybrid ion-exchange membranes. Homogeneous ion-exchange membranes are coherent ion-exchanger gels in the shape of disks, ribbons etc. The heterogeneous precipitate ion-exchange membranes consist of suitable colloidal ion-exchanger particles as electroactive materials embedded in a polymer (inert) binder, i.e., poly(vinyl chloride) (PVC) or epoxy resin (Araldite) or polystyrene, polyethylene, nylon, polymethylmethacrylate (PMMA), etc., by physical mixing or chemical reaction and have been extensively studied as potentiometric sensors [2-8]. Ion-exchange membranes also find applications in diverse processes such as electrodialysis, diffusion dialysis, electrodeionization, membrane electrolysis, fuel cells, storage batteries, electro-chemical synthesis etc.

Ion-selective electrodes are one of the important analytical tools, which are used for sensitive and selective determination of various ionic species in the wide range of concentration [9] in environmental, medical and industrial samples [10-12]. Mercury is well-known for its toxicity even in low concentration. Due to its toxicity mercury causes ill effects in human nervous system. Mercury also shows strong affinity for ligands containing S atoms and thus causing the blocking of
sulphydryl groups (-SH) of proteins, enzymes and membranes. Mercury(II) ions are also responsible for the injury of kidney and gastrointestinal track. Due to its serious hazardous effects to human health, there is strong requirement to extend new methods to determine mercury ions in wide variety of samples. Common methods are used to determine mercury such as, voltametry [13], spectrophotometry [14,15], X-ray fluorescence [16], flame and furnace atomic absorption spectrometry [17,18] fluorimetry [19,20], cold vapor atomic absorption spectrometry [21] and inductively coupled plasma [22]. But these methods involve expensive instrumentation and sample pretreatment which is time consuming and inconvenient. On the other hand ion-selective membrane electrodes commonly known as electrochemical sensors are important in view of the ability to make direct or indirect measurement in complex samples without the knowledge about the color of the sample or turbidity. The fact is that the use of ion-selective electrodes for such type of measurements requires relatively inexpensive equipment, which makes ion-selective electrodes attractive to scientist in many disciplines [23]. Thus, potentiometric sensors can offer an inexpensive and convenient method for the analysis of heavy metal ions in solutions provided acceptable sensitivity and selectivity. For this purpose many organic and inorganic compounds were studied as electroactive materials and used in the fabrication of ion-selective membrane electrode [24-32].

Now a days, the use of ‘organic-inorganic’ composite ion-exchange materials formed by the combination of inorganic precipitates and organic polymers as electroactive components in membrane electrodes has generated widespread
interest in developing new ISEs for sensor applications [33-38], especially for the
determination of heavy toxic metals.

The newly developed poly-o-toluidine Zr(IV) phosphate composite cation-
exchange material is highly selective for Hg(II) ions; (as shown in Chapter-3,
Section 3.2.4.6.). The further research work was carried out to obtain new
heterogeneous precipitate based membrane ion-selective electrodes by means of this
composite as electroactive phase for the determination of Hg(II) ions, present in the
solutions. This chapter represents the preparation, characterization and fabrication
of ion-exchange membranes and ion-selective membrane electrode based on the
aforesaid composite material.
4.2. EXPERIMENTAL

4.2.1. Reagents and Instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical reagent grade.

The stock solution of $1 \times 10^{-1}$ M Hg(II) was prepared in double distilled water (DMW). The solution was standardized by complexometric titration [39]. The working standard of Hg(II) solutions ($1 \times 10^{-1}$ M to $1 \times 10^{-9}$ M) were prepared by proper dilution of the stock solution.

A digital pH-meter (Elico LI-10, India), a double beam atomic absorption spectrophotometer (GBC 902, Australia), a digital potentiometer (Equiptronics EQ 609, India; accuracy $\pm 0.1 \ mV$) with a saturated calomel electrode as reference electrode, an electronic balance (digital) – (Sartorius 21 OS, Japan) and a mortar pastel were used.

4.2.2. Preparation of Electroactive Phase: Poly-o-toluidine Zr(IV) phosphate Composite Cation-Exchanger

A number of samples of ‘poly-o-toluidine Zr(IV) phosphate’ composite cation-exchange material was prepared as described in Chapter – 2 (Section 2.2.3.). But the samplies S-5 (Table 2.1) was chosen as electroactive phase for the potentiometric studies.
4.2.3. Preparation of Ion-Exchange Membranes

The ion-exchange membranes were prepared by employing an electroactive ion-exchange material into a polymer binder. For this purpose, electroactive component poly-o-toluidine Zr(IV) phosphate (S-5) composite cation-exchange material was taken to be embedded in polyvinyl chloride (PVC).

4.2.3.1. Preparation of Poly-o-toluidine Zr(IV) phosphate Membrane

The composite cation-exchange membrane was prepared by the adaptation of the method of Coetzee and Benson [40]. The poly-o-toluidine Zr(IV) phosphate cation-exchange material as an electroactive component for the preparation of membrane was grinded to fine powder and was mixed thoroughly with a fixed amounts of PVC dissolved in 10 ml tetrahydrofuran (THF) and finally mixed with 10 drops of dioctylphthalate used as a plastisizer [41]. The mixing ratio of ion-exchange was vary with fix ratio of PVC for the purpose to obtain a composition, which gave the membrane showing the best performance, and the resulting solutions were carefully poured into a glass casting ring (diameter 10mm) resting on a glass plate. These rings were left for slow evaporation of THF to obtain thin films. In this way four sheets of different thickness of master membranes were obtained.

4.2.4. Characterization of Membranes

The precondition for understanding the performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the
determination of all such parameters that affects its electrochemical properties. These parameters are porosity, water content, swelling, thickness, etc. and were determined as described elsewhere [42-44].

4.2.4.1. Conditioning of the membrane

The membranes were conditioned by equilibrating with 1 M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH 5-6.5 (to neutralize the acid present in the film).

4.2.4.2. Water Content (% Total Wet Weight)

The conditioned membranes were first soaked in water to elute diffusible salt, blotted quickly with Whatman filter paper to remove surface moisture and immediately weighed. These were further dried to a constant weight in a vacuum over P$_2$O$_5$ for 24 h. The water content (% total wet weight) was calculated as:

\[
\% \text{ Total Wet Weight} = \frac{W_w - W_d}{W_w} \times 100
\]

where $W_w = \text{weight of the soaked/wet membrane}$ and $W_d = \text{weight of the dry membrane}$.

4.2.4.3. Porosity

Porosity ($\varepsilon$) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data.
\[ \varepsilon = \frac{W_w - W_d}{A L \rho_w} \]  

Where \( W_w \) = weight of the soaked/wet membrane, \( W_d \) = weight of the dry membrane, \( A \) = area of the membrane, \( L \) = thickness of the membrane and \( \rho_w \) = density of water.

4.2.4.4. Thickness and Swelling

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze.

Swelling is measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane.

4.2.5. Fabrication of Ion-Selective Membrane Electrode

The membrane sheet (M-1) of 0.14 mm thickness as obtained by the above procedure was cut in the shape of disc and mounted at the lower end of a pyrex glass tube (o.d. 0.8 cm, i.d. 0.6 cm) with Araldite. Finally the assembly was allowed to dry in air for 24 h. The glass tube was filled with solution of the ion (as internal reference) towards which the membrane is selective and kept dipped in an identical solution of the same ion at room temperature. In case of poly-o-toluidine Zr(IV) phosphate ion-selective membrane electrode, the glass tube was filled with 0.1 M mercury nitrate solution. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as external reference electrode. The whole arrangement can be shown as:
In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, electrode response curve, response time and working pH range.

4.2.5.1. Electrode Response or Membrane Potential

The potentiometric measurements of the membranes were carried out by setting up a cell of the above type. To determine the electrode response, a series of standard solutions to be studied of varying concentrations were prepared. External electrode and ion-selective membrane electrode are plugged in digital potentiometer and the potentials were recorded.

In advance of measurements of the electrode potential (at 25 ± 2 °C) for a series of standard solutions of Hg(NO₃)₂ (10⁻⁹ M – 10⁻¹ M), the membrane of the electrode was conditioned by soaking in 0.1 M Hg(NO₃)₂ solution for 5-7 days and for 1 hour at least before use. The experiments were conducted in air thermostat maintained at 25 ± 1 °C, when not in use the membrane electrode was removed from the test-solution and kept in a 0.1 M selective metal ion solution.

Potential measurements of the membrane electrode were plotted against the selected concentrations of the respective ions in aqueous medium using the
electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system.

4.2.5.2. Effect of pH

A series of solutions of varying pH in the range of 1 to 13 were prepared, keeping the concentration of the relevant ion constant (1 × 10^{-2} M). The pH variations were brought about the addition of dilute acid (HCl) or dilute alkali (NH₃) solutions. The value of electrode potential at each pH was recorded (Table 4.1) and plot of electrode potential versus pH was plotted.

4.2.5.3. Response Time

The response time is measured by recording the e.m.f. of the electrode as a function of time when it is immersed in the solution to be studied. The method of determining response time in the present work is being outlined as follows:

The electrode is usually first dipped in a 1 × 10^{-3} M solution of the ion concerned and immediately shifted to another solution (pH ≈ 4.0) of 1 × 10^{-2} M ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second, i.e. just after immediate dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 s (Table 4.2). The potentials were then plotted against the time. The time during which the potentials attain constant value represents the response time of the electrode.
Table 4.1

Effect of pH on electrode response of Hg$^{2+}$ ion-selective poly-o-toluidine Zr(IV) phosphate membrane electrode (at $1 \times 10^{-2}$ M)

<table>
<thead>
<tr>
<th>pH</th>
<th>Measured electrode potential (-mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>256</td>
</tr>
<tr>
<td>2</td>
<td>240</td>
</tr>
<tr>
<td>3</td>
<td>241</td>
</tr>
<tr>
<td>4</td>
<td>241</td>
</tr>
<tr>
<td>5</td>
<td>242</td>
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<tr>
<td>6</td>
<td>241</td>
</tr>
<tr>
<td>7</td>
<td>241</td>
</tr>
<tr>
<td>8</td>
<td>243</td>
</tr>
<tr>
<td>9</td>
<td>280</td>
</tr>
<tr>
<td>10</td>
<td>293</td>
</tr>
<tr>
<td>11</td>
<td>298</td>
</tr>
<tr>
<td>12</td>
<td>310</td>
</tr>
<tr>
<td>13</td>
<td>312</td>
</tr>
</tbody>
</table>
### Table 4.2
Response of Hg\(^{2+}\) ion-selective poly-o-toluidine Zr(IV) phosphate membrane electrode at different time interval (at \(1 \times 10^{-2}\) M)

<table>
<thead>
<tr>
<th>Membrane electrodes ⇒</th>
<th>Poly-o-toluidine Zr(IV) phosphate Measured electrode potential (-mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (Sec)</td>
<td></td>
</tr>
<tr>
<td>00</td>
<td>322</td>
</tr>
<tr>
<td>05</td>
<td>315</td>
</tr>
<tr>
<td>10</td>
<td>315</td>
</tr>
<tr>
<td>15</td>
<td>315</td>
</tr>
<tr>
<td>20</td>
<td>315</td>
</tr>
<tr>
<td>25</td>
<td>315</td>
</tr>
<tr>
<td>30</td>
<td>316</td>
</tr>
<tr>
<td>35</td>
<td>316</td>
</tr>
<tr>
<td>40</td>
<td>316</td>
</tr>
<tr>
<td>45</td>
<td>316</td>
</tr>
</tbody>
</table>
4.2.5.4. Selectivity Coefficients

To study the cationic interference due to other ions, the selectivity coefficients of various interfering cations for the ion-selective membrane electrode was determined by the mixed solution method as discussed elsewhere [45]. The method is discussed below. A beaker of constant volume contains a mixed solution having a fixed concentration of interfering ion (M") (1 \times 10^{-3} M) and varying concentrations (1 \times 10^{-1} to 1 \times 10^{-9}M) of the primary ion. Now the potential measurements were made using the membrane electrode assembly.

4.2.5.5. Life Span of Membrane

In order to find out the lifetime of the electrode, the electrode responses were noted every week and response curve is drawn for the data. The electrode response remains fairly constant over a period of time. After this period the electrode starts behaving irregular, therefore cannot be used for any measurements. This period over which the electrode response is constant can be termed as life of electrode.

4.3. RESULTS AND DISCUSSION

In this chapter, electrically conducting ‘organic-inorganic’ composite cation-exchanger ‘poly-o-toluidine Zr(IV) phosphate’ was used as a electroactive material embedded in inert polymer binder PVC for the preparation of heterogeneous ion-selective membrane electrode. The inert polymer binder provides sufficient mechanical strength for the membranes to be used in electrodes without a
strengthening support. This is simple and economical in use while their range of applications is typical of ion-selective electrodes and extends to the direct determination of activity with the help of calibration graphs, continuous monitoring and potentiometric titrations.

4.3.1. Characterization of Composite Cation-Exchanger Membranes

Preliminary experiments were carried out to find out an optimum membrane composition of good electrochemical performance for the fabrication of electrode. The optimized membrane was then used to test the performance of the membrane electrode. Therefore, four samples of poly-o-toluidine Zr(IV) phosphate cation-selective membranes were prepared using different mixing ratios of poly-o-toluidine Zr(IV) phosphate as an electroactive material and PVC as binder dissolved in tetrahydrofuran (THF) with a fixed amount (10 drops) of plasticizer dioctylphthalate. The amount of the ion-exchanger was varied to change the thickness of the membranes coating and the results are given in Table 4.3.

It is observed that as the amount of electroactive component of the membrane i.e. poly-o-toluidine Zr(IV) phosphate increased, the thickness, swelling, water content, porosity increased. Thus, the low orders of water content, swelling and porosity with less thickness of this membrane suggest that interstices are negligible and diffusion across the membrane would occur mainly through the exchange sites. Hence, membrane sample M-1 (thickness 0.14 mm) was selected for the preparation of the ion-selective electrode for further studies. However, further
Table 4.3

Characterization of ion-exchanger membranes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Membrane composition</th>
<th>PVC (mg)</th>
<th>Plasticizer (drops)</th>
<th>Thickness (mm)</th>
<th>Water content as % weight of wet membrane</th>
<th>Porosity</th>
<th>Swelling as % weight of wet membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>Poly-o-toluidine Zr(IV) phosphate (mg) 100</td>
<td>200</td>
<td>10</td>
<td>0.14</td>
<td>1.89</td>
<td>0.200</td>
<td>0.1</td>
</tr>
<tr>
<td>M-2</td>
<td>Poly-o-toluidine Zr(IV) phosphate (mg) 200</td>
<td>200</td>
<td>10</td>
<td>0.20</td>
<td>2.27</td>
<td>0.214</td>
<td>0.2</td>
</tr>
<tr>
<td>M-3</td>
<td>Poly-o-toluidine Zr(IV) phosphate (mg) 400</td>
<td>200</td>
<td>10</td>
<td>0.32</td>
<td>3.89</td>
<td>0.244</td>
<td>0.4</td>
</tr>
<tr>
<td>M-4</td>
<td>Poly-o-toluidine Zr(IV) phosphate (mg) 600</td>
<td>200</td>
<td>10</td>
<td>0.64</td>
<td>4.48</td>
<td>0.360</td>
<td>0.4</td>
</tr>
</tbody>
</table>
various characteristics are necessary for a membrane ion-selective electrode to be considered as suitable sensor for quantitative measurement of ions. The most important characteristics are slope, working concentration range, response time, pH, selectivity and life span of the membrane electrode.

4.3.2. Potentiometric Studies of Heterogeneous Poly-o-toluidine Zr(IV) phosphate Membrane Electrode

The membrane under investigation prepared from poly-o-toluidine Zr(IV) phosphate was fabricated into ion-selective electrode and the membrane electrode was placed in 0.1 M Hg(NO₃)₂ solution for 7 days to get it conditioned.

After conditioning of the electrode, the potentials for a series of standard solution of the mercury nitrate in the range 10⁻⁹ M - 10⁻¹ M were measured, maintaining a fixed concentration of Hg²⁺ ion as internal reference solution. It was observed that the most favorable concentration of reference solution, for smooth functioning of the proposed membrane sensor, is 0.1 M.

The potentiometric response of the membrane electrode prepared from membrane sample M-1 over a wide concentration range 10⁻¹-10⁻⁹ is shown in Fig. 4.1. The electrode showed a linear Nernstian response for Hg(II) ions in the concentration range 1× 10⁻¹–1 ×10⁻⁶ M with an over Nernstian slope of 30 mV per decade change in concentration. The limit of detection of the electrode as determined according to the IUPAC recommendation [46,47] from the intersection
Fig. 4.1. Calibration curve of poly-o-toluidine Zr(IV) phosphate-araldite membrane electrode in aqueous solutions of Hg(NO₃)₂
of two segments of calibration curve was $1 \times 10^{-6}$ M. The over-Nernstian response in electrode of this kind is common [48-50].

A calibration curve was made by measuring the electrode response to standard solutions prepared by serial dilution without the addition of extra in different salts. The ionic strength will increase linearly with an increase in concentration. This will lead to a gradual decrease of the activity coefficient, and the calibration curve [$E$ vs. $\log$(concentration)] showed a negative deviation from the straight line for concentrations above $10^{-3}$ to $10^{-2}$ M. This curvature of the calibration curve can be precluded by working at a constant ionic strength. This is commonly achieved by adding a large excess of an indifferent electrolyte, the ionic strength buffer.

As is evident from Fig. 4.3 that the response time of the poly-o-toluidine Zr(IV) phosphate membrane electrode was found 5 s, according to the IUPAC recommendations [51] to reach a potential within ±2 mV of its final equilibrium value. Although the solid contact electrodes are often criticized for their poor response and stability, the response of this electrode is quick and the lifetime is reasonable, at least 3 month. It is very important that the performance of any ion-selective electrode should be checked soon every time before using it for any analytical purpose. For the present poly-o-toluidine Zr(IV) phosphate membrane electrode, it was observed that the measured potential of $\text{Hg}^{2+}$ ions in a given concentration range of $10^{-1}$–$10^{-9}$ M was reproducible within ±2 mV and there was no significant change in the slope of the Nernst plot during the experiment over a
Fig. 4.3. Time response curve of poly-o-toluidine Zr(IV) phosphate membrane electrode
time period of 3 months. This suggests a longer electrode life and a stable electrode performance.

A comparison of the present Hg$^{2+}$-ISEs with those already reported in the literature is given in Table 4.5. From Table 4.5, it is clear that the performance of the proposed mercury(II) ion-selective membrane electrode based on the organic-inorganic composite cation-exchanger polyaniline Sn(IV) phosphate is comparable and better in many respects, such as the slope, response time, linear concentration range, life time, pH range and selectivity. It is clear from the Fig. 4.2 that the pH influenced on the response characteristics the proposed mercury(II) ion-selective membrane electrode that the potential remain unchanged within the pH range 2-8. After that pH, the electrode behaved in an erratic manner, which may be because mercury ions formed a hydroxyl complex and precipitated. Thus, we can say that the optimum pH range of operation of this electrode was pH = 4-7.

The selectivity of the composite cation-exchanger is dependent on the distribution coefficient pattern, while that of for the electrode upon the potentiometric selectivity coefficient values. Thus, the selectivity of the membrane electrode is one of the most important characteristics, which is a measure of its response for the primary ion in the presence of other ions i.e. interfering ions. The selectivity of the electrode is determined in terms of potentiometric selectivity coefficient $K_{\text{Hg}_M}^{\text{Pot}}$ by mixed solution methods [44]. The selectivity coefficients of various cations for the Hg(II) ion-selective poly-o-toluidine Zr(IV) phosphate membrane electrode at pH=4 were determined and the results are summarized in Table 4.4.
Table 4.4
Selectivity coefficient values $K'_{Hg\text{M}}$ for Hg$^{2+}$-selective poly-o-toluidine Zr(IV) phosphate membrane electrode for mercury ions.

<table>
<thead>
<tr>
<th>Interfering ions ($M^{n+}$)</th>
<th>Selectivity Coefficients values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>$5.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>$5.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$5.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>$5.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>$5.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cr$^{2+}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>$1 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Table 4.5.
Comparison of the response characteristics of different Hg\(^{2+}\) ion-selective electrodes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Working concentration range (M)</th>
<th>Life time</th>
<th>pH range</th>
<th>Response time</th>
<th>Slope (mV)/decade</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1 \times 10^{-1} \text{ to } 1 \times 10^{-6})</td>
<td>2 months</td>
<td>1.0-3.0</td>
<td>30 s</td>
<td>29</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>(1 \times 10^{-1} \text{ to } 1 \times 10^{-5})</td>
<td>4 months</td>
<td>2-4</td>
<td>6 min.</td>
<td>30-32</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>(1 \times 10^{-1} \text{ to } 1 \times 10^{-5})</td>
<td>5 weeks</td>
<td>1.0</td>
<td>4 min.</td>
<td>Not mentioned</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>(1 \times 10^{-1} \text{ to } 1 \times 10^{-5})</td>
<td>5 weeks</td>
<td>0-2.0</td>
<td>Less than 3 min.</td>
<td>28.5</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>(1 \times 10^{-1} \text{ to } 1 \times 10^{-5})</td>
<td>3 months</td>
<td>2.8-3.9</td>
<td>30-40 s</td>
<td>29.0</td>
<td>56</td>
</tr>
<tr>
<td>6</td>
<td>(1 \times 10^{-1} \text{ to } 1 \times 10^{-6})</td>
<td>2 months</td>
<td>Not mentioned</td>
<td>20-100 s</td>
<td>28.6</td>
<td>57</td>
</tr>
<tr>
<td>7</td>
<td>(1 \times 10^{-1} \text{ to } 1.41 \times 10^{-6})</td>
<td>4 months</td>
<td>2.5-5.0</td>
<td>18</td>
<td>30</td>
<td>58</td>
</tr>
<tr>
<td>8</td>
<td>(5 \times 10^{-2} \text{ to } 7.5 \times 10^{-6})</td>
<td>Not mentioned</td>
<td>6.5</td>
<td>20 s</td>
<td>61.1</td>
<td>59</td>
</tr>
<tr>
<td>9</td>
<td>(1 \times 10^{-2} \text{ to } 5 \times 10^{-6})</td>
<td>4.0</td>
<td>20 s</td>
<td>28.7</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>(1 \times 10^{-1} \text{ to } 5 \times 10^{-5})</td>
<td>3 months</td>
<td>1.3-4.0</td>
<td>20 s</td>
<td>27.3</td>
<td>60</td>
</tr>
<tr>
<td>11</td>
<td>(1 \times 10^{-1} \text{ to } 1 \times 10^{-6})</td>
<td>3 months</td>
<td>2-8</td>
<td>5 s</td>
<td>30</td>
<td>Proposed assembly</td>
</tr>
</tbody>
</table>
Fig. 4.2. Effect of pH on the potential response of the poly-o-toluidine Zr(IV) phosphate membrane electrode at $1 \times 10^{-2}$ M Hg$^{2+}$ concentrations
The selectivity pattern in Fig. 4.4 showed that the alkali and alkaline earth metal ions do not interfere with the determination of mercury ions, while Cu(II), Zn(II), Pb(II) and Mn(II) interfere to a very little extent, and the interference of Fe(III) and Al(III) was found to be negligible. Thus, the results revealed that the electrode was selective for Hg(II) in the presence of interfering cations. Therefore, it is understandable the poly-o-toluidine Zr(IV) phosphate interacts relatively strongly with Hg(II) ions and can be used successfully as a sensing agent for mercury-selective electrodes.

4.3.3. Determination of Hg(II) by Potentiometric Titration’s using Poly-o-toluidine Zr(IV) phosphate Composite Membrane Electrode

The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometric titration of a 0.01 M Hg(NO₃)₂ solution against an EDTA, oxalic acid and potassium dichromate solutions as titrants. The results are shown in Fig. 4.5. For this purpose 5 ml Hg(NO₃)₂ solutions were pipetted out in three different beakers, and volume of each beaker was raised upto 20 ml by adding demineralized water. The solutions were titrated against EDTA, oxalic acid and potassium dichromate solutions respectively; the electrode potential was measured after each addition of 0.5 ml. The necessary adjustment of pH (≈ 4) was made before adding the titrant. The addition of titrants causes a decrease in potential as a result of the decrease in free Hg(II) ion concentration due to formation of a complex with titrants. The amount of Hg(II)
Fig. 4.4. Selectivity coefficients of various interfering ions for poly-o-toluidine Zr(IV) phosphate membrane electrode.
Fig. 4.5. Precipitation titration of Hg(II) against EDTA, oxalic acid and potassium dichromate solutions.
ions in solutions can be accurately determined from the resulting neat titration curves providing a sharp end point. The potentiometric titration of Hg(II) were also successfully carried out in the presence of $1 \times 10^{-5}$ M Ni(II), Cu(II) and Zn(II). Hence demonstrating its applications as a sensor developed for potentiometric determination of Hg(II) in mixtures. Poly-o-toluidine Zr(IV) phosphate, Hg$^{2+}$ ion-selective membrane electrodes was also applied to the direct measurement of Hg$^{2+}$ in the drain water collected from Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India. The samples were collected by a routine technique from five different locations of drains and preserved with HNO$_3$, stored in glass bottles and analyzed within 12 h after collection. Since the samples contain particulate matters, they were centrifuged and the potentials were measured after adjusting the pH $\approx 4$ with HNO$_3$ or NH$_3$. Three replicate measurements were done to obtain the Hg(II) contents in five samples with this electrode using the membrane sensor’s calibration graph. The concentration of mercury in the sample was $10^{-3}$ M and the reproducibility of the results was checked to three times.
REFERENCES


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