Preparation and characterization of transition metal ion-selective membrane electrodes

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Ion selective electrodes of transition metal ions Co(II), Cu(II) and Zn(II) have been fabricated using the corresponding hydroxamate complexes. These electrodes have been systematically characterized by studying the response time, electrode response, pH range and selectivity coefficients over closely associated metals. The electrode response in non-aqueous and the stability over the medium have been studied.

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The increasing demand for chemical surveillance in environmental protection, medicine and many industrial processes has created the need for sensors with features such as high selectivity, sensitivity, reliability and sturdiness. These demands can often be satisfied by ion selective electrodes (ISEs), which are commonly used owing to their simplicity, lower cost and fast provision for analytical results.

Copper ion selective electrodes are used as sensor. Conventional liquid membrane electrodes were replaced by carbon rod supported polymer membrane electrodes and coated wire ISES. A few electrodes have been reported for Co(II) and Zn(II)10-13.

In the present investigation, solid state electrodes were fabricated for sensing Co(II), Cu(II), and Zn(II). The chelating ability of hydroxamic acid to form very strong complexes with transition metal12 has prompted the use of metal hydroxamates as the electro-active material for the preparation of membranes and further for the fabrication of membrane ion selective electrode (MISE).

Experimental Procedure

Chemicals

All the chemicals used were of A. R. or G.R. grades of E. Merck and B.D. H., respectively unless otherwise specified. Ion free double distilled water was used throughout the experiment.

Metal salt solutions

The stock solutions of the metal ions were prepared by dissolving weighed quantities of the nitrates and final concentrations were determined volumetrically and by atomic absorption spectrophotometry.

Instruments

A Philips DC-Micro Model PP 9004 with a saturated calomel electrode as reference electrode were used for potential measurements controlled pH analyser, PHAN 6E488, was used for the pH measurements. The conductance was measured on a Systronics Model 303 direct measuring conductivity meter. The metal ion concentrations were determined by GBC 902 atomic absorption spectrophotometer. All measurements were made at 25 ± 1°C.

Preparation of membranes

The electro active materials required for the preparation of MISE were the corresponding metal-hydroxamates of N-phenylbenzohydroxamic acid (PBHA). The reagent PBHA was synthesised by the reported method16. The metal hydroxamate were prepared by following the general method of precipitation by the proper control of pH (Co: 5.5-6.5 pH, Cu: 3.6 - 6.0 pH and Zn: 5.3-6.8 pH). The
purity of the complexes was checked by elemental analysis.

The electroactive material (200 mg) was mixed with PVC (100 mg) in 6 mL tetrahydrofuran (THF) and finally mixed with two drops of di-octylphthalate. The resulting solution was carefully cast into a slide glass and left for slow evaporation to get a thin membrane.

Characterization of membranes

The physicochemical properties of the membrane, viz., thickness, water content, exchange capacity etc. were determined after conditioning the membrane as described earlier.

Conditioning of the membrane

The membranes were conditioned for testing by equilibrating with 1 M sodium chloride and a few mL of sodium acetate to adjust the pH 5-6.5 (to neutralize the acid present in the film) for 24 h, prolonged equilibration in 0.1 M sodium chloride preceded all measurements.

Electrolyte absorption

For the determination of electrolyte absorption, the membranes were immersed in 1 M sodium chloride solution until equilibration was attained, afterwards taken out, wiped free of adhering electrolyte, and dipped in 25 mL of conductivity water for 2-4 h with intermittent shaking. The solution was transferred into a 100 mL measuring flask. The process was repeated thrice and the entire solution was collected in a measuring flask and made up to mark with conductivity water. The conductivity of the solution was measured.

Specific conductance

For electrical conductance measurements, the membranes were cemented between two half cells with 0.1 M sodium chloride solution. After equilibration, the solution of sodium chloride was replaced by mercury previously equilibrated with sodium chloride solution. The conductance was measured by connecting platinum electrodes dipped in the mercury to the conductivity bridge.

Fabrication of MISE

The MISE were fabricated by the reported procedure. Membranes of appropriate sizes were cut from these master membranes and were mounted at the lower end of the glass tube. A 0.1 mol dm$^{-3}$ metal solution was used as internal reference solution.

Functioning of electrodes

The electrochemical behaviour of precipitate ion-selective electrodes is based on solubility equilibria and precipitate exchange reactions, existing at the phase boundaries of the electrode membrane. The phase boundary potential of the electrode in solutions containing only the primary ion, $i$, as the precipitate of the electrode membrane, is given by

$$E = E_0 + \frac{RT}{Z_i F} \ln \frac{(ai)}{(ai)_w};$$

where $E$ is the electrode potential, $E_0$, the standard electrode potential, $(ai)$ and $(ai)_w$ are the activities of the primary ion in the solution and in the membrane phase.

The selectivity of MISE towards primary ion $i$ over the interfering ion $k$ of activity $a_k$ can be expressed as

$$E = \text{constant} + S \log \left( \frac{a_i + K_{i,k}a_k}{a_i} \right),$$

where $K_{i,k}$ is the selectivity coefficient, $Z_i$ and $Z_k$ are the valences of $i$ and $k$ and $S$ is the slope of the electrode per decade change in activity.

Results and Discussion

The properties of the membranes, viz., water content, porosity, swelling, electrolyte absorption and specific conductance are given in Table 1. The electrodes for the transition metals Co(II), Cu(II) and Zn(II), have been prepared and were characterized by studying the electrode response, response time, pH range, and selectivity factor. The data are given in Table 2.

<table>
<thead>
<tr>
<th>Name of the hydroxamate membrane</th>
<th>Thickness (mm)</th>
<th>Water content as % weight of wet membrane</th>
<th>Porosity</th>
<th>Swelling % wt. of wet membrane</th>
<th>Electrolyte absorption NaCl $g$ of wet membrane $\mu g$</th>
<th>Specific conductivity ohm$^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>1.38</td>
<td>25.70</td>
<td>0.207</td>
<td>0.513</td>
<td>27</td>
<td>$2.43 \times 10^4$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.67</td>
<td>25.60</td>
<td>0.207</td>
<td>0.513</td>
<td>56</td>
<td>$2.44 \times 10^4$</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>1.25</td>
<td>14.70</td>
<td>0.065</td>
<td>0.337</td>
<td>45</td>
<td>$2.43 \times 10^4$</td>
</tr>
</tbody>
</table>
It can be seen from Table 2, that, the extent of swelling depends upon the thickness of the membrane; as the thickness decreases, the swelling increases. The order of porosity and water content of the membrane are:

Porosity: Zn < Co < Cu
Water content: Zn < Cu < Co

Generally, an ideal membrane should have less thickness, moderate swelling, porosity and water content capacity. To prepare a functional membrane for use in ion-selective electrodes, it is usually desirable to select a plasticizer in which the ionophore is soluble. For this reason, several plasticizers were studied. All ionophores were more soluble in dioctylphthalate and showed best response compared to dioctyl adipate, dioctyl phenyl phosphonate, diphenyl phthalate and bis (2-ethyl hexyl) sebacate and hence dioctylphthalate was used as the plasticizer throughout the study. The MISE fabricated from these membranes were characterized by studying the response, electrode response, electrode response in non-aqueous solvents, pH range and selectivity factor.

Response time

The electrode response was studied for the electrodes Co(II), Cu(II) and Zn(II). The response time is usually measured by recording the emf of the electrodes as a function of time, when they are immersed in the solution to be studied. The electrode is first dipped in 0.1 to 0.01 dm$^3$ solution of the ions studied and immediately shifted to another solution of ten fold concentration of the ion. The potential of the solution gives the reading at zero second and after immediately dipping the electrode in the second solution, the potential is noted at 5 s intervals. The potentials are then plotted against time. The time taken by the electrode to obtain a steady potential is the response time of the electrode (Table 2). All the electrodes studied showed very prompt response, with response time between 20 and 40 s.

Electrode response

To determine the electrode response of MISE, the electrode potential was measured in a series of solutions with the concentrations ranging from 0.1 to 1 × 10$^{-1}$ mol dm$^{-3}$.

The response curve is linear up to a particular concentration, after which the curve tends to become parallel to the activity or concentration axis. Suitable concentrations were chosen corresponding to the sloping portion of the linear curve for the measurement of potentials. The point when the curve becomes parallel to the activity or concentration axis is known as lower detection limit of the electrode (Table 2).

A linear response was observed in the concentration range 1 × 10$^{-3}$ - 1 × 10$^{-1}$ mol dm$^{-3}$ in the case of Cu(II) electrode and up to 1 × 10$^{-3}$ mol dm$^{-3}$ for Co(II) and Zn(II) electrodes (Fig. 1). The slopes derived from the linear curves have a near Nernstian slope for Co(II) and sub-Nernstian response for Cu(II) and Zn(II) electrodes. The MISE electrode response depends upon the chemical structure, solubility products, stability and the physical properties of the ligand and the precipitate. The deviation from the Nernstian response for Cu(II) and Zn(II) electrodes may be due to

![Fig. 1—Calibration curve for Co(II), Zn(II) & Cu(II)](image)

<table>
<thead>
<tr>
<th>Table 2—Characteristics of the electrodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
</tr>
<tr>
<td>--------------</td>
</tr>
<tr>
<td>Co(II)</td>
</tr>
<tr>
<td>Cu(II)</td>
</tr>
<tr>
<td>Zn(II)</td>
</tr>
</tbody>
</table>
principally ionic conduction through the membrane and also to the point defects in the crystal lattice which leads to a deviation. However, since a linearity is observed in the electrode response, these electrodes are used for the quantitative determination of these metals.

The electrode response was studied in various non-aqueous solvents, to find out the viability of application in non-aqueous systems. The solvents chosen were ethanol, methanol, dioxane, DMF, DMSO and acetone in 30-70% in water.

The calibration curve is plotted in each case and the slope of the curve is compared with the aqueous system. The studies were repeated after every 5 h to find out stability of the electrode in the various non-aqueous solvents.

The response studies showed, that, the electrodes are stable only in ethanol and methanol systems whereas in all other solvent systems the deviation of slopes is observed compared to aqueous systems.

The electrode response of Co(II) in various solvents and in 50% methanol and ethanol systems with time is given here in Table 3 as a representative case, which shows that the response is steady up to 30 h after which the potential gets deviated.

The electrode response was checked periodically to get the lifetime of the electrodes. The electrodes have a life time between 3 and 5 months (Table 2).

**Effect of pH**

The pH studies have also been carried out in the two concentration ranges 10⁻² and 10⁻¹ M in different pH between 1.0 and 13.0 and results are given in Table 2. The data reveals that the electrodes have a wide working range of pH 2-10 (Fig. 2).

**Selectivity coefficients**

The selectivity coefficients depend upon the experimental conditions, predominating on the activities of the primary ions (a₁) and of interfering ions (a₂) and the ionic strength.

The selectivity coefficients of the various electrodes were studied with respect to closely associated metals by the mixed solution method, and the $K_{selec}$ is calculated as discussed elsewhere. In most of the cases the fixed concentration of 10⁻² and 10⁻¹ M interfering ions were used against the varying concentration of primary ion. The selectivity coefficient obtained by the calculation method and graphical method were comparable (Table 4).

Of the electrodes, Zn(II) exhibits maximum selectivity and can be correlated with the low porosity of the membrane, water content, swelling and specific conductivity which are theoretically responsible for high selectivity. Here the diffusion will be only through the electroactive material and not through the interstitial liquid film.

![Fig. 2—Effect of pH on the potential of Co(II). Zn(II) & Cu(II)](image)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Slope (mV decade⁻¹)</th>
<th>Methanol</th>
<th>Dimethyl formamide</th>
<th>Slope (mV decade⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>33</td>
<td>33</td>
<td>Dimethyl formamide</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>33</td>
<td>33</td>
<td>Acetone</td>
<td>15</td>
</tr>
<tr>
<td>15</td>
<td>33</td>
<td>33</td>
<td>Dioxane</td>
<td>12</td>
</tr>
<tr>
<td>20</td>
<td>33</td>
<td>33</td>
<td>Dimethyl sulfoxide</td>
<td>10</td>
</tr>
<tr>
<td>25</td>
<td>32.5</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>33</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>28</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>30</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>27</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>18</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
These electrodes were selective over their closely associated metals, Zn(II) electrode exhibited selectivity over Pb(II) and Cd(II) which are the metals quite often associated with each other. The interference of Pb(II) in Cu(II) electrode was very small with $K_{\text{Zn,Pb}}^{\text{Cu}} = 0.078$. Further the Zn(II) electrode, with very closely associated metals like Cd(II) and Hg(II) show very negligible interference $K_{\text{Zn,Cd}}^{\text{Cu}} = 0.029$ and $K_{\text{Zn,Hg}}^{\text{Cu}} = 0.032$.

The extent of interference of Be(II) in Cu(II) electrode may be due to the similarity of their ionization potentials [Be(II)=27.52eV; Cu(II)=28.03eV] and so also is the case with Hg(II) in Cu(II) electrode [Hg(II)=28.94eV]. Ionization potentials are only one of the factors for the precipitate exchange reactions at the phase boundary of the electrode during the sensing of co-ion by the precipitate based membrane. The precipitate based membranes are prepared from metal complexes by the reaction of a complexing agent with metal cations and the action of the precipitate undergoes precipitate exchange reaction with the co-ions of the test solution. Since the formation and stability of the hydroxamate complexes depend on the ionization potential of the metal cation, the precipitate exchange may depend on the ionization potential of the cation of the precipitate and the co-ions, which are getting exchanged.

Similarly, ionization potential is only one of the factors for interference. Zn(II) and Be(II) possess almost same ionization potentials [Zn(II)=27.29eV; Be(II)=27.52eV]. However, Be(II) does not interfere with Zn(II) electrode. These responses may be related with the stability of their respective metal hydroxamate and

### Table 4—Selectivity coefficient $K^{\text{Cu}}_{\text{Be}}$ for transition metal ion sensors

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Ba(II)</th>
<th>Be(II)</th>
<th>Ca(II)</th>
<th>Cd(II)</th>
<th>Cu(II)</th>
<th>Hg(II)</th>
<th>Mg(II)</th>
<th>Pb(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>0.165</td>
<td>0.835</td>
<td>0.165</td>
<td>0.580</td>
<td>—</td>
<td>0.461</td>
<td>0.792</td>
<td>0.052</td>
<td>0.360</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.461</td>
<td>0.835</td>
<td>0.164</td>
<td>0.461</td>
<td>0.256</td>
<td>—</td>
<td>0.576</td>
<td>0.355</td>
<td>0.078</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.021</td>
<td>0.000</td>
<td>0.20</td>
<td>0.029</td>
<td>0.025</td>
<td>0.029</td>
<td>0.032</td>
<td>0.000</td>
<td>0.035</td>
</tr>
</tbody>
</table>

### Table 5—Applicability of ISE in environmental sample analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>Metals found, ppm</th>
<th>Co(II)</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ISE</td>
<td>AAS</td>
<td>ISE</td>
<td>AAS</td>
</tr>
<tr>
<td>Apple</td>
<td>0.02 ± 0.01</td>
<td>0.02</td>
<td>1.20 ± 0.02</td>
<td>1.18</td>
</tr>
<tr>
<td>Orange</td>
<td>0.04 ± 0.02</td>
<td>0.03</td>
<td>1.21 ± 0.02</td>
<td>1.20</td>
</tr>
<tr>
<td>Potato</td>
<td>0.04 ± 0.01</td>
<td>0.05</td>
<td>2.80 ± 0.03</td>
<td>2.80</td>
</tr>
<tr>
<td>Bean</td>
<td>0.04 ± 0.02</td>
<td>0.04</td>
<td>3.50 ± 0.03</td>
<td>3.49</td>
</tr>
<tr>
<td>Corn</td>
<td>0.03 ± 0.00</td>
<td>0.03</td>
<td>4.00 ± 0.05</td>
<td>4.00</td>
</tr>
<tr>
<td>Urine</td>
<td>0.05 ± 0.01</td>
<td>0.05</td>
<td>5.20 ± 0.03</td>
<td>5.19</td>
</tr>
<tr>
<td>Blood</td>
<td>0.03 ± 0.01</td>
<td>0.02</td>
<td>0.07 ± 0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>River water</td>
<td>0.07 ± 0.02</td>
<td>0.06</td>
<td>0.20 ± 0.01</td>
<td>0.20</td>
</tr>
<tr>
<td>Effluent</td>
<td>3.50 ± 0.05</td>
<td>3.48</td>
<td>7.50 ± 0.05</td>
<td>7.50</td>
</tr>
</tbody>
</table>

1 Average of 15 determinations, 2 Sabarmati river, Ahmedabad, 3 Effluents from Dyes Industries of Vatva, Ahmedabad.
their relative solubilities. The less selectivity of Cu(II)-
membrane electrodes compared with the other electrode
may be due to the high porosity of the membrane.

The selectivity of the electrodes was also
investigated in solutions of several inorganic anions
such as chloride, sulphate, acetate, nitrate, bromide,
iodide and thiocyanate using the same mixed solution
method and found that almost 100 times excess of
these ions do not change the potential and cause
interference.

The fabricated electrodes have been used for the
determination of Co(II), Cu(II) and zinc(II) in blood
and environmental samples. The known weight of the
sample (0.5-1.0 g) was transferred into 200 mL Borosil
beaker, 25 mL of perchloric acid (60%) and 5 mL of
concentrated nitric acid was added, followed by
digestion on a sand-bath for 1 h and evaporation to
dryness. The residue was heated with 10-15 mL
concentrated hydrochloric acid along with 0.5 g of
ammonium persulphate, centrifuged and the solution
was diluted with distilled water to 100 mL. The
concentration of the metal ions were determined with
ion selective electrodes. The concentration of zinc and
cobalt in the samples was determined by standard
addition method27. The reliability of the method was
compared with AAS and results given in Table 5 are
in good agreement.

Conclusion

The analytical characteristics of the membrane
electrodes investigated here, mostly depend on the
physical properties of the membrane, the stability of
the respective metal hydroxamates and their relative
solubilities. The selectivity and sensitivity of Zn(II)
electrode was better than Co(II) and Cu(II) electrodes.
The membrane electrodes fabricated are stable and can
be successfully used for non-aqueous studies and
stability constant determinations28.

References

2. (CRC, Boca Raton, FL), 1979, 90.