Review Article

Zinc(II) Ion Selective Electrodes

Rimal Isaac.R.S[1*], Praseetha P.K[1]
[1]Dept of Nanotechnology, Noorul Islam Centre for Higher Education, Kumaracoil, Thuckalay, Kanyakumari District, Tamilnadu, India.
***Corresponding author's E-mail:** rimalisaac@gmail.com

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ABSTRACT

Ion selective electrodes are used for the detection of a particular ion owing to its selectivity arising from the type of ionophore used. Zinc(II) when present in large quantities in the environment causes environmental pollution and can damage the microbial community. Zinc(II) is also an necessary metal for the normal metabolism in living beings and it is also widely used in industries. The importance of Zinc(II) makes way to detect its presence in the samples, this can be achieved by the use of ion selective electrodes with ionophores selective towards Zinc(II). In this work the available Zinc(II) ionophores and the properties of the electrodes with these ionophores are summarized.

Keywords: Zinc(II), Ion selective electrode, ionophore, electrochemistry, sensor.

INTRODUCTION

Electroanalytical techniques deal with the measurement of electrical quantities such as current, potential or charge and their relation towards chemical parameters. The birth of bio electrochemistry took place 200 years ago (1791) in Bologna, Italy, where Luigi Aloisio Galvani was dissecting a frog.[1] He discovered that the legs of the dead frog twitched when struck with electricity. Most of this field was concerned with the study of changes in chemical reactions caused by passing electrical current through the reaction mixture and the production of electrical energy by chemical reactions. Electrochemical reactions take place in the liquid-electrode interface in contrast to chemical reactions that occur in bulk solutions. At least two electrodes (conductors) and a sample (electrolyte) solution is required for these techniques, which constitute the electrochemical cell (Fig. 1). The electrode that responds to the target electrode is the indicator (or working) electrode and the other electrode is termed as the reference electrode which is at a constant potential (independent of the properties of the solution).

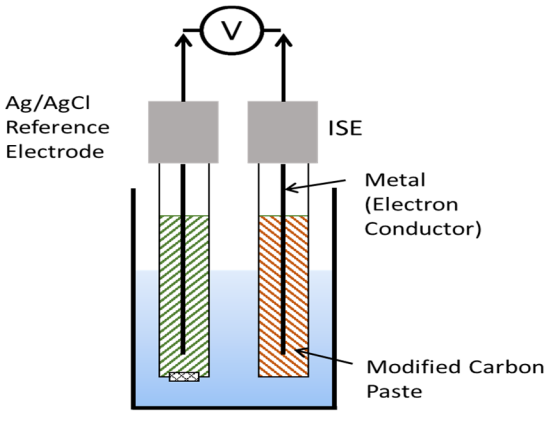

Figure 1: Representation of an electrochemical cell for the measurement of potential.

Potentiometry is an important technique in electroanalysis, which gives information about the sample composition by measuring the potential established across a membrane. Different types of membranes are produced with different ion recognition materials to increase the selectivity and sensitivity. These electrodes are used for decades for the detection of various ionic species like hydrogen, potassium, calcium, and fluoride in complex samples. In contrary, potentiostatic technique deals with the study of charge transfer at the liquid-electrode interface. Here the electrode potential is used to derive an electron transfer reaction, and the resultant current is measured. Electroanalysis can be carried out only when the medium between the two electrodes is conducting.[2] These techniques offer low detection limit, high sensitivity, large linear dynamic range, precision and accuracy with a low cost instrumentation. There are a number of important benefits associated with the use of electroanalytical techniques:[3]

- Selectivity and specificity.
- Low detection limit with high sensitivity.
- Choice of electrode material.
- Results are real time or near real time.
- Miniaturization of the sensors.

ISEs are capable of selectively measuring a particular ionic species. These electrodes are classified as membrane electrodes containing an ion permissible membrane that separates the sample from the internals of the electrode. The main advantage of using ISEs are that they are insensitive to colour, viscosity or suspended solids. They are also tolerant to small changes in pH.[4] Response time and reversibility are critical for the performance of this sensor. The problem of reversibility considering all electrochemical processes as equilibrium processes are the contribution of Nernst. Nernst equation states that

the change in potential is proportional to the change in ion activity (in logarithmic units) of the system. ISE measurement involves the use of two electrodes, one is the working (indicator) electrode, and the other electrode is the reference electrode whose potential is fixed irrespective of the solution used. The potential that is proportional to the activity of the sample ion is measured across these two electrodes.

The serious environmental and health effects of Zn makes it essential to develop more sensitive, accurate and rapid analytical techniques to detect its presence up to trace level in the environment, industries, biological samples and in pharmaceuticals. There are so many existing analytical techniques available for the detection of Zn, including potentiometry,[5] flame atomic absorption spectrometry,[6] UV-Vis spectroscopy,[7] fluorescence methods,[8] and Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES).[9] The electronic configuration of Zn is given by $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$, which shows a totally filled d-orbital thereby making it unsuitable for techniques that require magnetic or spectroscopic signals.[10] Among the above mentioned analytical techniques, potentiometric technique involving ISEs offer better response, selectivity and repeatability in a cost effective manner. There is a wide use of ISEs for the detection of metal ion pollutants mainly because of their simplicity and faster response.[11-15] ISEs employing polymeric membranes are developed for the determination of Zn ions.[10,16-26]

The Calibration Curve

When the membrane in the ISE separates the two solutions of different ionic strengths (a_1 and a_2), the electromotive force (EMF) is given by the equations Equation (1) and Equation (2):[27]

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1} \qquad \text{Equation (1)}$$

$$E = E^0 + S \log a_I \qquad \text{Equation (2)}$$

Here E is the measured EMF, E^0 is the EMF at $a_I = 0$, a_I is the activity and S is the response slope. The slope $S = \frac{dE}{d \log a_I} = 2.3026 \frac{RT}{F}$, where T is the absolute temperature, R is the gas constant, and F is the Faraday constant. The ideal value of slope at 25 °C is $S_{25} = \frac{59.18}{Z_I}$ mV, Z_I is the charge number of the target analyte.

An ideal electrode will give a Nernstian response, but it may not be ideal due to interference from other ions. The slope depends on the complex that forms at the solution-membrane interface.[28] The value of the slope also depends on different factors like the composition of the electrode, pH of the media and choice of ionophore. The slope of the ISE can be improved by choosing a suitable ionophore that forms a better complex with the analyte ion or by choosing a better composition of the electrode.[29]

A calibration plot is obtained by plotting EMF vs log a_I as shown in Fig. 2. From the calibration graph the values of S and E^0 can be obtained. From this the activity of the target analyte can be calculated as follows:

$$a_I = 10^{\frac{E - E^0}{S}} \qquad \text{Equation (3)}$$

From the calibration graph, the linear range is calculated as the linear part of the graph. The linear range is always narrower than the working range of the sensor. Working concentration is the range over which the electrode produces a measurable response.

The performance characteristics of sensor such as the linear range, interference and detection limit can be obtained from the calibration graph. Most ISEs are highly selective to a particular type of analyte ion, but some ISEs suffer from interference from ions with similar chemical properties or structure.

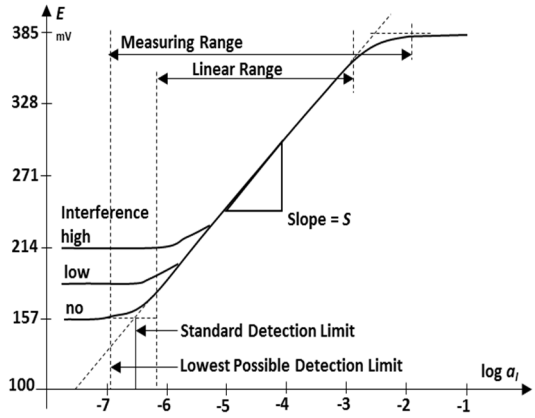

Figure 2: Calibration curve of ISE.

The Selectivity Coefficient

Selectivity is an important property of the sensor. It depends on the composition of the electrode, amount of analyte ion and interfering ion and pH of the solution. IUPAC classifies the interfering ion as the ion other than the analyte ion, whose presence in the solution interferes with the EMF of the cell. Selectivity coefficient values are used to define the selectivity of the electrode towards particular ion.

The selectivity coefficient is described by Nikolsky equation as follows

$$E = E^0 + \frac{2.303\,RT}{z_I F} \log a_I + \sum_{J=1}^{n} K_{IJ}^{Pot} a_J^{\frac{z_I}{z_J}} \qquad \text{Equation (4)}$$

Where a_J is the activity of interfering ion (I refers to the analyte ion for which the electrode is designed, and J refers to the interfering ion), z_I, z_J are the charges of the

ions I and J respectively, K_{IJ}^{Pot} refers to the selectivity coefficient of the electrode in the presence of J ion[30].

Selectivity coefficient can be determined by the following two models.

1) Separate - solution techniques
2) Mixed-solution techniques

Zinc Ions

Metals having density > 5 g/cm^3 is termed as heavy metals.[31] These heavy metals are found in municipal and industrial effluents; they pollute the ecosystem by modifying its properties.[32] Zinc (Zn) is one such heavy metal which imposes severe environmental and health risks. The properties of Zn is given in Table 1.[33]

Table 1: Properties of Zinc Metal.

Atomic number	30
State at 20°C	Solid
Atomic mass	65.38 g mol^{-1}
Density	7.134 g cm^{-3}
Melting point	419.527°C
Boiling point	907°C
Vander Waals radius	0.138 nm
Ionic radius	0.074 nm (+2)

In the human body, the heavy metal Zn is found abundantly. It is an essential nutrient for microorganisms, plant species and animals. In human serum, Zn concentration is in the order of 1.0 mg/L.[34] About 2 g of Zn is found in the human body of which 60% is found in skeletal muscles and 30% in bones. Highest amount of Zn is found in brain and prostatic secretions.[35] A healthy human requires 15 mg of Zn daily for his organs to function normally.[36,37] More than 300 enzymes require Zn for their proper function and to maintain structure. Some important enzymes that require zinc are carboxypeptidase, carbonic anhydrase, lactate dehydrogenase, RNA polymerase, and Insulin contains zinc when it is stored in the pancreas.[35] Zn deficiency is a major health issue in developing nations, annually nearly 2 billion people are affected by zinc deficiency.[38] This deficiency causes diseases like Anorexia,[39] impaired spermatogenesis, hyperkeratosis, chronic liver disease, chronic kidney disease, sickle-cell anaemia, eczema, diabetes mellitus, cancer, and other persistent illnesses.[40]

Zinc toxicity is seen when the intake of Zn is greater than 1000 mg/day. Excess of Zn causes gastric ulcer, tremors, microcytic hypo chronic anaemia, fever chills pulmonary manifestation, vomiting, pulmonary fibrosis, diarrhoea and gastroenteritis.[25] Zn also acts as an effective antioxidant and anti-inflammatory agent.[41-44] The industrial uses of Zn includes plating of iron and steel with Zn to prevent rusting, die casting and in alloys. The oxide of Zn is used in dyes, cosmetics, medicines, detergents and fabrics. Due to industrial and human activities zinc is released to the environment in levels exceeding the normal levels, this pollutes the environment and in turn this effects the soil microbial flora.[45,46] Excess levels of Zn in the environment contaminates food and agricultural wastes.[47]

Ionophores for Zinc (II) ISE

Before 1979, there were certain ISEs fabricated for the detection of Zn ions, but for them to work properly certain modifications should be carried out in the sample.[48-50] In 1979, a polymeric membrane ISE using a Zn salt of di(2-ethylhexyl)phosphoric acid dissolved in tri(2-ethylhexyl)phosphate as the ionophore was developed for the detection of Zn ion without any sample modification.[16] Rocheleau and Purdy developed a coated wire ion selective electrode (CWISE) for the determination of Zn ions in chloride or cyanide containing solutions. Interference was reported only from the transition metal ions such as copper, mercury and cadmium.[51]

A membrane electrode made with poly(vinyl chloride) (PVC) was developed by Kojima and Kamata using tetrabutyl thiuram disulfide neutral carrier as ionophore for the detection of Zn ions. From the calibration graph, the response slope was found to be 28.0 mV per decade which showed a Nernstian response with a linear range of 0.1 M to 1.0 mM at 25±1°C. The fabricated Zn^{2+} electrode exhibited a detection limit of 0.42 µM. The response of the electrode was studied at different temperatures, viz. 5 and 45°C. It was observed that the electrodes showed a Nernstian response in these temperatures. The time taken by the electrode to reach an equilibrium potential varied between 2 s and 10 s for an increase or decrease in Zn ion concentration by a factor of 100. The prepared electrode was useful over a pH range of 3.5 to 6.5. The electrode is proposed to be used in the detection of Zn in electroplating process and industrial effluents.[20]

Zn selective ISE based on PVC membrane was developed using 2,2,2-cryptand as ionophore by Srivastava. The PVC membrane was prepared by mixing PVC, ionophore, and dibutyl phthalate in tetrahydrofuran. The prepared PVC membrane was pasted on to the end of a Pyrex glass tube using araldite and used for further studies. The optimized electrode produced a Nernstian slope of 22.0 mV per decade. From the obtained calibration graph, the linear response range of the electrode was found in a concentration range of 0.1 M to 0.0315 mM. The electrode had a response time < 10 s in all the test solutions. The developed electrode also had a life time of 3 months and the response of the electrode was not affected when the pH of the solution was in between 2.8 and 7.0, showed a stable Nernstian response. The electrode response was also measured in a partially non aqueous solutions and it was observed that up to 25% (v/v) alcoholic content in the sample solution did not affect the response of the electrode.

The electrode worked well in the presence of cationic surfactant, cetyltrimethylammonium bromide at a concentration ≤ 0.01 mM.

The electrode was used for the specific determination of Zn ion in the potentiometric titration of Zn ion with EDTA.[52]

Gupta developed a Zn^{2+} ISE using a Zn complex of Diisooctyldithiophosphinic acid as the ionophore along with sodium tetraphenylborate (NaTPB) as the anion excluder and dibutyl(butyl)phosphonate (DBBP) as the solvent mediator.

From the calibration graph, it was observed that the electrode had a linear response in the concentration range of 0.1 M to 0.028 mM and requires 15 s to reach an equilibrium potential.

The electrode presented an unchanging response in a solution of pH between 2.1 and 6.9.

The fabricated ISE was used for the specific determination of the Zn ions by the end point obtained in the potentiometric titration of this metal ion with EDTA.

The selectivity of the electrode was studied for different metal ions and the selectivity coefficient value was higher for Cu^{2+} compared to all the other metal ions under investigation and it was found that Cu^{2+} causes interference at certain concentration levels.[53]

A PVC membrane electrode was developed for Zn^{2+} detection using a macrocyclic compound 12-crown-4 (Fig. 3.) as ionophore by Gupta. In the preparation of electrode NaTPB was used as the anion excluder and dibutylphthalate (DBP) and dioctylphthalate (DOP) as plasticizers.

The membrane composition was optimised and the optimised membrane was prepared with the composition of 12-crown-4: NaTPB: PVC: DOP as 1:1:10:10.

In this composition, the sensor showed a linear response slope in the concentration range of 0.1 M to 0.07 mM with a Nernstian slope of 29.5±1.0 mV per decade of Zn concentration.

The response time of the electrode was studied and it was found out that the electrode took a time < 10 s to reach the equilibrium potential. The fabricated electrode also had a life time over 3 months. During this period the electrode exhibited a stable response.

The electrode exhibited a stable response when the pH of the solution used for the study is in between 2.8 and 5.5 and also showed a stable response in non-aqueous solutions containing alcohol quantity up to a level of 25% (v/v). Real-world application of the electrode was validated by conducting potentiometric titration of Zn^{2+} with EDTA and also used for the estimation of Zn^{2+} in river water.[54]

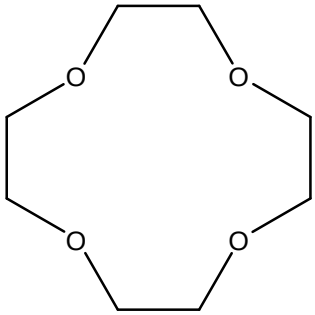

Figure 3: Structure of 12-crown-4.

A benzo-substituted macrocyclic diamide (1,13-diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione) was utilized as an ionophore for the fabrication of a Zn^{2+} ISE by Shamsipur. Calibration graph was plotted for the fabricated sensor and it was found out that the electrode showed linear response in the concentration range of 0.1 M to 0.09 mM with a Nernstian slope of 30.0±1.0 mV per decade of Zn^{2+} concentration. The optimal equilibration time is found to be 24 h for the electrode to obtain a stable potential when kept in contact with Zn^{2+} solution. The fabricated sensor had a detection limit of 0.05 mM and the time taken for the sensor to reach an equilibrium potential was found to be 10 s. The electrode was used for the detection of Zn in waste water samples from the zinc acid baths acquired from Tehran Electroplating Factory.[17]

Fakhari fabricated a PVC membrane ISE for Zn^{2+} using 5,6,14,15-dibenzo-l,4-dioxa-8,12-diazacyclopentadecane-5,14-diene (DBDA15C4) as the ionophore. The optimized membrane with the composition PVC (31%), acetophenone (59%), DBDA15C4 (3%), and oleic acid (7%) gave a linear response in the concentration range of 0.1 M to 0.05 mM with a Nernstian response slope of 22.0 mV/decade. The time for which the electrode has to be equilibrated before sample measurement was found to be 48 h. The time taken for the electrode to attain an equilibrium potential during sample measurement was found to be less than 5 s. The fabricated electrode had a longer life time of 11 month. During this period there was no notable change in the potentiometric response of the electrode. The electrode produced a stable response slope when the pH of the analyte solution was in between 1.5 and 7.0. The electrode was used for the determination of Zn ions in cosmetic creams contain zinc as zinc oxide and also used as an indicator electrode in the potentiometric titration of Zn ions with EDTA.[55]

$Zn(TIDAN)_2$ complex was used by Dumkiewicz for the fabrication of a Zn^{2+} PVC membrane ISE. The optimized electrode exhibited a Nernstian slope of 29.0±0.2 mV per decade over a linear concentration range of 0.1 M to 5.6 µM and a response time of 10 s. The detection limit of the fabricated electrode was found to be 5.6 µM. The response of the electrode was measured at solutions of different pH and it was found that when the pH is between 4 and 8 the electrode showed a stable response. The life of the electrode was studied and during this

period the electrode showed no deviation in its response slope and it was found to be 6 weeks. The electrode was used for the estimation of Zn in vitamin samples.[56]

Gupta developed a Zn ISE using dimethyl-8,13-divinyl-3,7,12,17-tetramethyl-21H, 23H-porphine-2,18-dipropionate as the ionophore. The developed sensor had a life time over 5 months. From the calibration graph, the developed sensor had linear response in the concentration range of 0.1 M to 0.015 mM and produced a Nernstian slope of 29.0±1.0 mV per decade of Zn ion. The time taken by the sensor to reach an equilibrium potential was found to be 10 s. The selectivity of the fabricated electrode towards different ions was studied and it was observed that sodium and cobalt ions had higher selectivity coefficient values thereby causes interference if present in the sample solution. It was observed that Na^+ concentration ≤ 0.052 mM and Co^{2+} concentration ≤ 0.045 mM is tolerable in the detection of Zn. The electrode was also tested for use as an electrode to detect the end point in the potentiometric titration of Zn^{2+} against EDTA.[57]

A sulipride drug, N-[(ethyl-1 pyrrolidinyl-2)methyl] methoxy-2 sulfamoyl-5 benzamide was utilized as an ionophore for the fabrication Zn ISE by Saleh and Gaber. The calibration graph showed that the fabricated PVC membrane electrode had a Nernstian slope of 29.3 mV per decade and had a liner range of 0.1 M to 0.01 mM. The prepared ISE was used in potentiometric titration as well as for the detection of Zn in rock samples. This electrode was responsive to Cu^{2+} and Cd^{2+} and can be used for their estimation in the concentration range of 0.1 M – 0.1 mM.[18]

Gupta developed a Zn^{2+} ISE using 5,10,15,20-tetraphenyl-21H,23H-porphine as the ionophore. From the calibration graph, the linear range of the developed sensor was calculated and it was found to be in the range of 0.1 M to 6.2 µM and also showed a Nernstian slope of 29.0±1.0 mV per decade of activity. The fabricated PVC membranes without the presence of any solvent mediator showed a very slow response time of 1 to 2 min during the measurement of Zn ions. But the response time was improved when solvent mediator was added to the PVC membrane. The electrode had a lifetime of over 6 months with a fast response time of 12 s to attain a stable potential. The effect of pH on the response of the electrode was studied and it was observed that the electrode showed a stable response when the pH of the solution is in between 3.8 and 7.7. Interference was caused from Na^+ and Mg^{2+} ions in the measurement of Zn^{2+} ions. It was found that if the concentration of Na^+ and Mg^{2+} was ≤ 0.05 mM, it did not cause any interference in the measurement. The sensor was used as an indicator electrode for the titrimetric determination of Zn^{2+} and also used to detect the amount of Zn^{2+} present in Eveready battery waste.[58]

Fakhari developed a PVC membrane Zn ISE using tetra(2-aminophenyl) porphyrin (TAPP) (Fig. 4.) as the ionophore. The best Nernstian response characteristics were acquired from the electrode with a membrane composition of PVC (30%), acetophenone (55%), TAPP (5%) and oleic acid (10%). The membrane was equilibrated in a Zn^{2+} solution before measurements so that it produces a stable potential. The optimal equilibration time required for the electrode before the sample measurement in a Zn solution to obtain a stable response was found to be 48 h. The electrode gave a Nernstian slope of 26.5 mV per decade over a concentration range of 0.1 M to 0.05 mM and a detection limit of 0.03 mM. Within 10 s of immersion of the electrode in the test solution, it showed a stable response and the electrode also showed a stable response when the pH of the solution is in between 3.0 and 7.0. The electrode also had a working life time of about 8 months. The electrode was utilized as an indicator electrode in the titration of Zn^{2+} with EDTA. It was also used for the direct estimation of Zn present in cosmetic samples containing zinc oxide.[59]

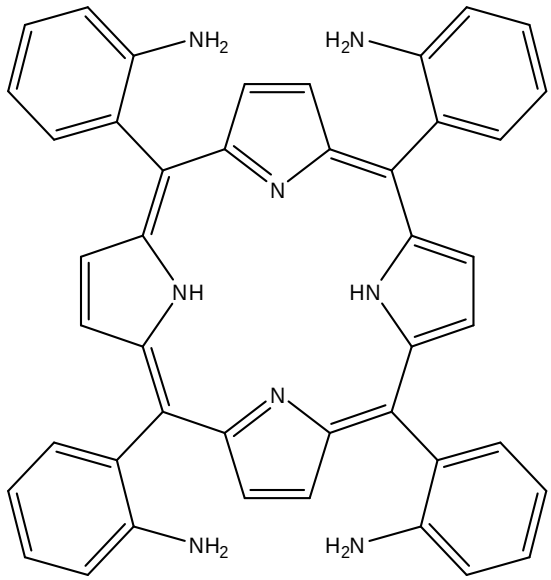

Figure 4: Structure of tetra(2-aminophenyl) porphyrin.

Zn ISE was developed using chalcogenide glassy As_2Se_3–Sb_2Se_3–ZnSe and $GeSe_2$–ZnSe–ZnTe membranes by Boycheva. The electrode conditioned for 15 min provided better and stable results. The electrode compositions were optimized and the electrodes with codes 1 ASZ and 7 ASZ gave better response with 1ASZ gave a slope of 38 mV per decade and 7 ASZ with a slope of 41 mV per decade. Both the fabricated electrodes exhibited a stable potentiometric response when the pH of the analyte solution is in between 3.0 and 7.0. The ASZ system gave a stable response with in a time of 2 to 30 s and the GZZ system gave a stable response with in a time of 5 to 50 s.[60]

A Hematoporphyrin IX based PVC membrane sensor was developed for the determination Zn^{2+} by Jain. The fabricated electrode had a linear concentration range of 0.1 M to 0.05 mM with a Nernstian slope of 28.6 mV per decade. The potentiometric response of the electrode

was studied in solutions of various pH and also in nonaqueous solutions. From the results, it was observed that the electrode was usable over a pH range of 2.0 to 5.5 without any deviation in the measured potential. Also the electrode showed a stable response in the measured potential for a period of over 3 months. These ISE was used for the specific determination of the Zn ions by the end point obtained in the potentiometric titration of this metal ion with EDTA and also used for the detection of Zn^{2+} in the waste water obtained from electroplating industry.[61]

A Zn^{2+} ISE was developed using bis(2-nitrophenyl)disulphide as the ionophore by Gholivand and Mozaffari. The fabricated PVC membrane electrode was utilized for the direct potentiometric determination of Zn in real samples such as human hair, urine, and alloys. The acquired results were compared by investigating the same samples for Zn ion concentration using AAS. The prepared electrode showed a Nernstian response in all the test solutions with pH in between 2.0 and 9.0. The electrode is usable over a concentration range of 0.032 M to 0.29 µM and exhibited a Nernstian slope of 29.9±0.4. The electrode was also used to detect the end point in the potentiometric titration of Zn^{2+} against EDTA.[62]

In another Zn ISE, Gupta utilized Porphyrin IX disodium salt as the ionophore. The electrode showed a Nernstian slope of 30.0 mV per decade and the calibration graph showed that the linear range is from 0.1 M to 0.013 mM. The sensors worked over a pH range of 3.0 to 7.4 with a response time of 10 s within which the electrode reached the equilibrium potential. The electrode response is checked in partially aqueous media methanol-water, ethanol-water and acetone-water. From the results it was observed that the electrode worked well in a media with alcohol content of 40 % (v/v). Interference was caused from Na^{+} and Cd^{2+} ions in the measurement. The electrode was used to detect the end point in the potentiometric titration of Zn^{2+} against EDTA and it also had a lifetime of 2 months.[26]

A highly lipophilic $[(CH_3)_3N(C_{43}H_{79}O_3)]_2Zn(SCN)_4$ ion exchanger was used as an ionophore to detect the presence of Zn^{2+} in environmental samples like water and soil by Rakhman'ko. The electrode showed a stable response in all the solutions with different pH in between 2 and 9. The electrode showed a response slope of 27 to 28 mV per decade under the test conditions. The developed procedure can be used to detect the amount of Zn^{2+} in environmental samples in the concentration range of 0.05 to 500 mg/L.[63]

A Zn^{2+} ISE was developed by Gupta for the detection of Zn in Eveready Battery waste. The electrode was fabricated with dibenzo-24-crown-8 as the ionophore. The electrode with the composition Ionophore:PVC:NaTPB: dioctylphthalate (DOP) in the ratio 10:200:2:100 (w/w) showed a linear working range from the concentration 0.1 M to 0.092 mM and the Nernstian slope calculated from the calibration graph was found to be 29.0±0.5 mV per decade. The fabricated electrode reached an equilibrium potential with in a time of 12 s. Response was measured in partially non-aqueous media and it was found that the electrode worked well in a medium of composition methanol–water, ethanol–water and acetone–water mixtures up to a concentration of 10% (v/v) of methanol, ethanol or acetone. The electrode was also used as an indicator electrode for Zn^{2+} against EDTA and to detect the amount of Zn^{2+} in Eveready Battery waste. The electrode had a lifetime of over 4 months.[64]

Zn^{2+} PVC membrane ISE was developed using 3-[(2-furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one (FTT) as the ionophore by Ganjali. Computational methods were adopted in this work to study the binding affinity of FTT with metal ions. The electrode with the composition PVC (30%), nitrobenzene (NB) (62%), FTT (3%) and NaTPB (5%) produced the best response. From the obtained calibration graph, the slope was found to be 29.3 ± 0.3 mV per decade in the linear range of 0.01 M to 1.0 µM. The detection limit of the electrode was found to be 0.85 µM. The electrode was found to work well in solutions with pH in between 3.0 and 7.0. The sensor was successfully utilized for the direct determination of Zn in wastewater which is obtained from zinc electroplating industries.[65]

N,N′-bis(acetylacetone)ethylenediimine was used as an ionophore in a Zn^{2+} PVC membrane ISE developed by Gupta. The calibration graph was drawn from the sensor response and the linear range of the sensor was found to be from 0.1 M to 1.0 µM and the slope was calculated as 30.0±0.5 mV per decade. The electrode had a lifetime of more than 3 months. The response of the electrode was stable when the pH of the analyte solution was in between 3.2 and 7.1. The electrode worked well in partially non-aqueous media with an alcohol content of 30% (v/v). The presence of copper in the sample at higher concentration caused interference, but this can be overcome by reducing copper by using ascorbic acid and copper can be masked from causing interference. The fabricated sensor was used for the detection of Zn^{2+} in blood samples and as an indicator electrode for the titrimetric determination of Zn^{2+}.[19]

4-tert-butylcalix[4]arene was successfully utilized as an ionophore in the fabrication of a PVC membrane base Zn^{2+} ISE by Gupta. The membrane with composition Ionophore: NaTPB: tri-*n*-butylphosphate (TBP):PVC in the ratio 8:5:100:200 (w/w) produced good response characteristics with a linear range of 0.1 M to 9.8 µM. The fabricated electrode also produced a Nernstian slope of 28.0±1.0 mV per decade. The response of the electrode towards solutions of different pH was studies and it was found out that when the solution pH is in between 2.5 and 4.3, the electrode produced stable response. The electrode also worked well in partially non-aqueous media containing methyl alcohol, ethyl alcohol and propanone up to a concentration of 15% (v/v). The

electrode was used as an indicator electrode in detecting the endpoint in the potentiometric titration of Zn^{2+} against EDTA.[66]

$Bzo_2Me_2Ph_2$(16)hexaeneN_4 was used as an ionophore in a Zn^{2+} PVC membrane ISE by Singh. The membrane composition was optimized and calibration graph was plotted for the optimized electrode, from the graph the linear response of the electrode was found to be in between the concentration range of 0.1 M to 2.82 µM and also had a Nernstian slope of 28.5±0.2 mV/decade. The electrode produced stable response when the pH of the analyte solution was in between 2.5 and 8.5. The membrane worked well in the presence of methanol, ethanol and acetonitrile up to a concentration of 30% (v/v) of aqueous medium. The sensor was used as an indicator electrode for the detection of Zn ions as well as in the determination of Zn ions in health drink/baby food powders.[67]

Potassium hydrotris(N-tert-butyl-2-thioimidazolyl) borate [$KTt^{t\text{-}Bu}$] and potassium hydrotris(3-tert-butyl-5-isopropyl-l-pyrazolyl)borate [$KTp^{t\text{-}Bu,i\text{-}Pr}$] was synthesized by Singh and used as an ionophore for the fabrication of a PVC membrane electrode for the estimation of Zn^{2+}. The sensor with the composition: [$KTt^{t\text{-}Bu}$] (15 mg), PVC (150 mg), dibutyl phthalate (DBP) (275 mg), and NaTPB (4 mg) gave better response with a Nernstian slope of 29.4±0.2 mV per decade and the electrode also had a liner concentration range of 0.1 M to 0.14 µM. The prepared membranes were equilibrated for 72 h before measurement of the samples so that it produced a stable response. The electrode had a faster response time of 12 s in reaching the equilibrium potential and a detection limit of 0.095 µM. The electrode was used as an indicator electrode for the potentiometric titration of Zn^{2+} against EDTA, it was also used for the detection of Zn^{2+} in water from industry waste and river and urine.[68]

Gupta developed a Zn^{2+} PVC membrane ISE using 9,10-Bis(N-[2-(dimethylamino)ethyl]methylaminomethyl)anthracene as the ionophore. The prepared electrode was used as an indicator electrode in Zn^{2+} determination, and for the determination of Zn^{2+} in brass, dry cell, pharmaceutical sample and tobacco leaves. The electrode exhibited a Nernstian slope of 30.0±0.5 mV per decade and a detection range of 0.1 M to 0.01 µM. The fabricated electrode also had a detection limit of 1.5 µM. The electrode took 15 s to reach the equilibrium potential in the test solution and worked well when the pH of the solution is in between 3.0 and 7.5.[69]

1,12,14-triaza-5,8-dioxo-3(4),9(10)-dibenzoyl-1,12,14-triene was used as an ionophore by Chandra and Singh for the fabrication of a PVC membrane Zn^{2+} ISE. The fabricate ISE worked over a concentration range of 0.1 M to 0.13 µM with a Nernstian slope of 29.2 ± 0.4 mV per decade and the detection limit of the electrode was found to be 0.01 µM. The electrode was used as an indicator electrode for detecting the end point in the potentiometric titration of Zn^{2+} against EDTA and also used in the estimation of Zn^{2+} in human hair samples and waste water. The electrode worked well when the pH of the solution is in between 3.5 and 9.2.[25]

Akl and El-Aziz developed PVC membrane electrode for the determination of Zn^{2+} using different ionophores 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), dibenzo 18-crown-6 and calix[6]arene (Fig. 5.). The electrodes fabricated with the ionophores 18-crown-6 and dibenzo 18-crown-6 and dioctylphenylphosphonate (DOPP) as plasticizer in the ratio (w/w) PVC: ionophore:DOPP (60:2:120) gave a better response in terms of the measured slope. The electrode with 18-crown-6 as the ionophore gave a Nernstian slope of 30.0 mV per decade and with the ionopre dibenzo 18-crown-6 gave a Nernstian slope of 29.0 mV per decade over a concentration range of 0.1 µM to 0.01 mM. Both the electrodes suffered interference from Pb and Ag ions. The electrodes were used successfully for the determination of Zn^{2+} in Devarde's Alloy samples.[70]

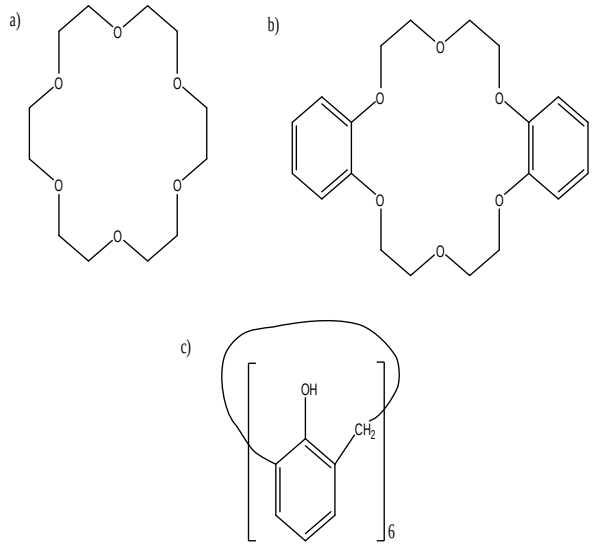

Figure 5: Structure of a) 18-crown-6, b) dibenzo 18-crown-6 and c) calix[6]arene.

Multiwalled Carbon Nanotubes (MWCNT) were chemically modified using trimethoxysilylpropylamine (TMSPA) and 2-hydroxybenzaldehyde (2-HBA). This modified MWCNT is used in the preparation of a Zn^{2+} selective CPE by Ghaedi. The electrode fabricated with the optimal composition showed a Nernstian slope of 29.70 mV per decade over a wide concentration range of 0.05 M to 0.1 µM. The electrode produced a stable response in the test solutions with pH in between 3.5 and 6.5 and also the electrode reached an equilibrium potential with in a time of 5 s. The fabricated electrode was also used as an indicator electrode to detect the end point in the potentiometric titration of Zn^{2+} against EDTA.[71]

Hosseini developed an electrode for the selective determination of Zn^{2+} using N,N′-phenylenebis (salicylideaminato) as ionophore. By examining the

calibration graph, the electrode showed a Nernstian slope of 29.4±0.2 mV per decade over a Zn^{2+} concentration range of 0.1 M to 0.5 µM with a detection limit of 0.26 µM. The electrode produced an equilibrium potential with in a time < 10 s. The electrode is usable in the pH of the solution in between 3.0 and 7.0. The stability of the electrode was studied and the electrode produced stable potential for all the measurements carried out during a period of over 2 months. The fabricated electrode was used for the detection of Zn^{2+} in mixture solution and also in waste water samples.[22]

Singh developed Zn^{2+} PVC membrane ISE based on the ionophores 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N_2-1,5-O_2 (L_1) and 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate- 9,12-N_2-1,5-O_2 (L_2). The optimized electrode with the composition L_2:PVC:TBP:NaTPB in the ratio of 4:37:57:2 (w/w; mg) gave better response characteristics in terms of the measured potential. The electrode response was measured using the optimized concentration of the prepared polymeric membrane electrode (PME) and coated graphite electrode (CGE). The potentiometric response characteristics of the CGE was much better when compared to the results of the PME with a 0.01 M to 0.19 µM and a detection limit of 0.079 µM with a response time of 10 s. The electrode was used as an indicator electrode for Zn^{2+} and also used for the detection of Zn^{2+} in water, biological samples, milk and tea samples.[72]

NiO nanostructures were functionalized with 12-crown-4 and used as an ionophore for the fabrication of PVC membrane ISE for the detection of Zn^{2+} by Abbasi. The fabricated electrode showed a slope of 36 mV per decade over a concentration range of 0.1 M to 1.0 µM. The electrode was used as an indicator electrode for the detection of end point in the potentiometric titration of Zn^{2+} against EDTA.[10]

Another PVC membrane sensor was fabricated by Dwivedi and Jain for the detection of Zn^{2+} using 12-crown-4 as the ionophore. The prepared sensor showed a wide response over a concentration range of 0.1 M to 0.0708 mM and a detection limit of 0.0141 mM. The electrode had a fast response time of 10 s with a Nernstian slope of 20.5 mV per decade. Selectivity of the sensor was studied and it showed good response to Zn^{2+} over the other studied ions and the sensor also showed stable response in solutions with pH in between of 4 and 7. The sensor was also used to detect the amount of Zn^{2+} ions in partially aqueous solutions and its practical application was demonstrated by using it as an indicator electrode in potentiometric titration.[73]

A PME based on the ionophore 2,6-diacetylpyridinebis (benzenesulfonylhydrazide) was developed by Isa. The membranes with the composition of ionophore: PVC: dibutylphthalate (DBP) in the ratio of 10:30:60 (w/w) produced better characteristics for the detection of Zn. The electrode fabricated with this composition gave a response slope of 29.06±0.1 mV per decade over a concentration range of 0.1 M to 1.0 µM. The electrode produced a stable response with in a time of 20 s and worked well when the pH of the solution is in between 4 and 12. The practical application of the electrode was proved by measuring the amount of Zn ion present in wastewater samples.[21]

CONCLUSION

This review clearly shows the presence of a large number of ionophores for the detection of the Zinc(II). The use of nanomaterials are of growing interest among researchers in the development of sensors. Some of the developed ionophores have the problem with interference. In this review all the ionophores available for Zinc(II) is reviewed which can serve as a database for researchers. Further development of sensors which surpasses the problems of interference can lead to the development of sensors for the use in fields of industries, environment and biomedical. In order to achieve this electrochemists should work in collaboration with synthetic organic chemists.

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