

Potentiometric Determination of Nickel (II) Ion Using Zirconium (IV) Antimono Tungstate as an Electroactive Material

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Authors' contributions

This work is a collective contribution of two Authors. Author HKS proposed the methodology; author PD and MSc student implemented the procedure to achieve the goal and also wrote the outline of the article. Authors HKS and PD analyzed the results and gave a final sketch to the manuscript. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Aims: The research work is based on the fabrication of ion selective Electrode based on Zirconium (IV) antimono tungstate.

Study Design: The Study was designed to make ion selective electrode for transition metal ions.

Place and Duration of Study: Department of Chemistry, M. M. University, Mullana (Ambala). It can be used for five months i.e Jan - May 2013, with a good reproducibility.

Methodology: Zirconium (IV) antimono tungstate having ion exchange capacity of 0.30 meq g⁻¹ for Na⁺ ion was synthesized by sol-gel method and characterized by physicochemical techniques. The proposed electrode was prepared by mixing the ionophore with the required amount of epoxy resin. Then potentiometric studies were carried out.

Results: Epoxy-based membrane of zirconium (IV) antimono tungstate (50% ZrSbW and 50% epoxy resin) reveals a sub-Nernstian potentiometric response with the slope of 20 mV per decade for Ni²⁺ over a wide concentration range (10⁻⁶ to 10⁻¹ M). The response time of the electrode is quite low and could be used for a period of 5 months with a good reproducibility. The proposed electrode reveals very high selectivity for Ni²⁺ in the presence

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of a wide variety of metal ions such as Zn^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Ce^{3+} , Na^+ , Ca^{2+} , Mg^{2+} , Pr^{3+} , Y^{3+} and Fe^{3+} at concentrations 1×10^{-3} M and 1×10^{-4} M. Effect of internal solution concentration was studied. The proposed sensor can be used in the pH range of 2.90 - 9.20. It was used as an indicator electrode in the potentiometric titration of Ni^{2+} ions against EDTA.

Conclusion: Zirconium (IV) antimonotungstate can be successfully used as electro-active material for making a nickel (II)-selective membrane electrode. The proposed electrodes have reasonably good lifetime, detection limit, pH range and selectivity coefficient. They can also be used as indicator electrodes for trace level determination of Nickel ions.

Keywords: ISE; Ni (II); FIM; Potentiometric titration.

1. INTRODUCTION

Over the years, nickel has been regarded as a potentially toxic metal. The main source of nickel in aquatic systems is decomposition or degradation of rocks and soil, biological cycles and especially industrial processes, and water disposal [1]. Nickel is well known as a toxic metal that can cause cancer of nasal lungs, dermatitis, asthma, and disorders of central nervous system [2]. The maximum recommended concentration of Ni^{2+} ions in drinking water for livestock is 2.5 mg/mL [3]. Thus, due to the urgent need for selective monitoring of Ni^{2+} in many industrial, environmental, and food samples, there have been a number of recent reports in the literature [4–8]. A number of methods, such as atomic absorption spectrometry (AAS), atomic absorption spectrometry-electrothermal atomization (AAS-ETA) [9–12], inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and flame photometry [13], can be used for determination of nickel. However, these methods generally require sample pretreatment and infrastructure backup and are, therefore, not very convenient for routine analysis of large number of environmental samples. Thus, there is critical need for the development of selective, portable, inexpensive diagnostic tool for the determination of nickel. Many optical chemical sensors utilize colored complexes [14–16] or redox reagents [17,18] immobilized in suitable matrix. Potentiometric sensor for determination of the ions in the real samples, offers interesting advantages such as simplicity, speed, relatively fast response, low cost, wide linear dynamic range and ease of preparation and procedures. There has been an increased interest in developing such sensors for transition metal ions recently many reports [19-33] have been given on various metal ions like:

Cr^{3+} , Mn^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} and Hg^+ etc.

Survey of literature shows that there are many reports on Ni^{2+} selective electrodes; based on organic Ionophores [34-39], however only few reports on Nickel selective electrode based on inorganic sensors are available. Therefore, it was interesting to use inorganic ion exchanger as an electro active material for our studies. Inorganic ion exchange membrane has many advantages over the organic ion exchangers, e.g. their ability to withstand high temperature and ionizing radiations without undergoing degradation and their remarkably high selectivity [40].

Inorganic ion exchanger zirconium (IV) antimonotungstate shows better selectivity for Ni^{2+} ions in comparison to other metal ions. Hence in this paper, results on the epoxy matrix for the determination of Ni^{2+} in aqueous solutions have been discussed.

2. MATERIALS AND METHODS

2.1 Chemical and Instruments

Zirconyl (IV) oxychloride, sodium tungstate needed for the preparation of Zirconium (IV) antimonotungstate were kindly supplied by C.D.H. Chemicals Ltd. India, while potassium pyroantimonate was supplied by S.D. Fine Chemicals Ltd., India. Transition metal halides were purchased from C.D.H. Chemicals Ltd., India. All the chemicals were of analytical grade and hence, were used as received. A solution of nickel (II) chloride was standardized against EDTA solution using Xylenol orange as an indicator. Double-distilled deionized water was used throughout the experiments. EMF measurements were made using a digital potentiometer (Equiptronics EQ-602, Mumbai, India) with accuracy of 0.1 mV. ISFET 701 pocket pH meter (Delta TRAK, INC., USA Model 240030) was used to measure pH of the solution.

2.2 Synthesis of Zirconium (IV) Antimonotungstate

Exchanger was prepared by adding zirconyl oxychloride (0.1M) to a continuously stirred equimolar mixture of potassium pyroantimonate and sodium tungstate at 60°C in a volume ratio of 2:1:1. Gelatinous white precipitates were obtained and the pH of the gel was adjusted to 1.0 by adding either HCl or NaOH solution. Precipitates were filtered, washed until free from halides and dried at 40°C. The dried product broke down into small granules when immersed in water. The material was converted into the H⁺ form by keeping it in HCl (0.1M) for 24 hours with intermittent changing of the acid and finally dried at 40°C. The product was washed with demineralized water to remove excess acid.

2.3 Ion Exchange Capacity

Ion- exchange capacity was determined by column operation, 0.5 g of zirconium (IV) antimonotungstate in the H⁺ form was placed in two glass columns having an internal diameter ~1cm with glass wool at the bottom. A 400 mL of 1M NaCl solution was passed slowly through these inorganic ion- exchange columns by adjusting the effluent to a rate of 8-10 drops/minutes. The complete replacement of H⁺ form the ion- exchanger by the Na⁺ was checked by pH meter. The eluted solution was titrated with the standard (0.1M) NaOH solution by using phenolphthalein as indicator. The volume of NaOH used gave the strength of the H⁺ ions given out by the exchanger, which in turn tells the ion- exchange capacity of the exchanger in meq g⁻¹.

2.4 Distribution Studies

Distribution coefficients (K_d) for different metal ions such as Ni²⁺, Fe²⁺, Ca²⁺, Cu²⁺, Mg²⁺, Y³⁺, Pb²⁺, Na⁺, Ce³⁺ and Cd²⁺ were determined by keeping 2 mL of 0.1 M (standardized solution) metal ion solutions, 18 mL of distilled water and 0.2 g of synthesized exchanger, overnight in a titration flask with intermittent shaking. The strength of the exchanged metal ion solution was obtained by titrating against 0.1M EDTA (standardized with Pb(NO₃)₂).

Then the distribution coefficient was determined by using the formula-

$$K_d = (I - F) / F.V / W$$

Where, I = Initial volume of EDTA (0.1M) consumed by cations before adding exchanger.
 F = Volume of EDTA (0.1M) consumed by cations after equilibrium.

V is the initial volume of the metal ion solution in mL for analysis and W is the initial dry mass of ion exchanger in mg. The distribution coefficient (K_d) values are given in Table 1.

Table 1. Distribution coefficient Values of various metal ions

Metal ions	Distribution coefficient (K_d) Values
Ni ²⁺	35.2
Cd ²⁺	20.0
Mg ²⁺	22.0
Pb ²⁺	17.0
Ca ²⁺	23.0
Cu ²⁺	28.0
Fe ²⁺	25.0
Na ⁺	15.0
Y ³⁺	21.0
Ce ³⁺	14.0

2.5 Preparation of the Membranes

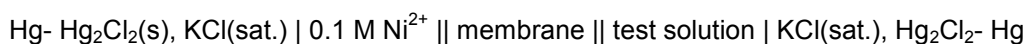
A number of membranes were prepared by using varying amount of epoxy resin as a binding material. ZrSbW in H⁺ form is used as an electro- active material during preparation of membranes. Desired amount of finely powdered exchanger was mixed thoroughly with epoxy resin in varying amounts (w/w) to make a near homogeneous paste which was then, spread between the folds of butter paper. Glass plates were kept below and above the paper folds as supports. In order to control the thickness of the membranes, pressure of 2.0 Kg cm⁻² was applied over the glass plates for 24 hours and left to dry. The sheet of membrane, thus obtained was then, dipped in distilled water to remove the paper from the membrane surface.

2.6 Storage of Electrode

Electrodes were stored in distilled water when not in use for more than one day. These were activated by keeping immersed in the 0.1 M Ni²⁺ ion solution for two hours, to compensate for any loss of metal ions in the membrane phase that might have taken place due to a long storage in distilled water. Electrodes were then washed thoroughly with distilled water before use.

2.7 EMF Measurements

The membrane was fixed to one end of glass tube 1.8 cm (internal dia.) using epoxy resin. These were then equilibrated with 0.1 M Ni²⁺ ion solution for 24 hours. The tube was filled with a solution of 0.1 M Ni²⁺ ion solution and immersed in a beaker containing test solutions of varying concentrations. All the emf measurements were carried out using the following cell assembly (Fig. 1):



A digital potentiometer (Equiptronics EQ-602, India) was used for the potential measurements at 25°C. Activities were calculated according to Debye- Huckel equation [41]. Test solutions of Ni²⁺ were obtained by gradual dilution of 0.1 M Ni²⁺ solution and their potential measurements were made in un- buffered solution.

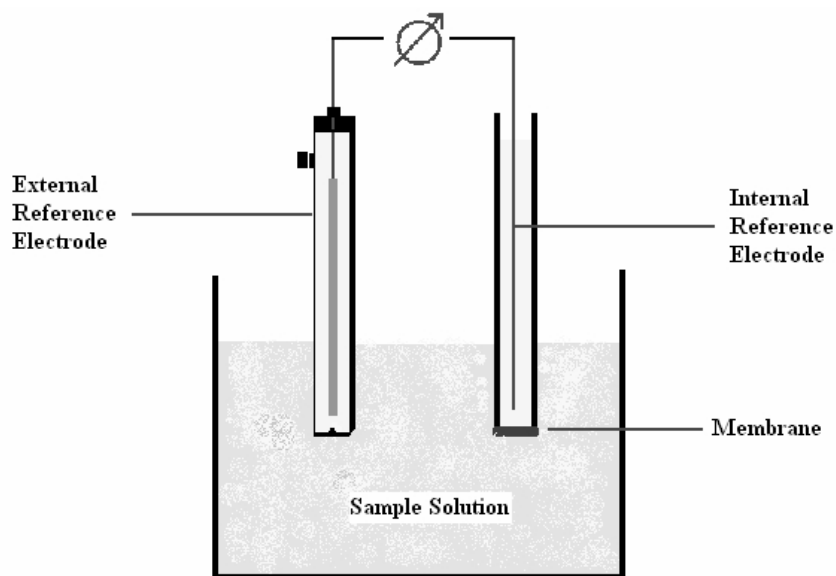


Fig. 1. Schematic diagram of an ion-selective potentiometric cell assembly.

Table 2. Optimization of Membrane Ingredients

Electrode No.	ZrSbW (%)	Binder	Slope (mV/decade)	Measuring Range (M)	Response Time (s)
1.	60	epoxy	20.0	$1.2 \times 10^{-6} - 10^{-1}$	15
2.	50	epoxy	20.0	$3.1 \times 10^{-6} - 10^{-1}$	10
3.	40	epoxy	35.0	$6.3 \times 10^{-6} - 10^{-1}$	15

3. CALIBRATION CURVE AND STASTICAL DATA

The potential response of the proposed sensor based on zirconium (IV) antimonotungstate (composition no. 2) at varying concentrations of nickel ions shows a linear response to the concentration of nickel ions in the range $1.0 \times 10^{-6} - 1.0 \times 10^{-1} \text{ mol L}^{-1}$, as shown in table 2 and Fig. 2. EMFs were plotted against log of activities of the Ni²⁺ ion. Experiment was repeated five times to check the reproducibility of the electrode system. A standard deviation of $\pm 0.9 \text{ mV}$ was observed. A representative calibration curve is shown in Fig. 2. The limit of detection, as determined from the intersection [42-43] of the two extrapolated segments of the calibration graph, was $3.1 \times 10^{-6} \text{ M}$.

Response time of electrodes was less than 10 seconds. The sensing behavior of the membrane remains unchanged when the potentials are measured either from low to high or from high to low concentration. It shows that the response was rapid and reversible. The non-Nernstian behavior of the electrode may be due to a possible discrepancy between the

ions activities in the bulk and at the phase boundary, i.e. the uptake of the ions by the membranes results in a depletion zone of the analyte ion from the nearest diffusion layer. This is supported by earlier reports of Jain et al. [44] and Malik et al. [45]. In terms of lifetime of the epoxy membrane electrodes, their response stability was observed for five months. The electrode was stored in 0.1M Ni^{2+} ion solution when not in use to avoid any change in the concentration in membrane phase.

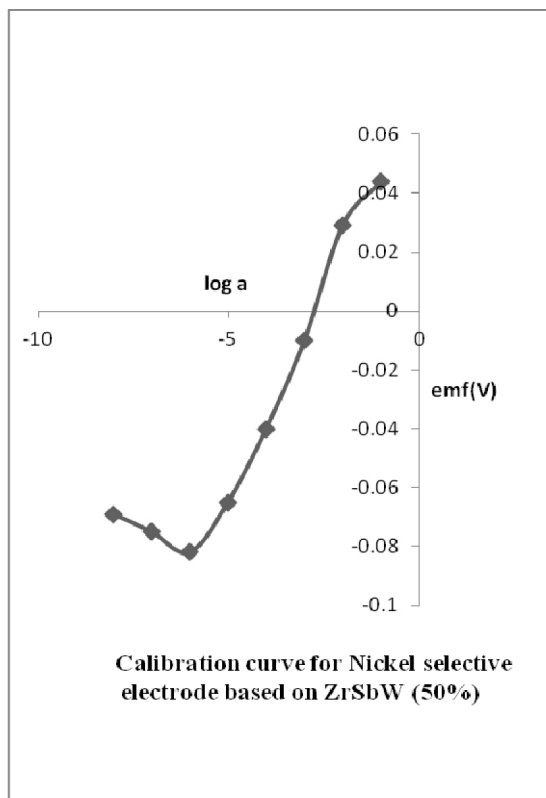


Fig. 2. Calibration curve for Nickel selective electrode based on ZrSbW (50%)

4. EFFECT OF INTERNAL SOLUTION CONCENTRATION

The effect of internal solution on the response of the proposed sensor for Ni^{2+} ion was studied using 10^{-1} M to 10^{-3} M internal solution concentration for ZrSbW. The results for the effect of internal solution for ZrSbW are given in Table 3 and Fig. 3. The results show that a variation in concentration of the internal solution does not have any significant effect on the response of the electrode expect for an expected change in the intercept of the curves as observed by Sharma et al. [46]. Internal Solution of conc. 1.0×10^{-3} was selected for further study.

Table 3. Effect of internal solution concentrations on response of Nickel (II) ion-selective electrode

Internal solution conc.(M)	Binder	Slope(mV/decade)	Detection limit (M)	Response time (Sec.)
1.0×10^{-1}	epoxy	20.0	3.1×10^{-7}	10
1.0×10^{-2}	epoxy	27.0	1.9×10^{-7}	15
1.0×10^{-3}	epoxy	28.0	1.0×10^{-7}	15

5. EFFECT OF pH

It is very important to find out the pH range where the electrode can work without interference from hydrogen ions present in aqueous solutions. The influence of pH on the potential response of the electrode was studied at 10^{-3} M internal solution concentration over a pH range of 1.5- 12. The results are shown in Fig. 4. pH was adjusted by introducing small drops of HCl (0.1M) or NaOH (0.1M) as per requirement. The potential is independent of the pH range 2.90 - 9.20. Hence, this pH range may be chosen as the working pH range for the electrode assembly. The variation above and below this pH range may be due to the formation of $\text{Ni}(\text{OH})_2$ and protonation of oxygen atoms of exchangers, respectively [47 - 48]. The hydroxyl formation significantly reduces the measured activity of free Nickel.

6. SELECTIVITY COEFFICIENT AND ANALYTICAL PROPERTIES OF Ni (II) – SELECTIVE ELECTRODE

Selectivity is one of most important characteristic of electrode, which defines the extent to which it may be employed in the determination of a particular ion in the presence of other interfering ions. Potentiometric selectivity coefficients of the nickel membrane electrode were evaluated by the fixed interference method (FIM) [42,43]. According to FIM, a calibration curve was plotted for the varying primary ion concentration in a constant backdrop of the interfering ion. The linear curve of the electrode was a function of the primary ion activity and was extrapolated until at the lower detection, it intersects with the observed potential for the background linear segment of the calibration curve. The selectivity coefficients are calculated from these two segments of the calibration curve by using formula:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}}$$

Where, a_A is the activity of the primary ion and a_B the activity of the interfering ion. z_A and z_B are their respective charges.

The results are given in Table 4. The electrode has a reasonably good selectivity over some common alkali, transition and rare earth metal ions. Selectivity coefficient values are better at lower interfering ion concentration.

Table 4. Selectivity coefficient values for Ni²⁺ - Selective electrode based on ZrSbW as calculated by FIM method

Interfering ion (B)	Selectivity co-efficient values	
	Interfering ion concentration (10 ⁻³ M)	Interfering ion concentration (10 ⁻⁴ M)
Zn ²⁺	0.20	0.0420
Cd ²⁺	0.71	0.0150
Mg ²⁺	0.42	0.0600
Ca ²⁺	0.31	0.0980
Pb ²⁺	0.20	0.1100
Ce ³⁺	0.45	0.0810
Pr ³⁺	0.61	0.0710
Na ⁺	0.35	0.0420
Fe ³⁺	0.90	0.0730
Y ³⁺	0.66	0.0720
Cu ²⁺	0.72	0.0924

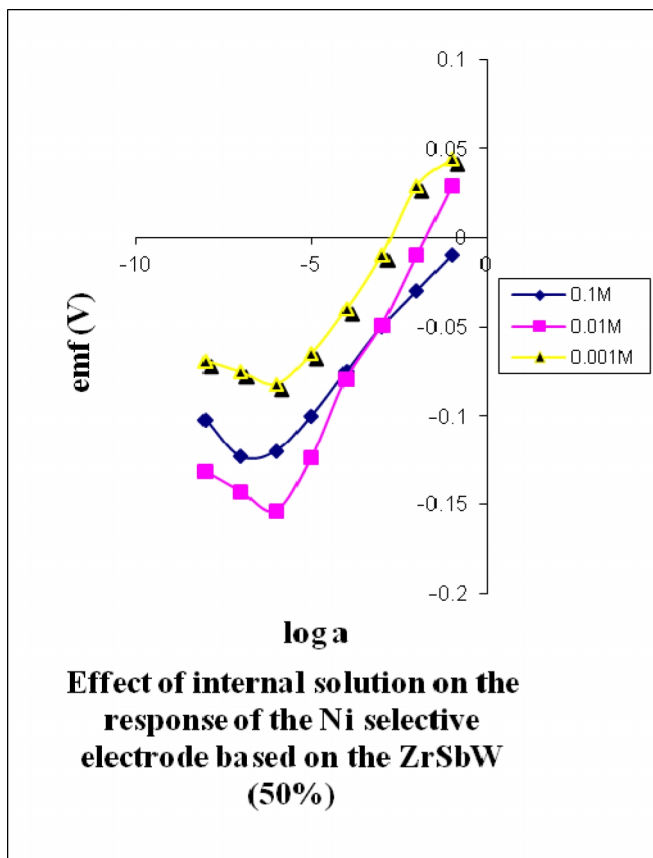


Fig. 3. Effect of internal solution on the response of the Ni selective electrode based on ZrSbW (50%)

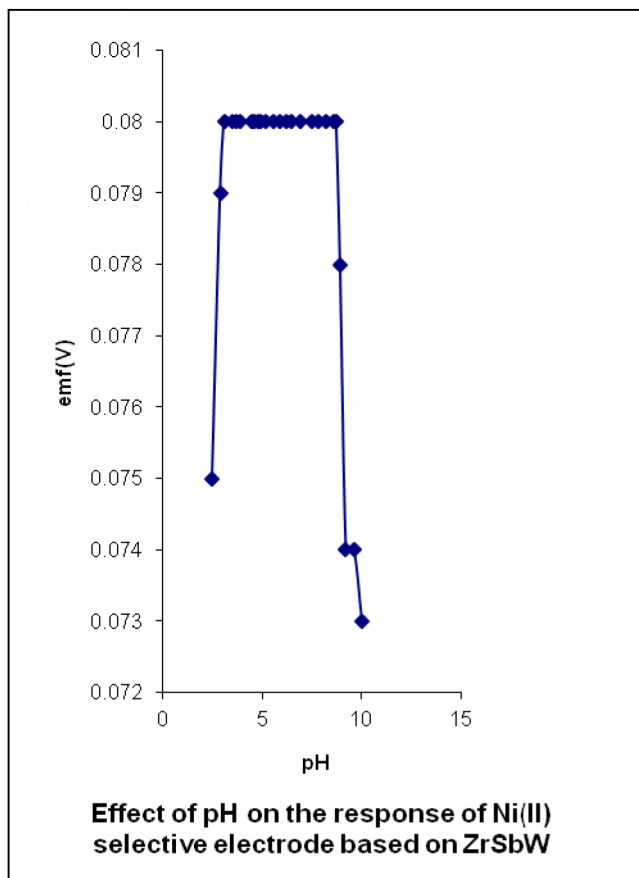


Fig. 4. Effect of pH on the response of Ni(II) selective electrode based on ZrSbW (50%)

7. POTENTIOMETRIC STUDIES

The proposed membrane electrodes were found to work well under laboratory conditions. The practical utility of ZrSbW membrane sensor was tested by its use as indicator electrode for the titration of 20 ml of 1.0×10^{-2} M Ni^{2+} ions with 5×10^{-2} M EDTA. The emf data was plotted against the volume of EDTA added. The titration curve is shown in Fig. 5. The curve shows a sharp inflection point at the titrant volume corresponding to the end point, which corresponds to 1:1 complexation between Ni^{2+} and EDTA. The sharp inflection point shows that these electrodes can be used for the determination of Ni (II) ion potentiometrically [48].

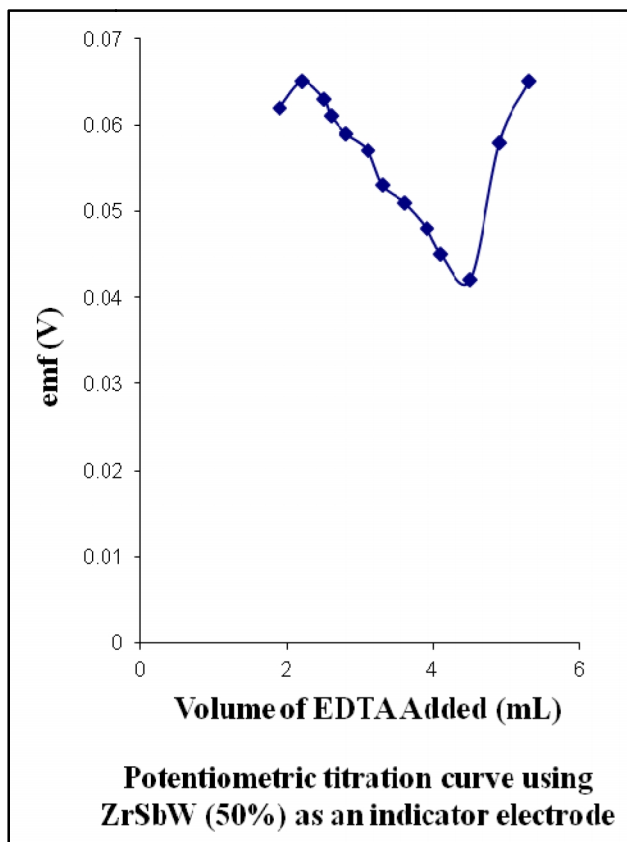


Fig. 5. Potentiometric titration curve using ZrSbW (50%) as an indicator electrode

8. A Comparative Study of Proposed ISE with Previously Reported in Literature

The present ISE based on zirconium (IV) antimonotungstate is comparable and superior in many results (such as selectivity, working linear range, response time, and working pH) than those reported in literature [49-53] (Table 5).

Table 5. Comparison studies of the proposed ISE with previously reported in literature

Cation	Ionophore	Slope (mV decade ⁻¹)	Linear Range (M)	Most Important Interfering ions (log K _{sel} > -2)	Ref.
Ni ²⁺	<i>N,N'</i> -bis-(4-dimethylaminobenzylidene)-benzene-1,2-diamine	30	$.0 \times 10^{-2}$ - 2.0×10^{-7}	Tl ⁺ , Ag ⁺	49
	<i>N</i> -(2-hydroxybenzyl)- <i>N'</i> -(2-hydroxybenzylidene)-ethylenediamine and <i>N</i> -(2-hydroxybenzylidene)-Al ³⁺ -(2-picolyl)ethylenediamine (II)	30 and 29	6.3×10^{-6} to 5.0×10^{-1} and 3.2×10^{-6} to 5.0×10^{-1}	Ag ⁺ , Co ²⁺ , Hg ²⁺	50
	1) N1,N2-bis((naphthalen-1-ylmethylene)ethane-1,2-diamine	29.9	1.0×10^{-1} - 5.0×10^{-6}	Na ⁺ , K ⁺ , Ba ²⁺ , Co ²⁺ , Ag ⁺ , Zn ²⁺	551
	2) 2-hydroxy-1-naphthylidene-N-cyanoacetohydrazone	22	1.5×10^{-7} - 10^{-1}	Zn ²⁺ , Co ²⁺ , Cd ²⁺ , Mg ²⁺ , Ca ²⁺	-
	N-[2-thienylmethylidene]-2-propanolamine (TNAIIP) and N-[2-thienylmethylidene]aminopropane (TNAP)	29	1.0×10^{-6} - 1.0×10^{-2}		52
Cu ²⁺ , Ni ²⁺	Electrodes 1 and 2 are based on mixed complexes of Cu(II) and Ni(II) with <i>N</i> -[2-thienylmethylidene]-2-aminopyridine as ligand and electrodes 3 and 4 are based on the mixed complexes with <i>N,N'</i> -[2,2'-bis-thienylmethylidene]tolylene	29	1.0×10^{-5} - 1.0×10^{-2}	Zn ²⁺	53
Ni ²⁺	Sulphamethaxazole dizonium resorcinol in PVC.	29	5.0×10^{-5} - 1.0×10^{-1}	Zn ²⁺ , Co ²⁺ , Cd ²⁺ , Mg ²⁺ , Ca ²⁺ , Zn ²⁺	54
Ni ²⁺	1,2-di(o-salicylaldiminophenylthio)ethane (H ₂ DSALPTE)	---	1.0×10^{-5} to 5.0×10^{-3} M.	Na ⁺ , K ⁺ , Ba ²⁺ , Zn ²⁺ , La ³⁺ , Zr ⁴⁺ , Cd ²⁺	55
Ni ²⁺					This report

4. CONCLUSION

Electrochemical studies have been done on zirconium (IV) antimonotungstate by preparing ion exchange membranes using epoxy resin as support material. (50% ZrSbW and 50% epoxy resin) reveals a sub-Nernstian potentiometric response with the slope of 20 mV per decade for Ni^{2+} over a wide concentration range (10^{-6} to 10^{-1} M). The response time of the electrode is quite low and could be used for a period of 5 months with a good reproducibility. The proposed electrode reveals very high selectivity for Ni^{2+} in the presence of a wide variety of metal ions such as Zn^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Ce^{3+} , Na^+ , Ca^{2+} , Mg^{2+} , Pr^{3+} , Y^{3+} and Fe^{3+} at concentrations 1×10^{-3} M and 1×10^{-4} M. Effect of internal solution concentration was studied. The proposed sensor can be used in the pH range of 2.90 - 9.20. It was used as an indicator electrode in the potentiometric titration of Ni^{2+} ions against EDTA. The proposed electrodes have reasonably good lifetime, detection limit, pH range and selectivity coefficient. This can also be used as indicator electrodes for trace level determination of Nickel ions. A comparative analysis of the proposed sensor, given in table 5, with the reported nickel sensors show that this sensor has good life time and pH range for working.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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