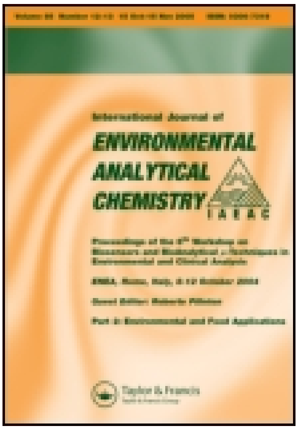

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Potentiometric determination of neodymium (III) ions using tin (IV) antimonotungstate and zirconium (IV) antimonotungstate as electro-active materials

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Potentiometric determination of neodymium (III) ions using tin (IV) antimonotungstate and zirconium (IV) antimonotungstate as electro-active materials

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Neodymium (III)-selective electrodes have been prepared by using tin (IV) antimonotungstate (SnSbW) and zirconium (IV) antimonotungstate (ZrSbW) as electro-active materials and epoxy resin as a binding material. In the case of SnSbW, best performance is exhibited by a membrane having the composition: tin (IV) antimonotungstate (50%) and epoxy resin (50%). It shows excellent response in the concentration range of 10^{-4} M to 10^{-1} M Nd (III) ion with a super-Nernstian slope of 40.0 mV/decade. It has a fast response time of 20 seconds and can be used for at least six months without any considerable divergence in potential. In the case of ZrSbW, best performance is exhibited by a membrane having the composition: zirconium (IV) antimonotungstate (40%) and epoxy resin (60%). It shows excellent response in the concentration range of 10^{-5} M to 10^{-1} M Nd (III) ion with a near-Nernstian slope of 25.0 mV/decade. It has a fast response time of 10 seconds and can be used for at least six months without any considerable divergence in potential. Effect of internal solution has been studied and the electrode was successfully used in partially non-aqueous medium, too. Selectivity coefficients have been determined by FIM method, with respect to alkali, alkaline earth, some transition and rare earth metal ions. ZrSbW electrode can be used in the pH range of 2.9–9.9 and SnSbW shows pH range 3.0–9.0. Both the electrodes have been used as indicator electrodes in the potentiometric titration of Nd (III) ions against EDTA.

Keywords: fixed interference method (FIM); inorganic ion exchanger; potentiometric titration; ion selective electrode (ISE)

1. Introduction

Nowadays more and more rare earth elements are being applied in agriculture as micro element fertiliser in China because of their ability to improve the yield and quality of crops [1,2]. Neodymium is an important member of the lanthanides family. It is suggested that Nd^{3+} had some biological effects similar to Ca^{2+} and could perform some functions of Ca^{2+} under given conditions [3]. Probably because of similarities to Ca^{2+}, Nd^{3+} has been reported to promote plant growth [4]. Due to several negative influences, it is very important to devise methods for its determination. The available methods for the trace determination of rare earth metal ions in solution include spectrophotometry, isotope

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dilution, mass spectroscopy, X-ray fluorescence, etc. [5–10]. These methods are either time consuming, involving multiple analysis or too expensive for most of the analytical laboratories.

Potentiometric sensors offer an inexpensive and convenient method for analysis of rare earth metal ions in solutions. There has been an increased interest in developing such sensors for rare earth metal ions recently and many reports [11–20] have been given on various metal ions like La^{3+}, Ce^{3+}, Sm^{3+} and Yb^{+3}, etc.

However, a survey of the literature shows that there are only a few reports on neodymium-selective electrodes. Neodymium-selective electrodes were prepared by Shamsipur *et al.* [21] and Ganjali *et al.* [22–24] using 5-Pyridino-2,8-dithia[9](2,9)-1, 10-phenanthroline-phane and N-(2-furylmethylene)pyridine-2,6-diamine),2-{[(6-Aminopyridin-2-yl)imino]methyl}-phenol,benzyl bis-thiosemicarbazone as electro-active materials, respectively. But all of these electrodes are based on neutral carriers.

Therefore, it was interesting to use inorganic ion exchanger as an electro-active material for our studies. Inorganic ion exchange membrane has several advantages over the organic ion exchangers, e.g. their ability to withstand ionising radiations and high temperature without undergoing degradation and their remarkably high selectivity [25]. Ion-selective electrodes employing inorganic ion exchanges as sensory molecules have been reviewed by Arnold and Solsky [26] and Buck [27]. It has been established that hydrous oxide combined with anion such as vanadates, phosphates, molybdates and tungstate produce superior ion exchangers [28–30]. Inorganic ion exchanger tin (IV) antimonato-tungstate (SnSbW) and zirconium (IV) antimonotungstate (ZrSbW) show better selectivity for neodymium (III) ions [31] in comparison to other rare earth metal ions. Hence they have been tried as electro-active materials for preparing neodymium (III) ion selective electrode.

2. Experimental

2.1 *Reagents*

Tin (IV) chloride and sodium tungstate needed for the preparation of tin (IV) antimonotungstate was procured from C.D.H. Chemicals, India, while potassium pyroantimonate was procured from S.D. Fine Chemicals, India. Neodymium (III) chloride and other rare earth chlorides were purchased from C.D.H. Chemicals, India. All the chemicals were of analytical grade and hence were used as such. A solution of neodymium (III) chloride was standardised against EDTA solution using xylenol orange as an indicator. Double-distilled deionised water was used throughout the experiments.

2.2 *Instruments*

EMF measurements were made using a digital potentiometer (Microsil EQ/602, India) with an accuracy of 0.1 mV.

2.3 *Preparation of tin (IV) antimonatotungstate (SnSbW)*

Tin (IV) antimonatotungstate was prepared by adding tin (IV) chloride (0.1 M) (containing hydrofluoric acid, 12 mL/L) to a continuously stirred equimolar mixture of potassium pyroantimonate and sodium tungstate solutions at 50°C in a volume ratio of

2 : 1 : 1. Gelatinous white precipitates are obtained and 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 phosphates, then 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 (0.1 M) for 24 hours with intermittent changing the acid and finally dried at 40°C. The product was washed with DMW in order to remove excess acid.

2.4 *Preparation of zirconium (IV) antimonatotungstate (ZrSbW)*

Zirconium (IV) antimonotungstate was prepared by adding zirconyl oxychloride (0.1 M, containing 12 mL/L hydrofluoric acid) 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 (0.1 M) for 24 hours with intermittent changing the acid and finally dried at 40°C. The product was washed with DMW to remove excess acid.

2.5 *Preparation of membranes*

A number of membranes were prepared using varying amount of epoxy resin as a binding material. ZrSbW and SnSbW in H^+-form are used as electro-active materials during preparation of the 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. A 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 *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 Nd (III) ion solution for 24 hours. The tube was filled with a solution of 0.1 M Nd (III) 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:

$$\mathbf{Hg{-}Hg_2Cl_2\,(s),\,KCl\ (sat.)|0.1M\ Nd\ \ (III)||membrane||test\ solution|}$$
$$\mathbf{KCl\ (sat.),\,Hg_2Cl_2{-}Hg}$$

A digital potentiometer (Microsil EQ/602, India) was used for the potential measurements at 25 ± 0.1°C. Activities were calculated according to Debye-Huckel equation [32]. Test solutions of Nd (III) were obtained by gradual dilution of 0.1 M Nd (III) solution and their potential measurements were made in unbuffered solution.

3. Results and discussion

3.1 *Optimisation of membrane composition and calibration curves*

The effect of membrane composition on the response of the electrode was studied. For this purpose, the performance parameters, such as slope of the calibration curve, measurement range and the response time were compared for prepared electrodes. The results are given in Table 1. Results show that the SnSbW electrode with composition: tin (IV) antimonotungstate (50%) and epoxy resin (50%) shows good excellent response in the concentration range of 10^{-4} M to 10^{-1} M Nd (III) ion with a super-Nernstian slope of 40.0 mV/decade. It has a response time of 20 seconds. In the case of ZrSbW, best performance is exhibited by a membrane having the composition: zirconium (IV) antimonotungstate (40%) and epoxy resin (60%). It shows good response in the concentration range of 10^{-5} M to 10^{-1} M Nd (III) ion with a near-Nernstian slope of 25.0 mV/decade. It has a fast response time of 10 seconds. So these two electrodes were selected for further studies.

Potential measurements were made on the selected electrode for different concentrations of Nd (III) ion solutions. EMFs were plotted against log of activities of the neodymium ion. Experiment was repeated five times to check the reproducibility of the electrode system. A standard deviation of ± 1.0 mV was observed for SnSbW and ZrSbW-based electrode. Representative calibration curves are shown in Figure 1. The slope was calculated according to IUPAC recommendation [27,33] from the intersection of the two extrapolated linear portions of the curve.

The over-Nernstian response of this kind of electrodes is common [34,35]. A higher slope may be due to poor permeability and incomplete perm selectivity of the membrane matrix for the neodymium ion. Membranes of this type sometimes show permeability for the anions [36] as well. The non-Nernstian behaviour of the electrode may also 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.* [34]. Pungor *et al.* [37,38] have also explained the Super-Nernstian slope observed for Ag^+ and I^- selective electrode. Hence the higher value of slope in no way hinders the determination of Nd (III) ion in the aqueous medium. Response time of electrodes was 10–20 seconds. The sensing behaviour of the membranes remain unchanged when the potentials are measured either from low to high or from high to low concentration. The electrode was stored in 0.1 M Nd (III) ion solution when not in use to avoid any change in the concentration in membrane phase.

Table 1. Optimisation of membrane ingredients.

Sensor	Electrode no.	(%) of sensor	Binder	Slope (mV/decade)	Measuring range (M)	Response time (s)
SnSbW	Nd-1	60(%)	Epoxy	45	10^{-4}–10^{-1}	20
	Nd-2	50(%)	Epoxy	40	10^{-4}–10^{-1}	20
	Nd-3	40(%)	Epoxy	36	5×10^{-3}–10^{-1}	25
ZrSbW	Nd-4	60(%)	Epoxy	29	2.5×10^{-5}–10^{-1}	15
	Nd-5	50(%)	Epoxy	27	1.0×10^{-5}–10^{-1}	25
	Nd-6	40(%)	Epoxy	25	6.3×10^{-6}–10^{-1}	10

3.2 *Effects of internal solution concentration*

The effect of internal solution on the response of the proposed for Nd (III) ion was studied using 10^{-1} M to 10^{-3} M internal solution concentration for SnSbW and by using 10^{-1} M to 10^{-3} M internal solution concentration for ZrSbW based electrodes. The results for the effect of interal solution for SnSbW and for ZrSbW are given in Table 2. The results show that a variation in concentration of the internal solution does not have any significant effect on the response of the electrode except for an expected change in the intercept of the curves as observed by Mittal *et al.* [18] and Ganjali *et al.* [39].

3.3 *Effect of pH*

The influence of pH on the potential response of the electrode was studied at 2×10^{-3} M over a pH range of 2.0–12.0 for the SnSbW and ZrSbW based electrode. The results are shown in Figure 2. The pH was adjusted by introducing small drops of HCl (0.1 M) or NaOH (0.1 M) as per requirement. The potential is independent of the pH range 3.0–9.0 and 2.9–9.9 for the SnSbW and ZrSbW based electrodes, respectively. Hence this pH range may be chosen as the working pH range for the electrode assembly. The variation above

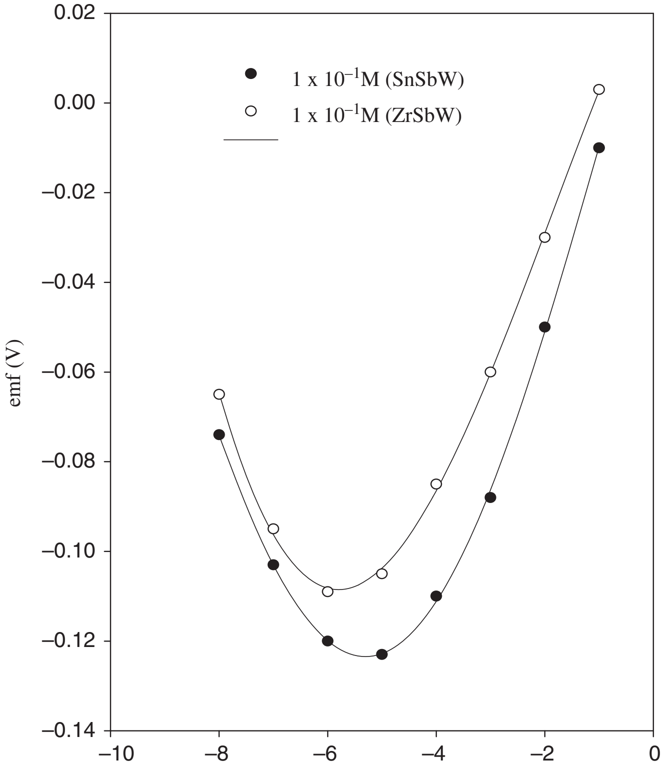

Figure 1. Calibration curve for Nd (III)-selective electrodes based on SnSbW and ZrSbW.

Table 2. Effect of internal solution concentrations on response of Nd (III) ion-selective electrodes based on ZrSbW and SnSbW.

Sensor	Composition of membrane	Internal soln. conc.	Binder	Slope (mV/decade)	Response time (S)
ZrSbW (%)	60%	10^{-1} M	Epoxy	29	15
		10^{-2} M	Epoxy	25	30
		10^{-3} M	Epoxy	30	30
	50%	10^{-1} M	Epoxy	27	25
		10^{-2} M	Epoxy	27	10
		10^{-3} M	Epoxy	28	20
	40%	10^{-1} M	Epoxy	25	20
		10^{-2} M	Epoxy	24	10
		10^{-3} M	Epoxy	22	20
SnSbW (%)	60%	10^{-1} M	Epoxy	39	20
		10^{-2} M	Epoxy	41	20
		10^{-3} M	Epoxy	38	20
	50%	10^{-1} M	Epoxy	40	10
		10^{-2} M	Epoxy	37	10
		10^{-3} M	Epoxy	40	20
	40%	10^{-1} M	Epoxy	38	20
		10^{-2} M	Epoxy	38	10
		10^{-3} M	Epoxy	35	20

and below this pH range may be due to the formation of Nd $(OH)_3$ and protonation of oxygen atoms of exchangers, respectively.

3.4 *Selectivity coefficient and analytical properties of Nd (III) selective electrodes*

Selectivity is one of the most important characteristics of electrode, which defines the nature of the device and 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 neodymium membrane electrode were evaluated by the fixed interference method (FIM) [27,33] at 1×10^{-3} M interfering ion concentration. According to this method, a calibration curve is drawn for the primary ion with a constant interfering ion background. The linear portion of the curve is extrapolated until it intersects with the second linear part of the curve in the low concentration region. The selectivity coefficients are calculated from these two segments of the calibration curve:

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

The results given in Table 3 show potentiometric selectivity coefficients of SnSbW and ZrSbW based sensors. Results are obvious that the electrode has a reasonably good selectivity with respect to rare earth metal ions, considering the fact that all rare earths have identical sizes and properties. It also has a good selectivity over some common alkali, alkaline earth and transition metal ions.

The results have been compared with previous reports [21,23] and have been found to be either comparable or in some cases even better. Further, selectivity studies for some new metal ions like Dy (III), Y (III), Fe (III), Tb (III), Al (III), Eu (III) and Pr (III) have been reported.

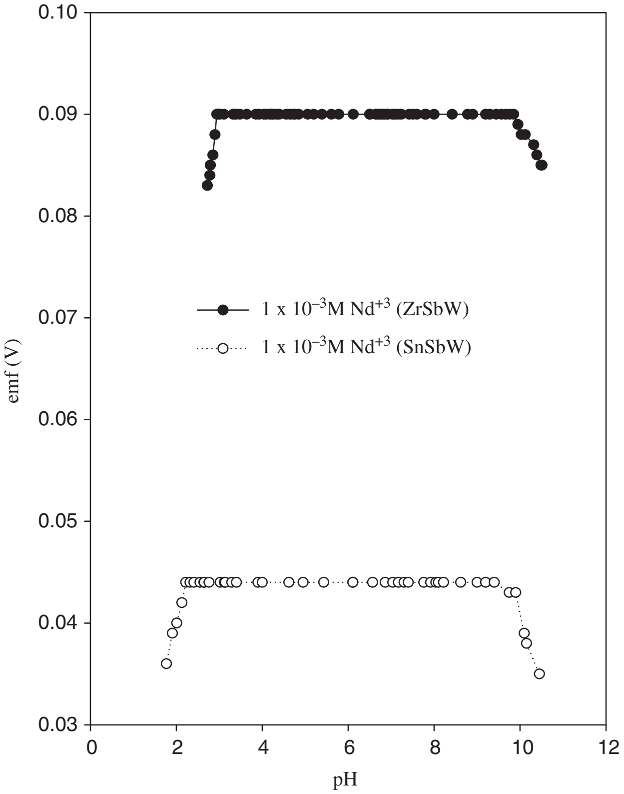

Figure 2. Effect of pH on the response of Nd (III)-selective electrodes based on ZrSbW and SnSbW.

Table 3. Selectivity coefficient values for Nd-(III) selective electrodes.

Interfering ion (B)	Selectivity coefficient values $K_{A,B}$			
	(With sensor SnSbW)	(With sensor ZrSbW)	Ref. No. 21 (log $K_{A,B}$)	Ref. No. 23
La(III)	0.015	0.0190	1.5 ± 0.2	2.5×10^{-2}
Sm(III)	0.019	0.0125	1.9 ± 0.1	2.7×10^{-2}
Gd(III)	0.006	0.0060	1.3 ± 0.1	1.5×10^{-2}
Eu(III)	0.025	0.0150	–	–
Pr(III)	0.250	0.0120	–	–
Ce(III)	0.062	0.0125	1.3 ± 0.1	2.7×10^{-2}
Dy(III)	0.079	–	–	–
Y(III)	0.039	–	–	–
Fe(III)	0.012	–	–	–
Ca(III)	0.004	–	2.6 ± 0.2	–
Tb(III)	–	0.0390	–	–
Al(III)	–	0.0310	–	–
Pb(II)	–	0.0015	1.7 ± 0.2	–
Cu(II)	–	0.0010	1.4 ± 0.2	–
Na(I)	–	0.0005	2.5 ± 0.1	2.1×10^{-3}

Table 4. Effect of partially non-aqueous media on the working of Nd(III)-selective electrodes ZrSbW and SnSbW.

		Sensor ZrSbW		Sensor SnSbW	
Solvent	Percentage (v/v)	Slope (mV/decade)	Measuring range (M)	Slope (mV/decade)	Measuring range (M)
Acetone	30%	23	5.0×10^{-6}	42	4.9×10^{-4}
	20%	24	3.9×10^{-6}	42	4.9×10^{-4}
	10%	30	3.9×10^{-6}	42	3.9×10^{-4}
Ethanol	30%	20	6.3×10^{-6}	36	4.7×10^{-4}
	20%	22	3.9×10^{-6}	39	4.4×10^{-4}
	10%	24	1.9×10^{-5}	39	4.4×10^{-4}
Methanol	30%	23	1.2×10^{-5}	39	3.9×10^{-4}
	20%	20	7.9×10^{-6}	42	4.9×10^{-4}
	10%	23	1.5×10^{-5}	40	3.6×10^{-4}

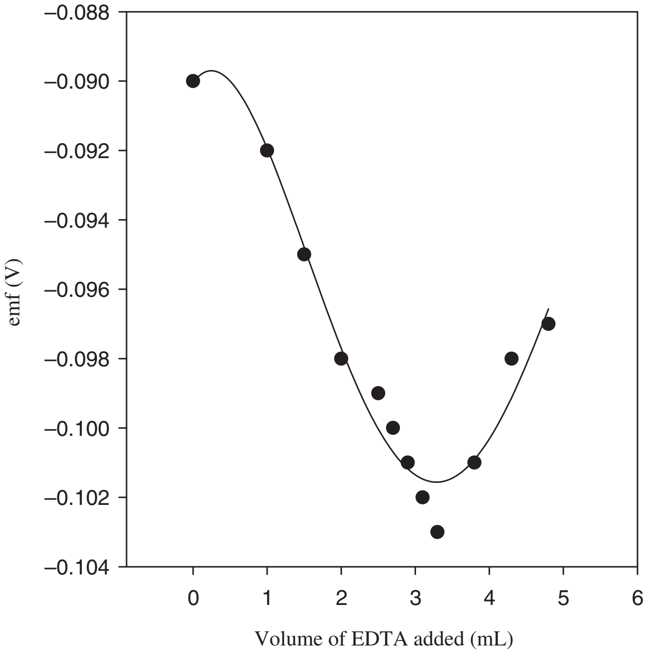

Figure 3. Potentiometric titration curves using proposed SnSbW sensor as an indicator electrode.

3.5 *Effect of partially non-aqueous medium on the working of Nd (III) electrodes*

The proposed sensors are investigated in partially non-aqueous media using acetone, ethanol and methanol. The slope remains unaltered with the addition of non-aqueous solvents. Hence the proposed sensor can be used in partially non-aqueous solvents. The results are given in Table 4 for ZrSbW and for SnSbW.

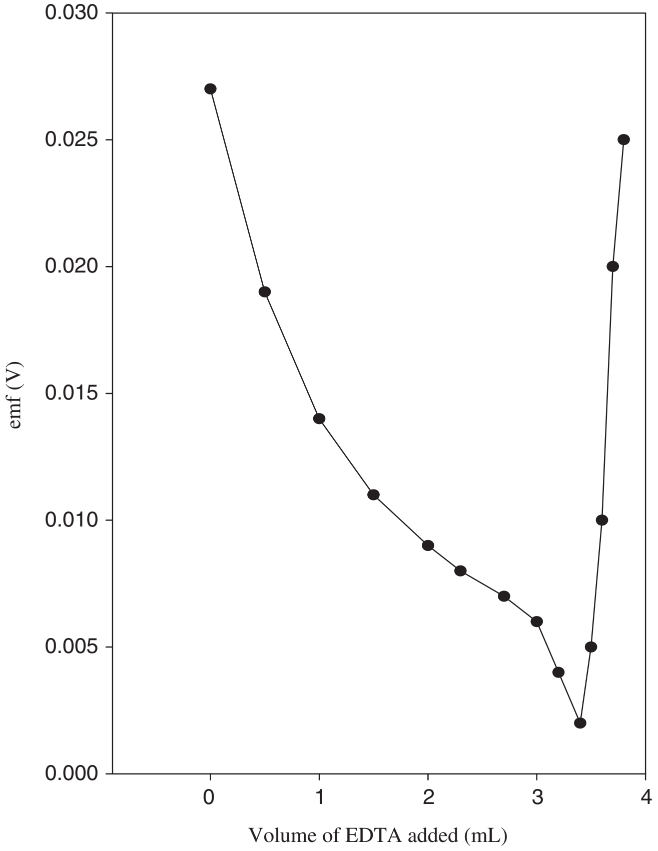

Figure 4. Potentiometric titration curves using proposed ZrSbW sensor as an indicator electrode.

3.6 *Potentiometric titration*

The practical utility of both SnSbW and ZrSbW membrane sensors were tested by their use as indicator electrodes for the titration of 20 ml of 10^{-3} M Nd (III) ions vs. 5×10^{-3} M EDTA and the emf data was plotted against volume of EDTA added. The titration curve for SnSbW sensor is shown in Figure 3. Figure 4 shows the results of 20 ml of 10^{-3} M Nd (III) ions vs. 5×10^{-3} M EDTA titration for ZrSbW based sensor electrode. The curves show a sharp inflection point at the titrant volume corresponding to the end point, which corresponds to 1 : 1 complexation between Nd (III) and EDTA. The sharp inflection point shows that these electrodes can be used for the determination of Nd (III) ion potentiometrically.

3.7 *Life time of electrode*

The proposed sensor can be used for at least six months without much deviation in the results obtained.

4. Conclusion

Zirconium (IV) antimonotungstate and tin (IV) antimonotungstate can both be successfully used as electro-active materials for making a neodymium (III)-selective membrane electrode. The electrodes have reasonably good lifetime, detection limit, pH range and selectivity coefficient and can be successfully used in partially non-aqueous mediums. They can also be used as indicator electrodes. However, on comparing the performance of the two sensors, it can be concluded that the one based on ZrSbW is better in terms of better measuring range, response time, Nernstian response and pH range.

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