Studies on PVC based chelating inorganic ion exchange resin membrane sensor for neodymium(III) ion

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Tetracycline sorbed zirconium(IV) tungstophosphate (TC-ZWP) has been used as a chelating agent for determination of rare earth metal ions i.e Nd(III). The poly(vinyl-chloride)-based membrane electrode exhibits a Nernstian response for Nd(III) ions over a wide concentration range (1 x 10⁻¹ to 5 x 10⁻⁵ M) with detection limit of 5 x 10⁻⁶ M. It has 25 s response time and can be used upto 45 days without any divergence in its potentials. The proposed membrane sensor reveals good selectivity for Nd(III) ions within the pH range of 3-7. Analytical application of electrode has been investigated for the quantitative determination of Nd(III) against standard EDTA solution.

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The recovery and concentration of metal ion at traces and ultra trace level from aqueous solution has been a subject of great interest for both analytical and industrial applications. The literature survey reveals that limited work has been done in the field of ion selective electrode for the rare earth metal ions. Recently, neutral carrier membrane electrode has been reported¹⁻³ using calix⁴ arenes as ionophores for the preparation of membranes. A lanthanum(III) electrode has been reported⁴⁻⁵, using crown ethers as electroactive material. Many ISEs for Sm(III) have been developed⁶⁻⁷. The present paper reports the studies of poly (vinyl chloride) based tetracyclined sorbed zirconium(IV) tungstophosphate ion exchange resin membrane sensor. The sensor exhibits significant selectivity for Nd(III).

Experimental Procedure

Materials
All chemicals and reagents for the preparation of the membrane and ion exchanger were of analytical grade. Metal solutions were prepared in conductivity water and standardization was carried out using standard methods.

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Instruments
A digital potentiometer (Equiptronics India) with a saturated calomel electrode as reference electrode was used for the potentiometric measurements and a digital pH-meter (Century CP-90) was used for the pH measurements. All the measurements were made at room temp. of about 27±1°C.

Preparation of membrane
Tetracycline sorbed zirconium (IV) tungstophosphate (TC-ZWP) as a chelating inorganic ion exchanger was prepared as described⁴. 0.6 g poly (vinyl chloride) dissolved in 6-8 mL tetra hydrofuran (THF)⁹ and 0.2 g tetracycline zirconium(IV) tungstophosphate in powdered form was mixed with PVC-THF solution to make a homogenous paste. The resulting paste was carefully spread evenly over a previously leveled plane glass plate and THF was allowed to evaporate to get a membrane. It was cut down into required size for further studies.

Characterization of membrane
After the conditioning of the membrane the physico-chemical properties of the membrane i.e water content, thickness, swelling and porosity were determined as described earlier⁸⁻¹³.
Water content (% total wet weight)
The membrane was first soaked in water to elute diffusible salt, blotted quickly with the Whatmann paper to remove surface moisture and weighed immediately. The membrane was further dried to a constant weight in vacuum over silica gel for 24 h. The water content (% total wet weight) was calculated using the equation,

\[
\frac{W_w - W_d \times 100}{W_w}
\]

where \( W_w \) is the wet weight of the membrane, and \( W_d \) is the dry weight of the membrane.

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

Porosity
Porosity (E) was determined as the volume of water incorporated in the cavities per unit membrane volume using the water content data,

\[
E = \frac{W_w - W_d}{AL\delta_w}
\]

where \( W_w \) is the wet weight, \( W_d \) is the dry weight, \( A \) is the area, \( L \) is the thickness of the membrane under study, and \( \delta_w \) is the density of water.

Fabrication of MISE
The membrane ion selective electrode MISE was fabricated as described by Craggs et al. An appropriate size of the membrane was cut from the parent membrane and was mounted at the lower end of the glass tube. A 0.1 M metal solution was used as the internal solution.

Potential measurements
The TC-ZWP based membrane electrode was used as an indicator electrode and a saturated calomel electrode (SCE) as the reference electrode in all potentiometric measurements. The potentiometric sensitivity towards Nd(III) was measured in freshly prepared solution of NdCl\(_3\) (1 x 10\(^{-7}\) to 1 x 10\(^{-1}\)) M at 27 ±10°C. The solutions were stirred for 1 min and the potential readings were taken after stabilization of potentials.

Determination of neodymium in sibaiya phosphate ore
0.2 g of sibaiya ore was dissolved in 20 mL of 60% nitric acid, the solution was heated to near dryness and the residue dissolved in least volume of water, the clear solution was adjusted to 4-6 pH. The prepared solution was analyzed for Nd(III) ions.

Results and Discussion
The physical characteristics of the heterogeneous chelating ion exchanger (TC-ZWP) PVC based membrane electrode have been analyzed to correlate the ions in the membrane phase, potential generated across it and the selectivity of ions of interest. The properties of the membrane determined were found to be as: water content - 28.33%, porosity of the membrane - 0.0025, thickness - 0.59mm and swelling - 0.17mm. The data show that the membrane is of less porosity and lesser swelling capacity under given experimental conditions.

Response and lifetimes
The tetracycline sorbed zirconium(IV) tungstophosphate (TC-ZWP) membrane sensor was equilibrated with 0.1 M NdCl\(_3\) solutions before potential measurements. The optimum equilibration time was 4-5 days after that membrane exhibits reproducible potentials and no drift in potentials was observed. The potentials of the cell were measured with a fixed concentration (0.1M) of Nd(III) as internal solution and varying the Nd(III) concentration in test solution in the range of 1 x 10\(^{-7}\) to 1 x 10\(^{-1}\) M. The static response time thus obtained was about 25 s. The potentials generated by the membrane remained stable for about 60 min and then deviate very slowly. The membrane was mechanically and chemically stable and was used over a period of 45 days only after that it shows major divergence in the potentials. The short life time of the electrode may be attributed to the gradual loss of the ion exchanging activity of TC-ZWP.

The potentials observed were plotted against Nd(III) concentration in Fig.1. It is clear from the calibration curve (Fig.1) that the membrane electrode shows the linear potential response in the concentration range of 5 x 10\(^{-8}\) to 1 x 10\(^{-4}\) M with the slope of 21.7 mV per decade change of concentration. The detection limit from the calibration curve was found to be 5 x 10\(^{-8}\) M.
Fig. 1—Calibration curve of Nd^{3+}-selective (TC-ZWP)-PVC based membrane electrode

Fig. 2—pH versus electrode potential for Nd^{3+}-selective (TC-ZWP)-PVC based membrane electrode

10^{-4} \text{ M}. According to the Nernst Equation, the slope must be 19.6 mV/decade concentration change; hence the slope value is stated to be moderately over-Nernstian.

pH effect

The pH dependence of the electrode potential has been tested over the pH range 1-13 for 1x10^{-5} \text{ M} of Nd(III) ions (Fig. 2), where the pH adjustments were made with the diluted acid and base. The useful working pH range was found to be between 3-7 pH in which potential remains constant. Beyond this pH range the sharp change in potentials occurs, which may be due to the hydrolysis of Nd(III) at higher pH values and H^+ ions co flux at lower pH values.

Non-aqueous effect

The performance of the proposed sensor system was also investigated in partially non-aqueous medium using water-ethanol and water-acetone mixtures up to 10\% v/v. In these mixtures, the working concentration range and slope remain almost the same. However above 10\% non-aqueous contents, the slope decreased appreciably which indicates that the sensor has become less sensitive to Nd(III) in non-aqueous media.

| Table 1 — Selectivity coefficients $K$ values of Nd(III) selective (TC-ZWP) PVC membrane electrode for lanthanide metal ions |
|----------------------------------|------------------|------------------|
| Metal ion | Selectivity coefficients values $K$ |
| La^{3+} | $15.87 \times 10^{-3}$ |
| Ce^{3+} | $15.87 \times 10^{-3}$ |
| Pr^{3+} | $20.0 \times 10^{-3}$ |
| Sm^{3+} | $20.0 \times 10^{-3}$ |
| Eu^{3+} | $71.42 \times 10^{-3}$ |
| Gd^{3+} | $2.0 \times 10^{-3}$ |
| Tb^{3+} | $71.42 \times 10^{-3}$ |
| Dy^{3+} | $33.33 \times 10^{-3}$ |

| Table 2 — Potentiometric determination of Nd(III) in sibaiya phosphatic ore using Nd(III) sensor based on tetracycline sorbed zirconium(IV) tungstophosphate (TC-ZWP) |
|------------------|------------------|
| Sample | Nd(III) ppm | Nd- sensor | AAS Analysis |
| Low grade phosphatic ore | 629.96 | 639.34 |
| Upper grade phosphatic ore | 739.36 | 745.89 |

Potentiometric selectivity

The suitability of the sensor for Nd(III) ion determination in the presence of other ions depends on selectivity co-efficient of other ions. A number of trivalent lanthanide metal ion were tested using fixed interference method. The results are given in Table 1. It is evident from the selectivity coefficients data that the sensor exhibits a higher preference for Nd(III) ion as compared to other closely trivalent lanthanide ions.

Analytical applications

The practical utility of the proposed membrane sensor has been tested by its use as an indicator electrode for titration of $1.0 \times 10^{2}$Nd(III) with $1 \times 10^{2}$ M EDTA solution. The necessary adjustments of pH were made before adding the titrant. A sharp inflection point and perfect stoichiometry show noteworthy features of the membrane electrode.

This electrode has been proved to be useful for the direct potentiometric determination of Nd(III) content in sibaiya low grade as well as in upper grade phosphate ore samples. The results have been compared
with reported results\textsuperscript{14} obtained by AAS analysis, in Table 2 which indicates that content of Nd(III) ions in ores measured by Nd(III) sensor are in good agreement with those obtained by AAS analysis.

Conclusion

The chelating ion exchange resin proves to be suitable electroactive material for the fabrication of membrane sensor. Poly(vinylchloride) based tetracycline sorbed zirconium(IV) tungstophosphate chelating inorganic ion exchange resin membrane sensor exhibits promising selectivity for Nd(III) ions and this sensor can be used to estimate Nd(III) over a wide range of concentration i.e. $1 \times 10^{-1}$ to $5 \times 10^{-5}$ M.

References

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