Short Communication

Yttrium (III) Selective Electrode Based On Zirconium (IV) Phosphoborate

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Abstract: *Zirconium phosphoborate based heterogeneous membrane electrode has been used as a sensor for yttrium ions in aqueous medium. The electrode shows reproducible and Nernstian behavior for yttrium ions in the concentration range $10^{-4}M$ to $10^{-1}M$ with an RSD of 2%. The electrode does not show any change in response within a pH range of 5-9. The effect of internal solution concentration on the calibration curve was also studied. The electrode performance was also studied in partially non-aqueous medium (5% - 20%) of acetone and ethanol. The system was used successfully as an indicator electrode in potentiometric titration of yttrium ions with EDTA.*

1. INTRODUCTION

Lanthanides are widely distributed in low concentration throughout the earth's crust and are being used for various applications in electronic gadgets and other materials of daily use. Trace level determination of yttrium is being carried out by various analytical techniques such as neutron activation analysis[1], mass spectrometry[2] X-ray fluorescence[3], spectrophotometric[4], voltametric and amperometric techniques[5,6]. These methods are either time consuming, need expert technical manpower and involve multiple sample manipulations, or are too expensive.

Potentiometric sensors offer a simple, faster and cost effective method for the analysis of rare earth metal ions in solution. Ion selective liquid membrane electrodes containing chelate ligand complexes, such as crown ethers and their open chain analogs entrapped in polymer, suffer from the problem of leaching of electro active component and plasticizer from polymer matrix into sample solutions[7]. Inorganic ion exchanger membranes have several advantages over organic ion exchangers, e.g. their ability to withstand ionizing radiations and high temperature, without undergoing degradation and their remarkably high selectivity[8]. In contrast to such operational problems, we hereby present a heterogeneous solid membrane electrode based on low solubility inorganic ion exchanger[9]. In ion exchange membranes, the charged groups attached to the polymer backbone are freely permeable to oppositely charged ions under influence of electric field[10-13]. In such processes, ion interaction happens in a complex fashion with membrane, water and with each other. Knowledge of electrokinetic properties of IEMs is a major contributing factor behind decisions on about their applicability in specific processes because of their effect on overall system performance[14-20]. A simpler, faster and inexpensive method is proposed for the Yttrium (III) estimation in the presence of some rare earth cations. Araldite based ion selective electrode containing the salt of heteropoly acid zirconium phosphoborate as an electro active material has shown excellent response and selectivity for yttrium ion.

2. EXPERIMENTAL

Reagents: ziconium oxychloride, boric acid and phosphoric acid required for the preparation of zirconium(IV) phosphoborate (ZrPB) were received from s.d. Fine Chemicals Ltd., India. Hydrofluoric acid was purchased from Ranbaxy, India. Samarium chloride and other rare earth chlorides were purchased from Indain Rare Earth Chemicals Ltd., India. All the chemicals used were of analytical grade. All the stock solutions of rare earth metal ions were standardized with EDTA using Xylenol orange as indicator.

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Double distilled de-ionized water was used throughout the experiments.
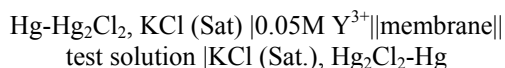
2.1. Preparation of Ion-Exchanger

The ion-exchanger was prepared by adding zirconyl oxychloride (0.1M) solution to a continuously stirred mixture of boric acid solution (0.1M) and phosphoric acid solution (0.1M) at 600 C, in the volume ratio 2:1:1. The gel produced in round bottomed flask was allowed to stand overnight. Then the gel was repeatedly washed with distilled water to remove chlorides from the mother liquor. The absence of chlorides in the mother liquor was tested with AgNO3 solution. After the gel became free from chlorides, it was filtered through Whatmann No.1 filter paper using Buchner funnel and suction pump. The gel was transferred from Buchner funnel to Petri dish. The precipitates in the Petri dish were dried in an air oven at 400C.When the gel dried completely, distilled water was added. Small granules of the ion-exchanger were formed with cracking sound.

2.2. Preparation of membrane

The required amount of finely powdered exchanger was mixed thoroughly with araldite in varying ratio (w/w) to make a nearly homogeneous paste, which was then spread between folds of the filter paper. The glass plates were kept above and below the paper for support. A pressure of 2.0 Kg/cm2 was applied over the glass plates for 24 h. The sheets of membranes thus obtained were then dipped in distilled water to remove the paper from membrane surface.

2.3. EMF Measurement

The membrane was fixed at one end of the glass tube of 1.8 cm (internal diameter) using araldite and then equilibrated with 0.05 M Y^{3+} and immersed in a beaker containing test solution of varying concentrations. All measurements were carried out using the following cell assembly:

$$\text{Hg-Hg}_2\text{Cl}_2, \text{KCl (Sat)} \,|0.05\text{M } Y^{3+}\|\text{membrane}\|$$
$$\text{test solution }|\text{KCl (Sat.), Hg}_2\text{Cl}_2\text{-Hg}$$

A digital potentiometer (Equiptrponics EQ-602, India) was used for potential measurements at 25 ± 0.1^0C. The activities were calculated according to Debye-Huckel equation[21]. Test solutions of Y^{3+} were obtained by gradual dilution of 0.1 M Y^{3+} solution, and potential measurements of them were taken in unbuffered solutions.

3. RESULTS AND DISCUSSIONS

3.1. Calibration Curve and Statistical Data

This membrane was investigated in detail as a Y(III) selective electrode, and all further studies were carried out on this membrane. The repeated monitoring of potential i.e. five identical measurements on the same portion of the concentration range, gave a standard deviation of ±1 mV (RSD 2%). The limit of detection $(1\times10^{-4}\text{M})$ was calculated according to IUPAC recommendations[22,23] from the intersection of two extrapolated linear portions of Figure 1. The response time of electrode is less than 15 second. The response time is still lower for relatively concentrated solutions as compared to dilute solutions. The sensing behavior of
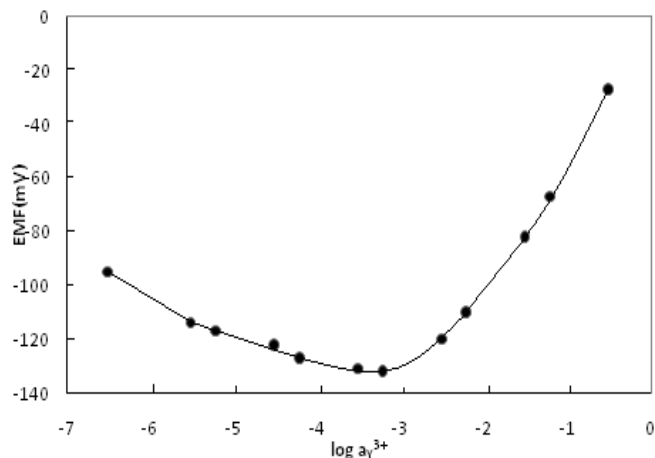

Figure 1. Calibration curve for Y(III)-selective electrode based on ZrPB
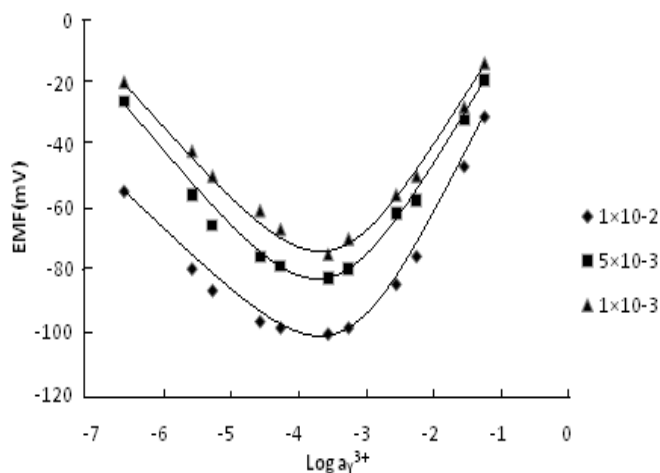

Figure 2. Effect of internal solution on response of Y(III)- Selective electrode based on ZrPB

the membranes remained unchanged when the potential is measured from low to high or from high to low concentration. These membranes could be used for at least four months without any measurable divergence. The electrodes were stored in Y(III) ion solution 0.05 M when not in use, to avoid any change in the metal ion concentration in membrane phase.

The ZrPB based electrode showed a near – Nernstian response. Membranes of this type sometimes show permeability for anions[24] as well. This preference for anions in lower concentration regions may also be responsible for non-Nernstian behavior of the electrode. Another reason for non-Nernstian behavior of electrode may also be the possible discrepancy between the ion activities in bulk and the phase boundary i.e. the uptake of ions by membranes results in depletion zone of analyte ions from the Nernst diffusion layer. This is supported by earlier reports of Jain et al.[25] and Malik et al.[26].
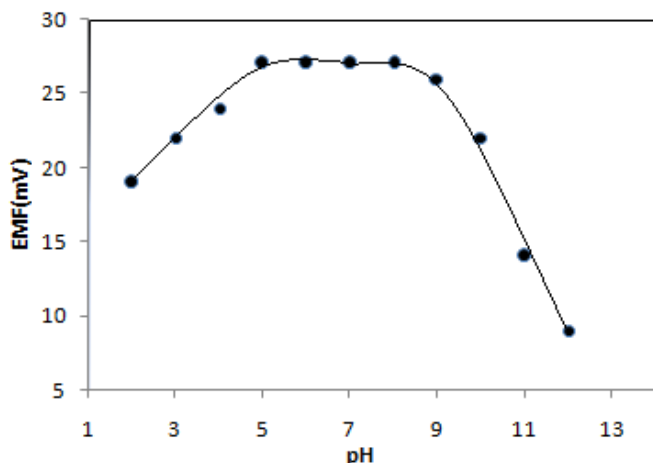
Figure 3. Effect of pH on the response of Y (III)-selective electrode based on ZrPB

Figure 4. Titration curve of Y (III) ions with EDTA solution using ZrPB based electrode

3.2. Effect of Internal Solution Concentration

The effect of internal solution on response of the proposed sensor for Y(III) ions was studied using 1×10^{-2}, 5×10^{-3} and 1×10^{-3} M internal solution concentration for ZrPB based electrodes. A variation in concentration of internal solution does not have any significant effect on the response of electrode except for change in intercept of curves as observed by Ganjali et al.[27].

3.3. Effect of pH

The influence of pH on potential response of the electrodes was studied using a Y(III) concentration of 1×10^{-3}M for the ZrPB based electrode. Experiments were conducted for number of Y^{3+} solutions, pH of which were adjusted between 2 to 12 by using suitable amounts of HCl and NaOH. Results are shown in Figure 3. EMF is independent of pH in the range 5.0-9.0 for Y (III) of concentration 5×10^{-2} M for the ZrPB based electrode. Variation above and below this pH range may be due to formation of $Y(OH)_3$ and protonation of oxygen atoms of metal oxide or –P=O type groups in the exchangers, due to their tendency to hydrolyze at higher pH ranges.

3.4. Selectivity coefficient values for Y (III)-selective electrodes based on ZrPB by FIM method

Selectivity is the single most important characteristic of any electrode which defines the nature of the device and extent to

which it may be employed in the determination of a particular ion in presence of other interfering ions. Potentiometric selectivity coefficients of the membrane were evaluated by fixed interference method [FIM][28,29] at 1×10^{-4} M and 1×10^{-5}M concentrations of the interfering ions. According to this method, a calibration curve is drawn for varying primary ion concentration in constant background of interfering ions. The linear response curve of the electrode is a function of primary ion activity and is extrapolated until at lower detection limit, it intersects with the observed potential for the background alone. The selectivity coefficients were calculated from these two extrapolated linear segments of the calibration curves. The log K_{ij} values for most of the lanthanides like Nd^{+3}, Pr^{+3}, Dy^{+3}, Tb^{+3} and Eu^{+3} were found to be in the range 0.4 to 0.9. The yttrium electrode was not very selective for other elements of the lanthanide series, being similar in chemical properties to that yttrium.

3.5. Potentiometric titrations

Potentiometric titrations were performed by using the proposed electrodes as indicator electrodes for titrations of Y^{3+} (1.0 x 10^{-3} M) with EDTA solution (1.0x 10^{-2} M). Titration curves are shown in Figure 4 for the ZrPB based sensors. The curves show sharp inflexion points at the titrant volume corresponding to the formation of a 1:1 complex.

4. ACKNOWLEDGEMENT

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Table 1. Effect of partially non aqueous media on the working of Y (III) –selective electrode based on ZrPB

Solvent	Volume of Solvent (v/v %)	Slope (mV/decade)	Measuring range (M)
Acetone	5	20.5	1×10^{-6} to 1×10^{-2}
	10	20.5	1×10^{-6} to 1×10^{-2}
	15	20.0	1×10^{-6} to 1×10^{-2}
	20	20.5	1×10^{-6} to 1×10^{-2}
Ethanol	5	21.2	1×10^{-6} to 1×10^{-2}
	10	21.0	1×10^{-6} to 1×10^{-2}
	15	20.0	1×10^{-6} to 1×10^{-2}
	20	20.0	1×10^{-6} to 1×10^{-2}

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