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Zirconium(IV) Phosphoborate-Based Ion Selective Membrane Electrode for Potentiometric Determination of Ba(II) Ions

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Zirconium phosphoborate based heterogeneous membrane electrode has been used as a chemical sensor in aqueous medium. The membrane demonstrates sub-Nernstian response in the concentration range of 10^{-5} to 10^{-1} mol L^{-1} Ba(II) ions, with a slope of 20.7 mV $decade^{-1}$. The designed sensor has a fast response time of 15 s and has a detection limit of 6.31×10^{-7} mol L^{-1} for Ba(II) ions. Effect of internal solution concentration on the slope of calibration curve was studied. The electrode was successfully used in partially non-aqueous medium. The proposed sensor shows good selectivity for Ba(II) ions with respect to rare earth metal and alkaline earth metal ions. The electrode does not show any change in response within pH range 3.5 to 9. The system was used successfully as an indicator electrode in potentiometric titration of Ba(II) ions with EDTA.

Keywords: Zirconium phosphoborate, Indicator electrode, Barium selective electrode, Potentiometric titration.

INTRODUCTION

Barium is a highly reactive metal that occurs naturally only in a combined state. It is widely spread in the earth's crust, especially in the sandstone, igneous rocks and shale [1]. Barium enters the environment through weathering of rocks and minerals. Anthropogenic releases are primarily associated with industrial processes. Barium is present in the atmosphere, surface water, soil and many foods. Barium exposure may be the source of several medical problems in human beings, including low blood potassium, respiratory failure, cardiac arrhythmias, muscle twitching, gastrointestinal dysfunction, paralysis and elevated blood pressure [2]. Even kidney damage, respiratory failure and death may be caused by barium toxicity [3]. Thus, the assay of barium is essential due to its toxic properties and other unfavourable effects.

The available methods for monitoring of barium ions *i.e.* inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [4,5], inductively coupled plasma-mass spectroscopy (ICP-MS) [6], electro-photometry [7] and atomic absorption spectroscopy (AAS) [8] are very expensive. The advantage of speed, ease of preparation and procedures, relatively fast response, reasonable selectivity through judicious choice of membrane active materials, wide linear dynamic range and low cost are offered by potentiometric detection based on ion-selective electrodes (ISEs) [9-11]. However, literature survey revealed only a small number of ion-selective electrodes for barium, based on ionophores but no reference of ion-selective electrodes employing inorganic ion exchanger is available.

Arnold & Solsky [12] and Buck & Lindner [13] have reviewed ion-selective electrodes (ISEs) employing inorganic ion-exchangers as sensory molecules. It has been recognized that anions such as vanadates, phosphates, molybdates combined with hydrous oxides produce better-quality ion exchangers [14-17].

In recent times, a number of selective and sensitive polyvinyl chloride (PVC) membrane ion-selective electrodes for different metal ions have been reported [18-29]. Only a few ion selective electrodes, based on inorganic ion exchangers, for alkaline earth metal ions other than barium, have been reported so far [30,31]. Now-a-days, various organic-inorganic ion exchange materials are being used for potentiometric determination of metal ions [32,33]. In present investigation, inorganic ion exchanger zirconium(IV) phosphoborate shows good selectivity for barium(II) ions. Hence, it has been tried as an electroactive material for preparing a low cost barium(II) ion selective electrode.

EXPERIMENTAL

Zirconyl oxychloride, boric acid and phosphoric acid required for the preparation of zirconium(IV) phosphoborate

(ZrPB) were purchased from S.D. Fine Chemicals Ltd., India. Hydrofluoric acid and barium chloride was purchased from Loba Chemicals Ltd., India. All rare earth chlorides were purchased from Indian 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 (ethylene diamine tetraacetic acid) using xylenol orange as indicator. Double distilled water was used throughout the experiments.

The characterization of zirconium(IV) phosphoborate ion exchanger was performed on X-ray diffractometer (XRD, PAN analytical, System No. DY 3190), the surface scanning electron microscope (SEM, JEOl, JSM-6510LV), transmission electron microscope (TEM, MIC JEM 2100), (Fourier transform infrared spectrometer (FTIR, Perkin Spectrum-400), magnetic stirrer, digital potentiometer (Systronic 318)

Zirconium (IV) phosphoborate ion-exchanger was prepared [34] by adding 0.1 mol L^{-1} zirconyl oxychloride solution to a continuously stirred mixture of 0.1 mol L^{-1} boric acid and 0.1 mol L^{-1} phosphoric acid solutions at 60 °C, in the volume ratio 2:1:1. The gel formed in round bottomed flask was permitted to stand overnight. The gel was repeatedly washed with distilled water to remove chlorides from the mother liquor. 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 40 °C. When the gel dried completely, distilled water was added. Small granules of ion-exchanger were formed with cracking sound.

The ion exchange capacity of zirconium(IV) phosphoborate ion exchanger was determined by column operation. The H$^+$ ions eluted from the ion exchanger column using 0.1 mol L^{-1} NaNO$_3$ solution as eluent, were determined titrimetrically using 0.01 mol L^{-1} solution of NaOH.

The cation exchanger was ground to a fine powder (approximately 200 μm) and mixed thoroughly with araldite in the ratio ZrPB:epoxy resin = 80:20 (w/w), with constant stirring till a homogeneous slurry was obtained. This slurry was spread between the folds of a glossy paper and a pressure of 2.0 Kg cm^{-2} was applied over the glass plates containing glossy paper for 24 h. Then slurry was dried in air to get three membranes of different thickness (0.45, 0.57, 0.65 mm). The dried membrane was dipped in distilled water to remove the glossy paper. The sheet of the membrane formed was cut with a sharp knife into circular discs.

All potential measurements were carried out at 27 ± 1 °C with the following assembly:

$$\text{SCE}\left|\text{Ba}^{2+}(0.05\text{ mol L}^{-1})\right\|\text{Membrane}\left\|\text{Ba}^{2+}(\text{test solution})\right|\text{SCE}$$

The solutions containing barium ions in 1 × 10^{-8} to 1 × 10^{-1} mol L^{-1} concentration range were used to determine the performance of electrode. The electrode was stored in 5 × 10^{-2} mol L^{-1} barium(II) chloride solution after the experiment.

The response time was measured by immersing the electrode in Ba(II) ion solution. The electrode potential was recorded as a function of time. In this study, 5 × 10^{-2} mol L^{-1} solution was taken inside the membrane electrode and 5 × 10^{-3} mol L^{-1} solution was used for investigation. The membrane potential was then plotted against time.

The effect of change in concentration of internal solution on the response of proposed membrane electrode for Ba(II) ions was studied using 1 × 10^{-2}, 5 × 10^{-3} and 1 × 10^{-3} mol L^{-1} internal solution concentrations. The value of electrode potential obtained is plotted against log [Ba(II)] at different concentrations.

The effect of addition of non-aqueous solvents to Ba(II) solution on the working of proposed membrane electrode was studied using 1 × 10^{-2} to 1 × 10^{-8} mol L^{-1} Ba(II) concentration. The electrode potential obtained is plotted against log [Ba(II)] at different concentrations.

The membrane electrode was tested for pH dependence using 1 × 10^{-3} mol L^{-1} Ba(II) solution in the pH range 2.0 to 12.0.

The analytical importance of membrane electrode has been established by employing it as an indicator electrode in potentiometric titration of Ba(II) (1.0 × 10^{-3} mol L^{-1}) solution against EDTA (1.0 × 10^{-2} mol L^{-1}) as titrant. Electrode potential values were plotted against volume of EDTA solution used.

Selectivity defines the extent to which an electrode may be employed for determination of a primary ion in presence of other secondary ions. Potentiometric selectivity coefficients of the membrane electrode were evaluated by fixed interference method [FIM]. The selectivity coefficients were calculated using equation given below:

$$K_{i,j}^{Pot} = \frac{a_i}{a_j^{\frac{z_i}{z_j}}} \qquad (1)$$

When not in use for more than one day, the electrode was stored in distilled water. The electrode was activated by keeping immersed in Ba(II) solution (0.05 mol L^{-1}) for 2 h, before use, 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. Before use, electrode was washed thoroughly with distilled water.

RESULTS AND DISCUSSION

The synthesized ion exchanger (ZrPB) was characterized by IR spectroscopy, morphology and topography determining techniques like SEM and XRD. The presence of various components in the composite was confirmed through IR spectrum (Fig. 1).

In the IR spectrum, broad band around 3400 cm^{-1} is assigned to O-H stretching of interstitial water and another broad band around 2410 cm^{-1} is assigned to P-OH (acidic) stretch. The sharp band at 1637 cm^{-1} is due to O-H deformation mode. A broad band at 1020 cm^{-1} is due to P=O stretching [35]. The absorption bands at 620 cm^{-1}, 517 cm^{-1} and 420 cm^{-1} are due to metal oxygen stretches like P-O, B-O and Zr-O [36] respectively.

XRD spectrum (Fig. 2) confirmed the semi crystalline nature of ZrPB ion exchanger. Fig. 3(a) shows the field emission scanning electron micrograph (FESEM) of ZrPB taken at 1,00,000X magnification. It consists of irregular aggregates of spherical particles with non-uniform size (marked area P, Fig. 3a).

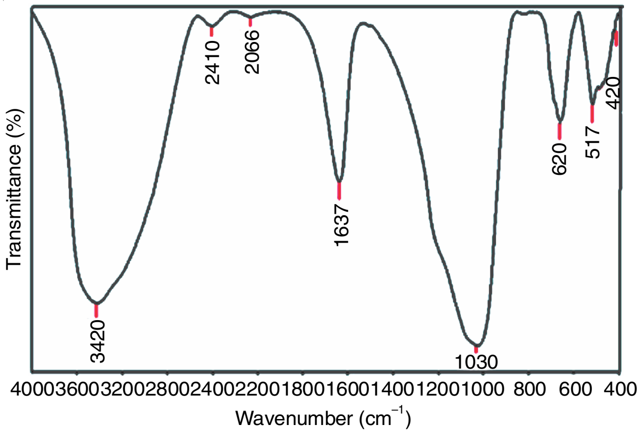

Fig. 1. IR spectrum of ZrPB ion exchanger

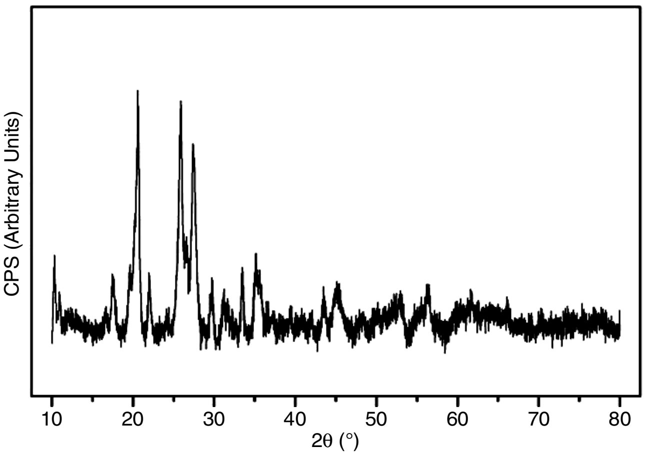

Fig. 2. X-ray diffraction pattern of ZrPB ion exchanger

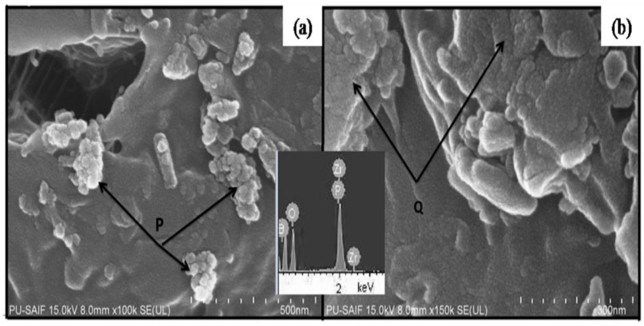

Fig. 3. Field emission scanning electron micrographs (FESEM) of ZrPB ion exchanger

These aggregates are due to the powder form of ZrPB sample taken in FESEM instrument. The non-uniform sizes of particles are due to stabilizing agent free synthesis of ZrPB.

The presence of Zr, P, B, C and O was confirmed from the EDX spectrum of ZrPB (inset of Fig. 3). Another underlying layer (marked as Q in Fig. 3b) has also been focused with FESEM at a high magnification of 1,50,000X. These layers also consist of aggregated spherical particles of ZrPB.

The ion exchange capacity of ZrPB ion exchanger was found to be 0.38 meq g^{-1} for Na^+ ions. The physico-chemical properties of membrane *i.e.* thickness, water content, swelling and porosity were determined. It is confirmed from Table-1 that ZrPB membrane M-1 has highest ion exchange capacity,

TABLE-1
PREPARATION AND CHARACTERIZATION OF
ZrPB CATION EXCHANGE MEMBRANE

Sample No.	Thickness (mm)	Water content (%)	Porosity	Na^+ ion exchange capacity (meq g^{-1})
M-1	0.45	12.22	3.5×10^{-2}	0.18
M-2	0.57	9.13	7.2×10^{-2}	0.14
M-3	0.65	6.12	5.3×10^{-2}	0.09

water content and least thickness. Hence, it was selected for fabrication of ion selective electrode.

The response time of the electrode was calculated by measuring the electrode potential as a function of time. The response time of ZrPB based membrane electrode was observed to be 15 s (Fig. 4).

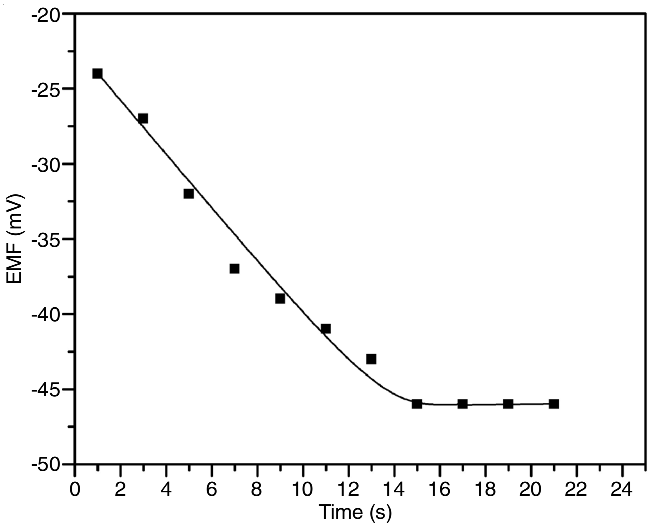

Fig. 4. Electrode potential of Ba(II) selective membrane electrode at different intervals of time

Potential measurements were made for different concentrations of Ba(II) ion solution in the range 10^{-8} mol L^{-1} to 1×10^{-1} mol L^{-1} on the outer side of the membrane while 0.05 mol L^{-1} Ba(II) solution was put inside the electrode tube. EMFs were plotted against log of activities of barium ions. Experiment was repeated five times to check the reproducibility of electrode system. A standard deviation of ± 1 mV was observed. A representative curve is shown in Fig. 5.

The limit of detection (6.31×10^{-7} mol L^{-1}) was calculated according to IUPAC recommendations [37,38] from the intersection of the two extrapolated linear portions of the curve [39-41]. Slope of the electrode was sub-Nernstian, being 20.7 mV $decade^{-1}$ for Ba(II) ions. The sub-Nernstian behaviour of the electrode may be due to possible discrepancy between the ion activities in the bulk and the phase boundary. Jain *et al.* [42] and Pungor *et al.* [43,44] have reported similar observations.

The effect of concentration of the internal solution on the response of proposed sensor for Ba(II) ions was studied using 1×10^{-2}, 5×10^{-3} and 1×10^{-3} mol L^{-1} concentrations of Ba(II) ions (Fig. 6).

As reported by Ganjali *et al*. [45], the results indicate that the variation in concentration of internal solution does not have any significant effect on the response of electrode except the change in intercept of curves.

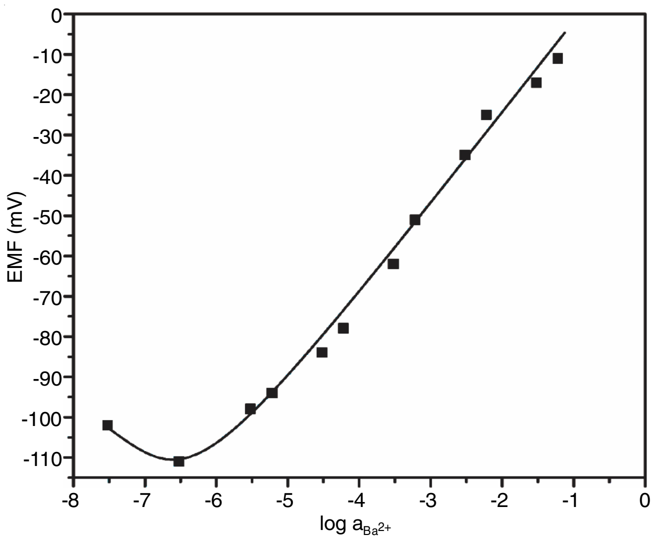

Fig. 5. Calibration curve for Ba(II) selective electrode

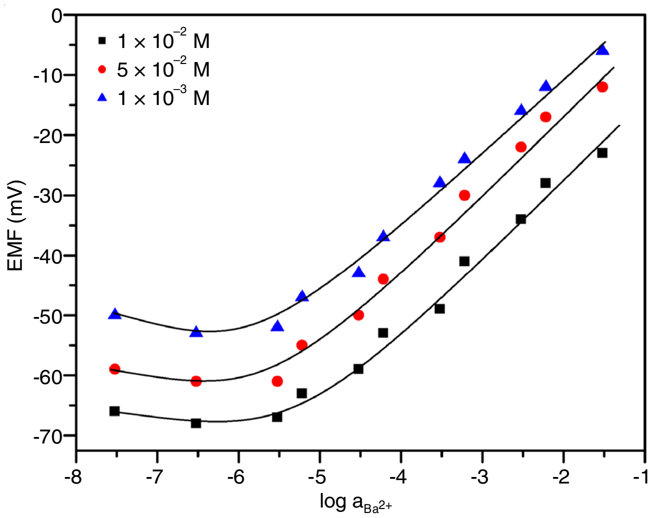

Fig. 6. Effect of change in concentration of internal solution on the potential response of Ba(II)-selective electrode

The proposed sensor was investigated in partially non-aqueous media using acetone and ethanol mixture with water. Table-2 indicates that with the addition of non-aqueous solvents, the slope remains almost unaffected. Hence, the proposed sensor can be used successfully in partially non-aqueous solvents also.

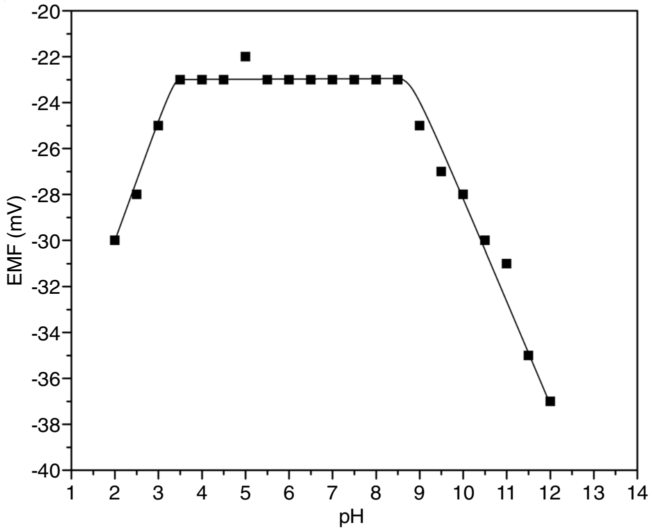

Fig. 7. The potential response of Ba(II) selective electrode at different pH

TABLE-2
EFFECT OF PARTIALLY NON AQUEOUS MEDIA ON THE WORKING OF Ba(II)-SELECTIVE ELECTRODE BASED ON ZrPB

Solvent	Volume of solvent (%, v/v)	Slope (mV decade^{-1})	Measuring range (mol L^{-1})
Acetone	5	20.5	1 × 10^{-5} to 1 × 10^{-1}
	10	20.5	1 × 10^{-5} to 1 × 10^{-1}
	15	21.0	1 × 10^{-5} to 1 × 10^{-1}
	20	20.5	1 × 10^{-5} to 1 × 10^{-1}
Ethanol	5	21.0	1 × 10^{-5} to 1 × 10^{-1}
	10	20.5	1 × 10^{-5} to 1 × 10^{-1}
	15	21.0	1 × 10^{-5} to 1 × 10^{-1}
	20	21.0	1 × 10^{-5} to 1 × 10^{-1}

As shown in Fig. 7, the potential of the electrode was found to be independent of pH value in the pH range 3.5-9. The sharp decrease in membrane potential at pH value below 3.5 and above 9 may be the result of promotion of oxygen atoms of exchanger and formation of $Ba(OH)_2$, respectively [46]. In fact, the Donnan exclusion phenomenon fails beyond the workable pH range and the electrode starts responding to species other than Ba^{2+} ions, leading to decrease in potential.

The single most important characteristic of any electrode is its selectivity that defines the nature of the device and the extent to which it may be employed for the determination of a particular ion in the presence of other interfering ions. Fixed interference method [FIM] [38] at 1 × 10^{-4} mol L^{-1} concentration of the interfering ions was employed to evaluate potentiometric selectivity coefficients of the membrane. According to this method, a calibration curve was drawn for varying primary ion concentration in a constant background concentration 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 back-ground alone. The selectivity coefficients were calculated from these two extrapolated linear segments of the calibration curves. The log K_{ij} values (Table-3) for most of the ions like Nd^{3+}, Pr^{3+}, Dy^{3+}, Tb^{3+}, Eu^{3+}, Sr^{2+}, Ca^{2+} and Cd^{2+} were found to be in the range 3.8 × 10^{-2} to 3.4 × 10^{-3}. The barium electrode was not very selective for other ions of the lanthanide series, which are similar to barium in chemical properties.

TABLE-3
SELECTIVITY COEFFICIENT VALUES FOR Ba(II)-SELECTIVE ELECTRODE BASED ON ZrPB BY FIXED INTERFERENCE METHOD

Interfering ion	A	Interfering ion	A
Tb(III)	3.4 × 10^{-3}	Sr(II)	6.1 × 10^{-2}
Dy(III)	3.4 × 10^{-3}	Ca(II)	4.3 × 10^{-2}
Pr(III)	5.4 × 10^{-3}	Mg(II)	3.2 × 10^{-2}
Eu(III)	3.4 × 10^{-3}	Cd(II)	3.8 × 10^{-2}
Nd(III)	8.5 × 10^{-3}	–	–

A = Selectivity coefficient values ($K^{pot}_{A,B}$) of ZrPB sensor at interfering ion concentration of 10^{-4} mol L^{-1}

Potentiometric titrations of Ba^{2+} ions (1.0 × 10^{-3} mol L^{-1}) were performed with EDTA solution (1.0 × 10^{-2} mol L^{-1}) by using the proposed membrane electrode as indicator electrode. Titration curves are shown in Fig. 8.

TABLE-4
COMPARISON OF PERFORMANCE CHARACTERISTICS OF ZIRCONIUM(IV) PHOSPHOBORATE BASED SENSOR WITH OTHER REPORTED Ba(II) ION SENSORS

Linear response (mol L^{-1})	Low detection limit (mol L^{-1})	Slope (mV $decade^{-1}$)	Slope in presence of non-aqueous solvent (mV $decade^{-1}$)	pH range	Response time (s)	Ref.
$1 \times 10^{-5} - 2 \times 10^{-2}$	–	58.9	–	–	20	[47]
$5 \times 10^{-5} - 10^{-1}$	2.50×10^{-6}	28.5	–	4.5-10.0	20	[48]
–	2.50×10^{-5}	24.0	–	5.5-9.6	15	[49]
$1 \times 10^{-5} - 1 \times 10^{-1}$	5.00×10^{-6}	30.0	–	4.0-9.0	–	[50]
$1 \times 10^{-6} - 1 \times 10^{-2}$	5.20×10^{-7}	29.7	–	3.4-10.6	15	[51]
$1 \times 10^{-6} - 1 \times 10^{-2}$	5.60×10^{-7}	29.6	–	2.6-11.0	15	[52]
$1 \times 10^{-5} - 1 \times 10^{-1}$	6.31×10^{-7}	20.7	20.5	3.5-9.0	15	Present study

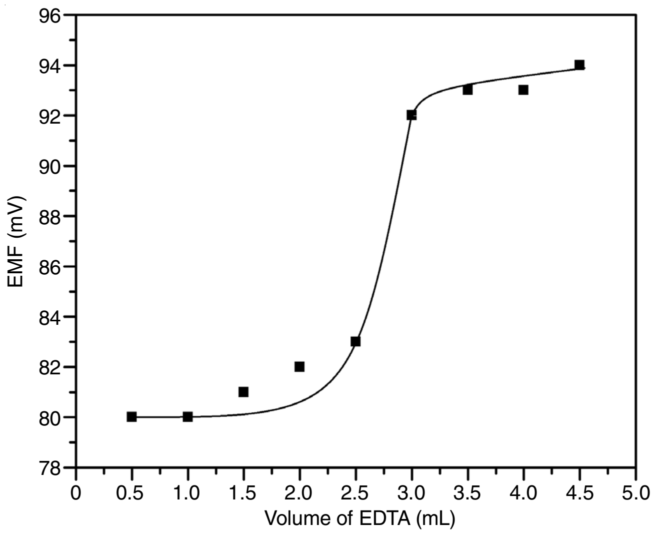

Fig. 8. Titration curve of Ba(II) ions with EDTA solution

Sharp inflexion points were shown by the curve at the titrant volume corresponding to the formation of a 1:1 complex. The sharp inflection shows that this electrode can be used for determination of Ba(II) ions potentiometrically.

As no other inorganic ion exchanger based Ba(II) selective electrode has been reported in literature, the response characteristics of proposed ZrPB electrode have been compared with some of the already reported ionophore based sensors for Ba(II) determination (Table-4).

The proposed sensor exhibits comparable linear range (1×10^{-5} to 1×10^{-1} mol L^{-1}), lower detection limit (6.31×10^{-7} mol L^{-1}), working pH range and similar response time in comparison to the other reported electrodes for Ba(II). The proposed electrode can also be used satisfactorily in partially non-aqueous media, whereas none of the other reported electrodes has been used in non-aqueous media. The life time of the proposed sensor is longer compared to other reported sensors.

Conclusion

Zirconium phosphoborate based ISE shows sub-Nernstian response characteristics in the concentration range of 10^{-5} to 10^{-1} mol L^{-1} Ba(II) ions with a slope of 20.7mV $decade^{-1}$. The detection limit was 6.31×10^{-7} mol L^{-1} with a fast response time of 15 s. The electrode potential of the proposed sensor remains almost constant with pH variation from 3.5 to 9. The sensor was used as an indicator electrode in the potentiometric titration of barium(II) ions with EDTA and could also be used for Ba^{2+} determination in rock samples. The proposed ISE can be safely used in partially non-aqueous media also.

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