

Samarium (III) Selective Membrane Sensor Based on Tin (IV) Boratophosphate

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Abstract: A number of Sm (III) selective membranes of varying compositions using tin (IV) boratophosphate as electroactive material were prepared. Polyvinyl chloride, polystyrene and epoxy resin were used as binding materials. Membrane having composition of 40% exchanger and 60% epoxy resin exhibited best performance. This membrane worked well over a wide concentration range of 1×10^{-5} M to 1×10^{-1} M of samarium ions with a Super-Nernstian slope of 40 mV/decade. It has a fast response time of less than 10 seconds and can be used for at least six months without any considerable divergence in potentials. The proposed sensor revealed good selectivities with respect to alkali, alkaline earth, some transition and rare earth metal ions and can be used in the pH range of 4.0-10.0. It was used as an indicator electrode in the potentiometric titration of Sm (III) ions against EDTA. Effect of internal solution was studied and the electrode was successfully used in non-aqueous media, too.

Keywords: Inorganic ion exchanger, ISE, Sm (III), FIM, potentiometric titration.

Introduction

The demand for the development of methods providing quantitative determination of trace metals in a variety of environmental matrices has increased as environmental protection has become a higher priority on the scientific agenda of the industrialized nations. However, the selective determination of these metal ions is complicated by the similarity of their chemical properties and the fact that they all exist primarily as trivalent cations in solution [1]. The vapors or the dusts of rare earth elements are very toxic when inhaled as they tend to remain in the lungs, liver, spleen and kidneys [2]. Samarium is an important member of this family and widely used as a gasoline cracking catalyst, polishing compound and in the iron and steel industries to remove sulphur, carbon and other electronegative elements from iron and steel [3]. Hence, it is important to find out methods for its quantitative determination in solution.

The available methods for the trace determination of rare earth metal ions in solution include spectrophotometry, inductive-coupled plasma atomic emission spectroscopy (ICP-AES), isotope dilution, mass spectrometry, neutron activation analysis, X-ray fluorescence, etc. [4-8]. 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 and provide acceptable sensitivity and selectivity. In recent decades, many intensive studies on the design and synthesis of highly selective ionophores as sensory molecules for ion-selective electrodes have been reported. However, there are only a limited number of reports on the development of selective electrodes for samarium [2, 9, 10]. Ion-selective liquid membrane electrodes containing organic exchangers suffer from the problems of leaching of the active component and plasticizer from the polymer matrix into the solution [11].

Ion-selective electrodes employing inorganic ion exchanger as sensory molecules have been reviewed by Arnold and Solsky [12] and Buck [13]. It has been established that hydrous oxides combined with anions such as phosphates, vanadates, molybdates and antimonates produce superior ion exchangers [14-17]. A new inorganic ion exchanger tin (IV) boratophosphate shows better selectivity for samarium (III) ions, in comparison to other rare earth metal ions, during distribution coefficient studies of the prepared exchanger. Hence, it has been tried as an electroactive material for preparing ion-selective electrodes for samarium (III) ions.

Experimental

Reagents

Tin (IV) chloride, boric acid, phosphoric acid needed for the preparation of tin (IV) boratophosphate [SnBP] were procured from S.D. fine chem. Ltd., India. Samarium (III) chloride and other rare earth chlorides needed for preparing stock solutions were purchased from Indian Rare Earth Chemicals Ltd., India. All the chemicals were of analytical grade and hence, used as such. All the rare earth metal ion solutions were standardized against EDTA solution using xylenol orange as an indicator. Double-distilled deionised water was used throughout the experiments.

Preparation of exchanger

Tin (IV) chloride (0.1 M, containing HF 12 mL/L) was added to a continuously stirred solution of boric acid (0.1 M) and orthophosphoric acid (0.1 M) at 90 °C in the volume ratio of 2:1:1. pH of the gel was adjusted to 2.0 by adding HCl or NaOH and stirred for half an hour at 90°C. It was then, filtered and washed till it was free from halides. The product was dried at 40 °C and on immersing in water broke into fine granules. It was converted to H⁺ form by treating with 0.1 M HCl for 24 hours, washed with double-distilled water and finally, dried at 40 °C. It was characterized as an ion exchanger using standard techniques.

Preparation of membranes

A number of membranes were prepared using varying amounts of binding materials such as an epoxy resin, PVC in THF solvent, polystyrene. SnBP is used as an electroactive material.

Preparation of epoxy resin-based membranes

Desired amount of finely powdered exchanger was mixed thoroughly with araldite in varying amounts (w/w) to make a near homogeneous paste, which was then, spread between the folds of a butter paper. Glass plates were kept below and above the paper folds as supports. A pressure of 2.0 kg/cm² 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.

Preparation of PVC membranes

Membranes of 0.2 mm thickness were obtained by mixing a solution made from varying amounts of PVC in 2-3 mL THF solvent at room temperature and desired weight of finely ground SnBP with constant stirring till a homogeneous slurry was obtained. The slurry was spread between the folds of a filter paper and dried in air. Dried membranes were dipped in distilled water to remove the paper and again dried at room temperature.

Preparation of PS membranes

A desired weight of finely ground exchanger was thoroughly mixed with powdered polystyrene and the mixture was heated at a temperature of 99 °C for 6 hours under pressure in the polymer film making equipment. The membranes obtained by various methods were cut in the shapes of discs of about 2.0 cm diameter using a sharp blade and those of good surface qualities were selected for further investigations.

EMF measurements

The membranes were fixed to one end of the glass tube of 1.8 cm (internal dia) using araldite. These were then equilibrated with 0.1 M Sm³⁺ ion solution for 24 hours. The tube was filled with a solution of

0.1 M Sm^{3+} 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:



A digital potentiometer (Equiptronics EQ-602, India) was used for the potential measurements at 25 ± 0.1 °C. Activities were calculated according to Debye-Huckel equation [18]. Test solutions of Sm^{3+} were obtained by gradual dilution of 0.1 M Sm^{3+} solution and their potential measurements were made in unbuffered solution.

Results and Discussions

Optimization of membrane composition

The effect of membrane composition on the response of the electrode was studied. For this purpose, the performance parameters, like slope of the calibration curve, measurement range and response time were compared for 7 electrodes. The results are given in Table 1. It is seen that the nature and amount of binding material hardly has any effect on the response of the electrode. All the electrodes showed a super-Nernstian slope in the range of 40 – 42 mV per decade and the response is linear in the range from 1×10^{-5} M to 1×10^{-1} M. Electrode No. 6 was selected for further studies because of its fast response and wide concentration range.

Table 1. Optimization of membrane ingredients.

Electrode No.	SnBP(%)	Binder	Medium	Slope (mV/decade)	Measuring Range (M)	Response Time (s)
1	30	PVC	THF	40	2.0×10^{-5} - 10^{-1}	20
2	40	PVC	THF	42	2.0×10^{-5} - 10^{-1}	20
3	10	Araldite	-	40	1.0×10^{-5} - 10^{-1}	15
4	20	Araldite	-	40	2.5×10^{-5} - 10^{-1}	15
5	30	Araldite	-	42	1.0×10^{-5} - 10^{-1}	15
6	40	Araldite	-	40	1.0×10^{-5} - 10^{-1}	10
7	40	Polystyrene	-	42	2.0×10^{-5} - 10^{-1}	15

Calibration curve and statistical data

Potential measurements were made on the selected electrode (No. 6) for different concentrations of Sm (III) ion solutions. EMFs were plotted against log of activities of the samarium ions. Experiments were repeated five times to check the reproducibility of the electrode system. A standard deviation of ± 0.9 mV was observed. A representative calibration curve is shown in Figure 1. The amount of the electroactive component (the ion exchanger) was varied over a range of 10–40% (w/w) as shown in Table 1. The membrane composition SnBP: Araldite as 40%:60% shows a linearity in the concentration range

1.0×10^{-5} M to 1.0×10^{-1} M with a slope of 40 mV/decade. The limit of detection (1×10^{-5} M) was calculated according to IUPAC recommendations [13, 19] from the intersection of the two extrapolated linear portions of the curve.

The over-Nernstian response of this kind of electrodes is common [20, 21]. A higher slope may be due to poor permeability and incomplete permselectivity of the membrane matrix for the samarium ions. Membranes of this type sometimes show permeability for the anions [22] as well. The non-Nernstian behavior of the electrode may also be due to a possible discrepancy between the ion 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 ions from the Nernst diffusion layer. This is supported by earlier reports of Jain, A.K. et al. [20] and Malik, W.U. et al. [21]. Pungor et al. [23, 24]. They have also explained the Super-Nernstian slope observed for Ag^+ - and I^- -selective electrodes.

Hence, the higher value of slope in no way hinders the determination of samarium (III) ions in the aqueous medium. Response time of the electrodes was less than 10 seconds. It is still lower for the relatively concentrated solution. The sensing behavior of the membrane remains unchanged when the potentials are measured either from low to high or high to low concentration. This membrane could be used for at least six months without any measurable divergence. The electrodes were stored in 0.1 M Sm (III) ion solution when not in use to avoid any change in metal ion concentration in the membrane phase.

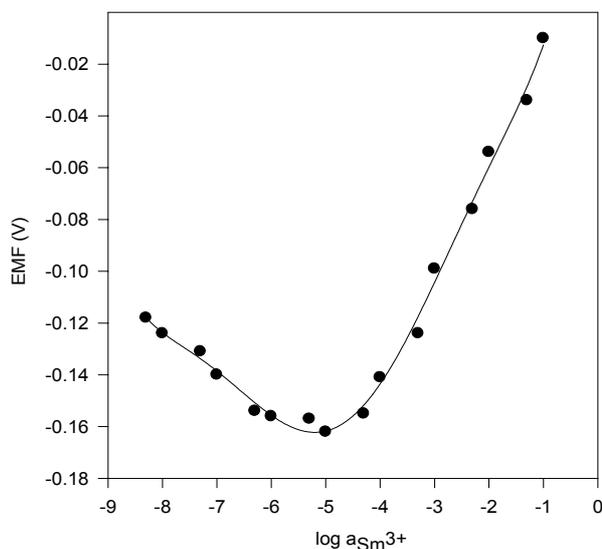


Figure 1. Calibration curve for Sm (III) selective electrode based on SnBP.

Effect of internal solution concentration

The effect of internal solution on the response of the proposed sensor for Sm (III) ions was studied using 10^{-1} M to 10^{-3} M internal solution concentrations. The results are shown in Figure 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 Ganjali et al. [2].

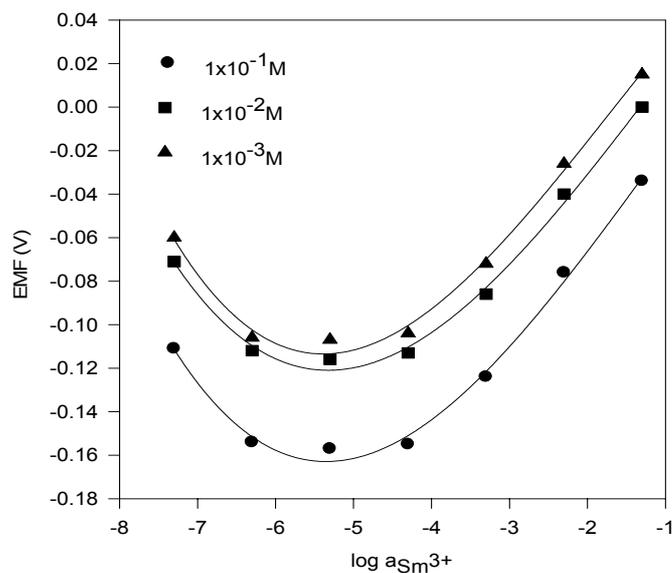


Figure 2. Effect of internal solution on potential response of the Sm (III) selective electrode based on SnBP.

Effect of pH

The influence of pH on the potential response of the electrode was studied at two different concentrations, $2 \times 10^{-2} M$ and $2 \times 10^{-3} M$ over a pH range of 2.0 to 12. The results are shown in Figure. 3. pH was adjusted by introducing small drops of HCl (0.1 M) or NaOH (0.1 M) as per requirement. The potential is independent on the pH in the range of 4.0-10.0 for $2 \times 10^{-2} M$ and pH 6.0-9.0 for $2 \times 10^{-3} M$ Sm (III) ions concentrations, respectively. Thus, this 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 $Sm(OH)_3$ and protonation of oxygen atoms of the exchanger, respectively.

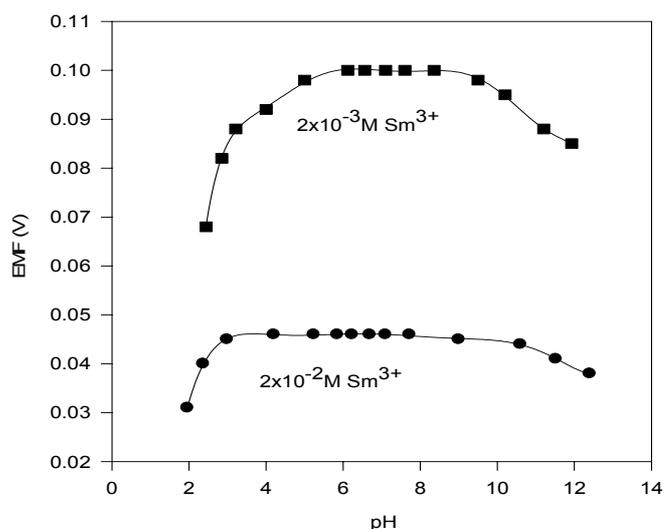


Figure 3. Effect of pH on the response of Sm (III) selective electrode based on SnBP.

Selectivity coefficients and analytical properties of Sm (III) selective electrode

Selectivity is one of the 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 the presence of other interfering ions. Potentiometric selectivity coefficients of the samarium membrane electrode were evaluated by the fixed interference method [FIM][13,19] at $1 \times 10^{-3} \text{ M}$ and $1 \times 10^{-4} \text{ M}$ interfering ion concentrations. 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 extrapolated linear segments of the calibration curve:

$$K_{i,j}^{pot} = \frac{a_i^{z_i/z_j}}{a_j} \quad (1)$$

The results are given in Table 2. It is obvious that the electrode has a reasonably good selectivity with respect to other 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. It is further obvious that as the concentration of the interfering ions decreases, the selectivity of the electrode increases. Table 2 shows the potentiometric selectivity coefficients of the SnBP-based sensor for samarium (III) ions in the presence of the interfering ions, commonly present along with samarium in its ores [25].

Table 2. Selectivity coefficient values for Sm (III) selective electrode based on SnBP as calculated by FIM method.

Interfering ion (B)	Selectivity Coefficient values ($K_{A,B}^{pot}$)	
	Interfering ion concentration	
	10^{-3} M	10^{-4} M
La(III)	0.31	0.40
Ce(III)	0.25	0.31
Nd(III)	0.40	0.50
Eu(III)	0.40	0.50
Pr(III)	0.50	0.63
Tb(III)	0.32	0.40
Dy(III)	0.40	0.40
Y(III)	0.31	0.40
Fe(III)	0.25	0.25
Al(III)	0.10	0.31
Ca(II)	0.50	0.50
Na(I)	0.50	0.63

Effect of partially non-aqueous medium on the working of Sm (III) electrode

The proposed sensor was investigated in partially non-aqueous media using acetone, ethanol and acetonitrile mixture with water. Table 3 indicates that the slope remains unaltered with the addition of non-aqueous solvents. Hence, the proposed sensor can be successfully used in partially non-aqueous medium. Plots of EMF vs. activity of Sm (III) ions for partially non-aqueous media are shown in Figure 4.

Table 3. Effect of partially non-aqueous media on the working of Sm (III) selective electrode.

Solvent	Percentage(v/v)	Slope (mV/decade)	Measuring range(M)
Acetone	5	40.0	1.0×10^{-5} to 10^{-1}
	10	40.0	3.2×10^{-5} to 10^{-1}
	15	40.0	3.2×10^{-5} to 10^{-1}
	20	40.0	1.0×10^{-5} to 10^{-1}
Ethanol	5	40.2	1.0×10^{-5} to 10^{-1}
	10	40.1	2.0×10^{-5} to 10^{-1}
	15	40.0	1.0×10^{-5} to 10^{-1}
	20	40.2	4.3×10^{-5} to 10^{-1}
Acetonitrile	5	40.0	1.0×10^{-5} to 10^{-1}
	10	40.1	1.0×10^{-5} to 10^{-1}
	15	40.0	2.3×10^{-5} to 10^{-1}
	20	40.0	1.0×10^{-5} to 10^{-1}

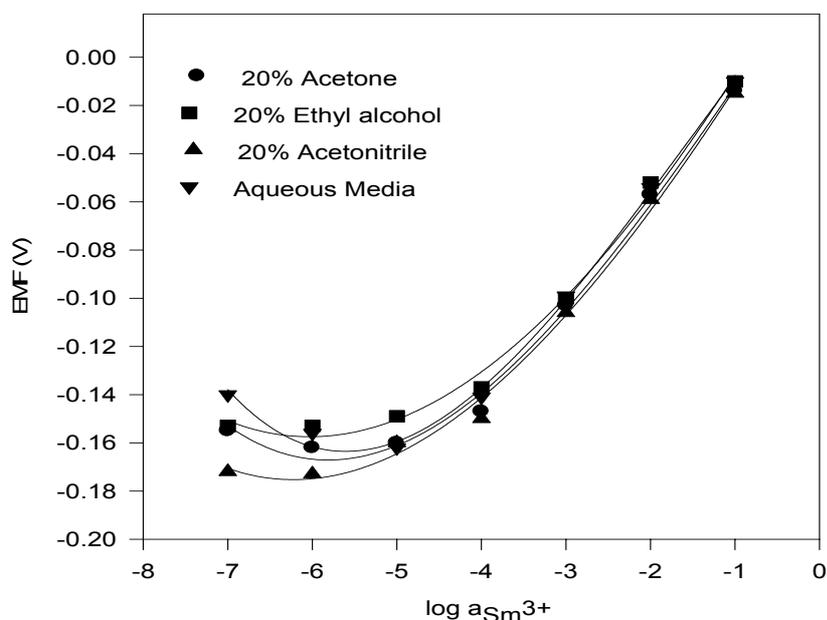


Figure 4. Effect of partially non-aqueous medium on potential response of Sm (III) selective electrode based on SnBP.

Potentiometric titration

A potentiometric titration was performed by using the proposed electrode as an indicator electrode for the titration of 15 mL of 2×10^{-2} M Sm^{3+} ions vs. 1×10^{-1} M EDTA. The titration curve is shown in Figure 5. The curve shows a sharp inflexion point at the titrant volume corresponding to the end point.

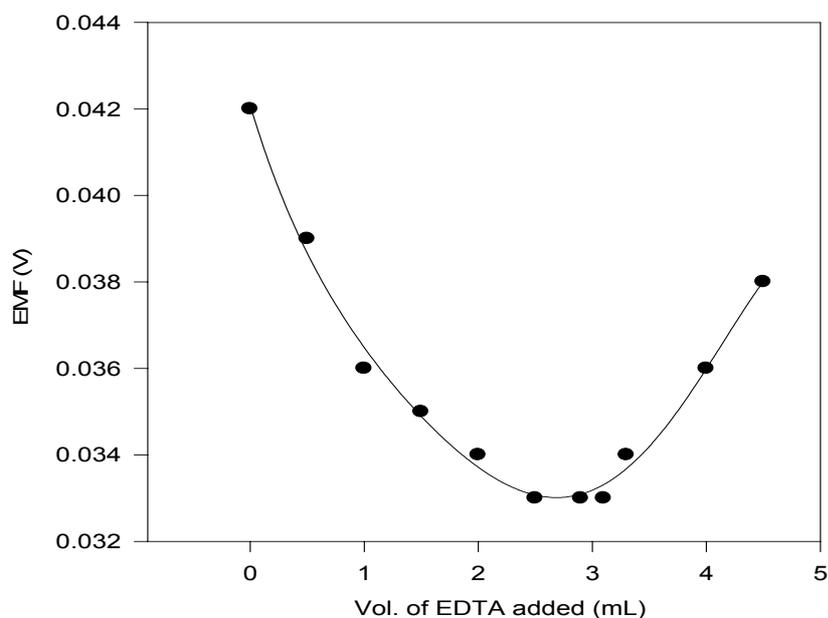


Figure 5. Titration curve of Sm (III) ions with EDTA solution using Sm (III) selective electrode based on SnBP.

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