Chemically Modified Carbon Paste Sensor Based on N^1,N^2 -Bis(salicylidine)butane-1,4-diamine for Determination of Nd(III)

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Fabrication of carbon paste sensor modified with N^1,N^2 -bis(salicylidine)butane-1,4-diamine (SAB) for Nd(III) has been demonstrated. The sensor having the composition of 90 % graphite and 10 % SAB exhibited best performance in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M. Nernstian slope of the sensor was found to be 19.5 ± 0.3 mV/decade. The sensor displayed fast response time of 10 s in the pH range 3.5 to 8.0. The detection limit is found to be 4.7×10^{-7} M. The proposed sensor can be used over a period of 5 weeks without any significant changes in its Nernstian behaviour. The sensor showed good selectivity for neodymium in presence of other metal ions such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Pb^{2+} , Ag^+ , Pr^{3+} , Sm^{3+} , La^{3+} and Gd^{3+} . The practical utility of the developed sensor was investigated in the determination of neodymium in binary mixtures. This electrode is also utilized as an indicator electrode in the potentiometric titration of Nd(III) ions with EDTA.

Keywords: Chemically modified carbon paste sensor, Neodymium ions, N^1,N^2 -Bis(salicylidine)butane-1,4-diamine, Potentiometry.

INTRODUCTION

Neodymium is one of the rare earth elements that can be found in house hold equipments such as television, fluorescent lamps and glasses. The most important use of neodymium is as a component in the alloys (Nd-Fe-B) used to make high strength permanent magnets. These magnets are used in computer data storing, in loud speakers and are part of modern vehicles. Oxides of lanthanides are extensively used in the fabrication of glass fibres for optical purposes, optical glasses, gasoline-cracking catalysts, polishing compounds and carbon arcs [1]. Neodymium is largely discarded in to the environment by petroleum producing industry and also when house hold equipments are thrown away. Neodymium is gradually accumulated in soil and water and lead to the increase in concentration in humans, animals and soil particles. Accumulation of neodymium in human body can damage the lungs and liver. So the trace level determination of neodymium in environmental and in biological materials is very important and has received increasing attention [2]. Different instrumental techniques that are accessible for the determination of neodymium are X-ray fluorescence [3] (AAS), neutron activation analysis [4], isotopic dilution method [5-7], inductively coupled plasma atomic emission spectroscopy (ICP AES) [8] and inductively

coupled plasma mass spectroscopy [9,10]. Although these methods are sensitive and precise, they require multiple sample preparation and are expensive. Potentiometric sensors offer a low cost and convenient method for analysis of metal ions in solution and provide acceptable sensitivity and selectivity. This paper introduces a highly selective and sensitive carbon paste sensor based on N^1,N^2 -bis(salicylidine)butane-1,4-diamine for neodymium.

EXPERIMENTAL

1,4-Diaminobutane, salicylaldehyde, dioctyl phthalate (DOP), dioctyl sebacate (DOS), dibutyl phthalate (DBP), dioctyl adipate (DOA) and sodium tetra phenyl borate (NaTBP) were obtained from Lancaster (UK) and were used as obtained. Lanthanide salts were obtained from IRE Ltd. (India) and other metal salts, high molecular weight PVC and dibutyl sebacate (DBS) were procured from Merck. Tetrahydrofuran (THF) and methanol were supplied by S.D. Fine-chem. Ltd, India and were distilled before use. High purity graphite powder was procured from Sigma Aldrich Corporation, USA. Double distilled water was used for the preparation of all metal salts solutions and solutions of different concentrations were made by serial dilution of the 1×10^{-1} M stock solution.

Synthesis of ionophore: The ion carrier, N^1,N^2 -bis(salicylidine)butane-1,4-diamine (SAB, Fig. 1) was prepared by refluxing salicylaldehyde (0.02 mol) and butane-1,4-diamine (0.01 mol) in 20 mL methanol for 3 h. The reaction mixture was then filtered and yellow product obtained is washed, dried and recrystallized from dichloromethane. The formation and purity of the product was confirmed by elemental analysis and spectroscopic techniques and results are given below.

CHN analysis: Found (%): C - 72.44, H - 6.30, N - 9.25; Calcd (%): C - 72.95, H - 6.80, N - 9.45.

Spectroscopic analysis: IR (KBr, $\nu_{\max}$, cm^{-1}): 1604 ($\text{CH}=\text{N}$, S), 1581, 1528, 3565, 2885, 1352, 149, 1282, 1223, 1047, 942, 893, 744, 750, 659; ^1H NMR (DMSO): 8.5 (2H, s, $\text{CH}=\text{N}$), 7.49 (2H, d, Ar-H), 7.3 (2H, t, Ar-H), 6.9 (2H, m, Ar-H), 6.7 (2H, m, Ar-H), 3.5 (4H, t, CH_2), 11.29 (2H, s, OH).

Fig. 1. Structure of N^1,N^2 -bis(salicylidine)butane-1,4-diamine (SAB)

Electrode preparation: Graphite and the ionophore (in varying %w/w ratios) were mixed thoroughly using a motor and pestle to give a homogeneous mixture. To this, acetone was added and this mixture was left overnight for the acetone to evaporate completely. It was made a paste by using binders. This paste was then packed to one end of the Teflon holder in which electrical contact was made with a copper rod through the centre of the electrode. Appropriate packing and a smooth surface was achieved by pressing the surface of the sensor against a filter paper. The sensor was conditioned in a 1.0×10^{-1} M solution of metal salt solution.

EMF measurements: The following cell assembly was used for the EMF measurements:

Potentials measurements were carried out by using a Metrohm 781 ion meter at 25 ± 0.1 °C.

RESULTS AND DISCUSSION

The structure of the ionophore (SAB) was confirmed by ^1H NMR, IR and elemental analysis (CHN). The $\nu_{\max}$ (cm^{-1}) at 1604 and δ at 8.5 indicates the presence of $\text{CH}=\text{N}$ in the structure of SAB. The close agreements between the theoretically and experimentally obtained CHN values also confirm the formation of SAB.

Based on previous report [11] which showed a strong interaction between SAB and Nd(III), SAB was used as a potential neutral ion carrier to prepare CPEs for a number of metal ions and potential response of the resulting sensors are shown in Fig. 2. As it is seen, neodymium ion demonstrates most sensitive response to the ionophore and is suitably determined by the developed sensor.

Fig. 2. Potential response of various CMCPE ion selective electrodes based on SAB

The extent of complexation of SAB towards different metal ions was studied conductometrically. Complexation of SAB with a number of metal ions such as Sm^{3+} , La^{3+} , Gd^{3+} , Nd^{3+} , Pr^{3+} and Pb^{2+} were investigated conductometrically in acetonitrile solution (1.0×10^{-4} M of cation solution and 1.0×10^{-2} M of ligand) at 25 ± 1 °C. 20 mL of each ion solution was titrated with 1.0×10^{-2} M of SAB solution and conductance of the resulting solution is measured after each addition. The ligand addition is continued until the desired ionophore to ion mole ratio is achieved. The 1:1 binding of the cation with the ionophore can be expressed by the following equilibrium:

The complex formation constant in terms of molar conductance can be expressed as:

$$K_f = \frac{[\text{ML}^{n+}]}{[\text{M}^{n+}][\text{L}]} = \frac{(\Lambda_M - \Lambda_{\text{obs}})}{(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]} \quad (2)$$

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{\text{obs}})}{(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})} \quad (3)$$

where, Λ_M is the molar conductance of the cation before the addition of the ionophore. Λ_{ML} is the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during the titration, C_L the analytical concentration of the added ionophore and C_M the analytical concentration of the cation salt. The complex formation constant of the complexes, K_f , of SAB towards different metal ions were performed by computer fitting of the molar conductance/molar ratio data with suitable equations [11-13] and results are summarized in Table-1. The ionophore SAB forms more stable complex with Nd^{3+} than other cations tested. Table-1 shows that the formation constant of the Nd-SAB complex is more than that of the other lanthanides studied. Thus, SAB may be used as a suitable ion carrier in the construction of neodymium selective membrane sensor.

Optimization of composition: The sensitivity and selectivity of a carbon paste sensor depends significantly on the composition of carbon paste and nature of the solvent mediator [14-17]. A set of seven CMCPE type sensors were developed

TABLE-1
FORMATION CONSTANTS OF SAB-Mⁿ⁺ COMPLEXES

Metal ion	log K _f
Nd ³⁺	4.35
Gd ³⁺	2.45
Sm ³⁺	2.29
Pr ³⁺	2.15
Pb ²⁺	2.53

by varying plasticizer and sensor composition. The results obtained are given in Table-2. It is well known that the use of plasticizer not only gives some permeable properties to the carbon paste but also enhances its mechanical stability by promoting binding between grains. Among the different binders tested DBS was found to be the most suitable one. Since the percentage of ionophore is known to strongly influence the sensitivity and selectivity of ISEs [18-21], the effect of ionophore percentage on the response of the CPE sensor incorporated SAB towards Nd(III) is also investigated and results are given in Table-2. From the data given in Table-2, it is obvious that the variation of ionophore percentage from 5 to 10 increases the working concentration range and slope of the sensor. The sensor Sb₆ with the composition ratio 90:10 (graphite:ionophore) (w/w %) exhibited best performance in terms of response time, working concentration range and the Nernstian slope. Further increase in the percentage of ionophore resulted in a super Nernstian slope.

Calibration curve and statistical data: The developed sensor was equilibrated in 1.0×10^{-1} M NdCl₃ and optimum equilibration time was found to be 24 h. The calibration curve of the sensor is shown in Fig. 3. The sensor displayed a linear

Fig. 3. Calibration graph for Nd(III) selective CMCPE sensor based on SAB

response in the range 1.0×10^{-6} to 1.0×10^{-2} M and slope of the calibration graph is found to be 19.5 ± 0.3 mV/decade. The detection limit is found to be 4.7×10^{-7} M. The membrane sensor could be used for at least 5 weeks without any measurable divergence from Nernstian response.

Response time: The response time required for Nd³⁺ sensor to reach a stable potential was measured by changing the Nd³⁺ concentration in the range 1×10^{-6} to 1×10^{-2} M. The sensor reached their equilibrium potential in very short time and was measured as 10 s over the entire concentration range. The practical reversibility of the sensor was evaluated by taking measurements for Nd³⁺ in the sequence of high-to-low concentration and *vice-versa*. The response of the sensor remained unchanged irrespective of the change in concentration of the metal salt solution.

Effect of pH: The effect of pH on the response of the newly developed sensor was studied over the pH range 1 - 11 at 1×10^{-4} M NdCl₃. The pH adjustments were carried out by adding suitable buffer solution. The results are shown in Fig. 4. It is obvious from the figure that potential remains constant despite the pH change in the range of 3.5 to 8.0. Beyond this pH range, drastic drift in potential is observed. Therefore, these intervals can be chosen as the working pH range for the sensor. The variation above the pH range may be due to the formation of some hydroxyl complex of Nd(III) in the solution and at the lower pH due to the response of the sensor to hydrogen ions.

Fig. 4. Effect of pH of test solution (1×10^{-4} M NdCl₃) on the response of Nd(III) sensor

Selectivity: Selectivity is the most important characteristics of any ion-selective electrode, which determines the

TABLE-2
OPTIMIZATION OF THE COMPOSITION OF CMCPE TYPE OF SENSOR

Sensor	Ionophore % (w/w)	Graphite % (w/w)	Binders	Concentration range (M)	Slope (mV/decade)
1	5	95	DBP	10^{-6} to 10^{-4}	10.9 ± 0.4
2	5	95	BEA	10^{-5} to 10^{-2}	13.5 ± 0.4
3	5	95	BES	10^{-5} to 10^{-2}	8.9 ± 0.5
4	5	95	BEP	10^{-5} to 10^{-2}	5.4 ± 0.4
5	5	95	DBS	10^{-6} to 10^{-2}	16.5 ± 0.3
6	10	90	DBS	10^{-6} to 10^{-2}	19.5 ± 0.3
7	12	88	DBS	10^{-5} to 10^{-2}	28.2 ± 0.4

ability of sensor to discriminate between target ion and interfering ions in the same solution. Potential response of the CPE sensor incorporated SAB towards Nd(III) in presence of other interfering ions were evaluated by fixed interference method (FIM) [22-24] at 10⁻² M concentration of interfering ions. The values of selectivity coefficients were calculated using the equation:

$$K_{A,B}^{\text{pot}} = \frac{a_A}{(a_B)^{Z_A/Z_B}}$$

where K_{A,B}^{pot} is the selectivity coefficient; a_A is the value obtained from the intersection of the extrapolated linear portions of the plot of EMF values *versus* the logarithm of the activity of the primary ion; a_B is the activity of the interfering ion which is fixed; Z_A and Z_B are the charge numbers of the primary ion, A and of the interfering ion, B. The selectivity coefficients so obtained are compiled in Table-3. It is evident from the selectivity coefficients data, that the sensor exhibits a high performance for neodymium ion compared with other metal ions.

TABLE-3

SELECTIVITY COEFFICIENTS FOR Nd(III) SENSOR USING FIXED INTERFERENCE METHODS OF INTERFERING IONS

Interfering ions	K _{sel}	Interfering ions	K _{sel}
Na ⁺	3.28 × 10 ⁻²	Ca ²⁺	4.36 × 10 ⁻³
K ⁺	3.49 × 10 ⁻²	Gd ³⁺	8.53 × 10 ⁻³
Mg ²⁺	2.45 × 10 ⁻²	Sm ³⁺	2.48 × 10 ⁻²
Pb ²⁺	2.48 × 10 ⁻²	La ³⁺	6.14 × 10 ⁻⁴
Ag ⁺	3.36 × 10 ⁻²	Pr ³⁺	9.54 × 10 ⁻⁴

Analytical application: The developed sensor was successfully utilized for the determination of neodymium ions in various binary mixtures. Concentration of both the components in each combination was made 5.0 × 10⁻⁴ M and the results are presented in Table-4. It was observed that the recoveries of Nd(III) ions are accurate in all cases and the sensors can be employed for the determination of Nd(III) in real samples having different analytical matrixes.

Comparison of the developed sensor with other Nd(III) sensors: Table-5 compares the response characteristics of newly developed sensors with those of the previously reported sensors in literature. The sensor showed comparable working concentration range, pH and response time with respect to the other Nd(III) selective sensors reported in literature [25-35].

TABLE-4
DETERMINATION OF NEODYMIUM IN BINARY MIXTURES

Nd ³⁺ (M) taken	Added cation (M)	Nd ³⁺ found (M)*
5.0 × 10 ⁻⁴	La ³⁺ (5.0 × 10 ⁻⁴)	4.8 × 10 ⁻⁴
5.0 × 10 ⁻⁴	Pr ³⁺ (5.0 × 10 ⁻⁴)	5.1 × 10 ⁻⁴
5.0 × 10 ⁻⁴	Pb ²⁺ (5.0 × 10 ⁻⁴)	4.9 × 10 ⁻⁴
5.0 × 10 ⁻⁴	Gd ³⁺ (5.0 × 10 ⁻⁴)	5.2 × 10 ⁻⁴
5.0 × 10 ⁻⁴	Na ⁺ (5.0 × 10 ⁻⁴)	4.7 × 10 ⁻⁴

*Average of six replicates

Conclusion

Carbon paste sensor based on N¹,N²-bis(salicylidine)-butane-1,4-diamine as ionophore was developed for the determination of Nd(III). This sensor showed a good Nernstian response over a wide concentration range with a fast response time. pH range of the developed sensor was found to be 3.5-8.0. The electrode showed better selectivity, working concentration range, slope and pH range in comparison to other Nd(III) selective sensors reported in literature (Table-4). The proposed sensor can be successfully applied for the direct determination of neodymium in binary mixtures.

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TABLE-5
COMPARISON OF THE RESPONSE CHARACTERISTICS OF THE DEVELOPED SENSOR WITH OTHER REPORTED NEODYMIUM SENSORS

Sensor No.	Working concentration range (M)	pH	Response time (s)	Slope (mV/decade)	Reference
1	5 × 10 ⁻⁷ to 1 × 10 ⁻²	4.0-8.0	10	19.8 ± 0.3	[26]
2	1 × 10 ⁻⁶ to 1 × 10 ⁻²	2.4-8.5	7	21.2 ± 0.2	[27]
3	1 × 10 ⁻⁶ to 1 × 10 ⁻²	3.7-8.3	< 10	19.7 ± 0.4	[28]
4	1 × 10 ⁻⁶ to 1 × 10 ⁻²	3.0-7.6	5	19.8 ± 0.4	[29]
5	1 × 10 ⁻⁶ to 1 × 10 ⁻²	3.0-7.0	< 15	19.4 ± 0.3	[30]
6	1 × 10 ⁻⁵ to 1 × 10 ⁻²	3.5-8.5	< 10	19.7 ± 0.3	[33]
7	1 × 10 ⁻⁵ to 1 × 10 ⁻²	4.0-8.0	15	19.6 ± 0.3	[32]
8	1 × 10 ⁻⁶ to 1 × 10 ⁻²	4.0-6.5	< 5	20.1	[31]
9	5 × 10 ⁻⁶ to 1 × 10 ⁻²	2.9-9.2	< 10	19.5 ± 0.4	[34]
10	1 × 10 ⁻⁶ to 1 × 10 ⁻²	2.7-8.1	5	20.2 ± 0.2	[35]
11	1 × 10 ⁻⁶ to 1 × 10 ⁻²	3.0-7.5	< 15	20.6 ± 0.3	[25]
12	1 × 10 ⁻⁶ to 1 × 10 ⁻²	3.5-8.0	< 10	19.5 ± 0.3	This work

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