Comparative evaluation of Dy(III) selective poly(vinyl) chloride based membrane electrodes of macrocyclic tetraimine Schiff's bases

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A B S T R A C T

Three different derivatives of macrocyclic tetraimine Schiff's base have been synthesized and explored as a neutral ionophores for preparing poly(vinyl chloride) based membrane sensors selective to Dy^{3+}. The addition of sodium tetraphenyl borate and various plasticizers, viz., *o*-NPOE, DBP, DBBP, DOP and CN has been found to substantially improve the performance of the sensors. The best performance was obtained with the sensor no. 1 having membrane of Schiff's base (SL-1) with composition (w/w) SL-1 (4.5%): PVC (30.5%): *o*-NPOE (59.5%): NaTPB (5.5%). This sensor exhibits Nernstian response with slope 19.4 mV/decade of activity in the concentration range of 10^{-8} to 1.0×10^{-2} M Dy^{3+}, performs satisfactorily over wide pH range of (2.8–7.2) with a fast response time (10 s). The sensor was also found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of acetonitrile, methanol or ethanol. The proposed sensor can be used over a period of 1.5 months without significant drift in potentials. The sensor has been also utilized for the determination of Dy^{3+} level in different soil samples.

1. Introduction

Although the dysprosium has negligible toxic effect on human beings, only mild toxicity can be produced by ingestion of soluble salts of dysprosium. It was calculated that a dose of 500 g or more would be needed to put a person's life at risk. Dysprosium has number of applications that make its analysis more advantageous. Dysprosium is used, in conjunction with vanadium and other elements, for making laser materials [1]. It is used for nuclear control rods; dysprosium oxide (also known as dysprosia) with nickel cement compounds which absorb neutrons readily without swelling or contracting under prolonged neutron bombardment, is being used for cooling rods in nuclear reactors [2]. Dysprosium also used in semiconductor device [3,4] and can be used in some metal alloys to provide strength [5]. Therefore its determination in mineral and salt solutions is very important

There are lots of techniques for the determination of dysprosium such as A.A.S [6], ICP-MS [7] and ICP-AES [8]. These methods either are time-consuming, involve multiple sample manipulations, or are too expensive for most analytical laboratories; ion-selective electrodes (ISE) provide analytical procedures for such situations as they are fast, convenient, having minimum sample pre-treatment requirement and may also be suitable for online analysis. In view of such advantages, a number of lanthanide ion selective sensors based on poly(vinyl) chloride have been developed such as La^{3+} [9,10], Yb^{3+} [11], Gd^{3+} [12], Sm^{3+} [13], Er^{3+} [14], Tb^{3+} [15] and also on Dy^{3+} [2,16,17–19]. Although lot of work has been done on Dy^{3+} selective membrane electrodes with good selective ranges, no one did comparative evaluation of Dy^{3+} selective membrane electrodes; therefore authors have been synthesized three different derivatives of macrocyclic tetraimine Schiff's base for comparative evaluation of Dy^{3+} selective membrane electrodes and improved the detection limit compared to reported work.

2. Experimental

2.1. Reagents and materials

1,2-ethanediamine, high molecular weight polyvinyl chloride (PVC), potassium tetra fluoroborate (KBF_4) and 1,4-butadiamine Aldrich (Wisconsin, USA), tri-*n*-butylphosphate (TBP) BDH (Poole, England), chloronapthalene (CN), dibutylphthalate (DBP) and dibutyl(butyl) phosphonate (DBBP) Mobile (Alabama, USA), *o*-nitrophenyl octyl ether (*o*-NPOE), Oleic acid (OA) Sisco research Lab (Mumbai, Maharashtra, India), dioctylphthalate (DOP) renkem (Gurgaon, India) and potassium tetrakis(4-chlorophenyl borate) (KTpClPB) fluka (Ronkonkoma, NY) were purchased and used as

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received. 0.1 M stock solutions were prepared by dissolving AR grade metal nitrates in double distilled water and standardized wherever necessary. The working solutions of different concentration were prepared by diluting the stock solutions.

2.2. Synthesis of ligands

2.2.1. Synthesis of bis(5-formyl-2-thienyl)methane, S_A [20]

A solution of bis(5-bromo-2-thienyl)methane [21] (6.3 g, 19.0 mmol) in dry ether (40 ml) was added over a period of 10 min to 15% buthyllithium–hexane solution (19.0 g) in dry diethyl ether (30 ml) at −40 to −50 °C under N_2 atmosphere. Then, N,N-dimethyl formamide (DMF) (2.8 g, 38 mmol) in dry diethyl ether (20 ml) was added over a period of 5 min; the mixture was stirred for 1 h at room temperature. After this, the solution was added to crushed ice (100 g); the ether layer was washed successively by a 5% HCl aqueous solution, a saturated $NaHCO_3$. After removing the solvent, the crude product was crystallized with ethanol to give colorless product.

Color: colorless; mp: 95 °C; I.R (KBr): 1645 cm^{-1} (CHO); ^{1}H NMR (CDCl$_3$): δ = 4.43 (2H, s), 7.00 (2H, d, J = 3.6 Hz), 7.62 (2H, d, J = 3.6 Hz) and 9.83 (2H, s, CHO); MS m/z 236 (M$^+$, 100%)

2.2.1.1. Synthesis of 31,32,33,34-tetrathia-3,6,18,21-tetraazapentacyclo[26.2.1.1^{8,11}.1^{13,16}.1^{23,26}] tetratriaconta-1(30), 2,6,8,10,13,15,17, 21,23,25,28-dodecaene, SL-1.
A solution of S_A (0.25 g, 1.0 mmol) in CHCl$_3$ (20 ml) and a solution of 1,2-ethanediamine (0.06 g, 1.0 mmol) in CHCl$_3$ (20 ml) were added simultaneously to the CHCl$_3$ (20 ml) over a period of 1.5 h with stirring at room temperature. After stirring for 30 min, the reaction mixture was filtered in order to remove any insoluble precipitate; the filtrate was then dried over Na_2SO_4 and concentrated. The yellow powder, thus obtained, was washed with ethanol (20 ml × 2) giving SL-1 (2.2 g, 83%). Color: colorless; mp: 158 °C; I.R (KBr) 2820, 1620, and 840 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 3.83 (8H, s), 4.20 (4H, s), 6.73 (4H, d, J = 3.6 Hz), 7.03 (4H, d, J = 3.6 Hz.) and 8.15 (4H, s); MS m/z 520 (M$^+$, 10%). Elemental analysis was corresponding to the structure as given in Fig. 1.

2.2.2. Synthesis of 12,12,27,27-tetramethyl-31,32,33,34-tetrathia-3,6,18,21-tetraazapentacyclo [26.2.1.1^{8,11}.1^{13,16}.1^{23,26}] tetratriaconta-1 (30), 2,6,8,10,13,15,17,21,23,25,28-dodecanene, SL-2

The solution of 2,2-bis(5-formyl-2-thienyl) propane, synthesized by the same procedure as given above [22] (2.6 g, 10 mmol) in CHCl$_3$ (50 ml) and 1,2-ethanediamine (0.6 g, 10 mmol) in CHCl$_3$ (100 ml) were added simultaneously to 50 ml of CHCl$_3$ over a period of 15 h with stirring at room temperature; the mixture was stirred for an additional 30 h. After usual work-up, the crude product was obtained as yellow powder, which was recrystalized with CHCl$_3$–hexane to give SL-2 (2.4 g, 84%). Color: pale-yellow; mp: 233 °C; I.R (KBr): 2970, 2930, 2830, 1630 and 800 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.80 (12H, s), 3.79 (8H, s), 6.74 (4H, d, J = 3.6 Hz), 6.99 (4H, d, J = 3.6 Hz); ^{13}C NMR (CDCl$_3$): δ = 32.41, 40.92, 61.07, 123.61, 130.04, 155.83 and MS m/z 576 (M$^+$, 26%). Elemental analysis corresponds to the structure given in Fig. 1.

2.2.3. Synthesis of 13,13,29,29,-tetramethyl-33,34,35,36-tetrathia -3,7,19,23-tetraazapentacyclo [28.2.1.1^{9,12}.1^{14,17}.1^{25,28}] hexatriaconta-1(32), 2,7,9,11,14,16,18,23,25,27,30-dodecaene, SL-3

The solution of 2,2-bis(5-formyl-2-thienyl) propane, synthesized by same procedure as given above (2.6 g, 10 mmol) in CHCl$_3$ (50 ml) and 1,3-propanediamine (0.6 g, 10 mmol) in CHCl$_3$ (100 ml) were added simultaneously to 50 ml of CHCl$_3$ over a period of 15 h with stirring at room temperature; the mixture was stirred
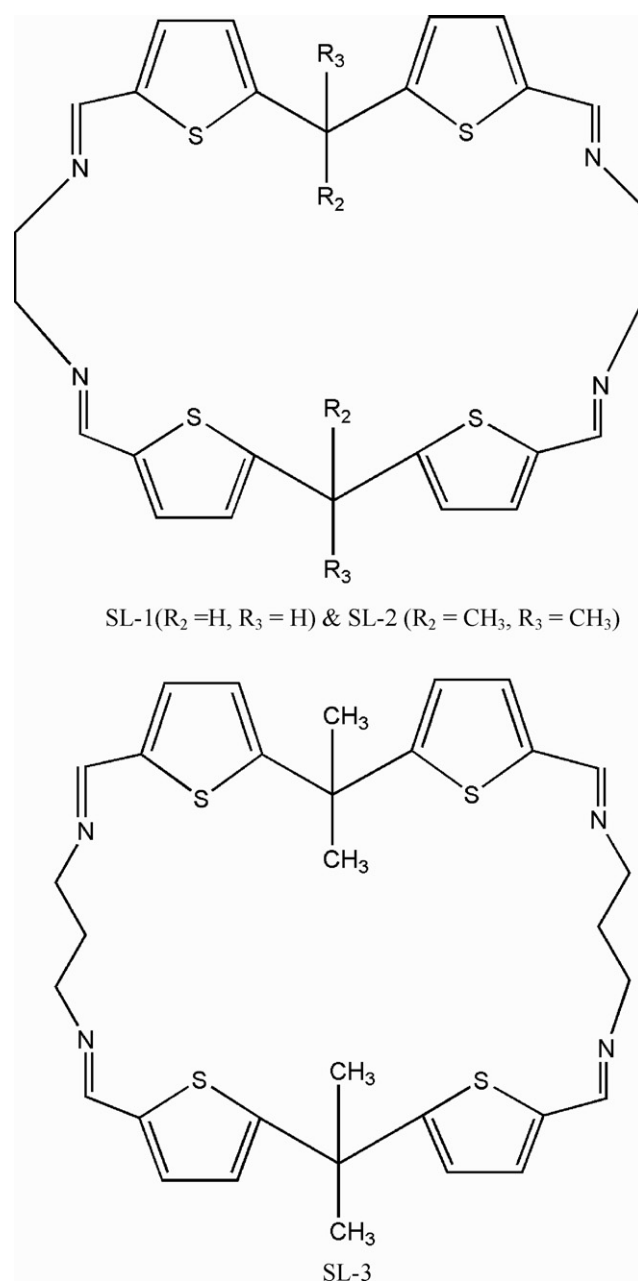

for an additional 30 h. After usual work-up, the crude product was obtained as colorless powder, which was recrystalized with CHCl$_3$–hexane to give SL-3 (14%). Color: colorless; mp: 270 °C; I.R (KBr): 2975, 2840 and 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.40–2.40 (16H, m), 3.53 (8H, t, J = 7.2 Hz), 6.76 (4H, d, J = 3.6 Hz), 7.00 (4H, d, J = 3.6 Hz) and 8.20 (4H, s); ^{13}C NMR (CDCl$_3$): δ = 31.74, 32.38, 40.89, 58.60, 123.54, 129.64, 140.56, 154.46 and 157.94 cm^{-1} MS m/z 604 (M$^+$, 1%). Elemental analysis corresponds to the structure given in Fig. 1.

2.3. Fabrication of electrodes

The membranes have been fabricated as suggested by Craggs et al. [23]. The PVC-based membranes have been prepared by dissolving appropriate amounts of Schiff's bases (SL-1 and SL-2), different anionic additives NaTPB, OA, KTpClPB, KBF4 and plasticizers DBP, o-NPOE, CN, DOP and PVC in THF (5 ml). The components were

Fig. 1. Structures of macrocycli Schiff's bases SL-1, SL-2 and SL-3.

SL-1(R$_2$ =H, R$_3$ = H) & SL-2 (R$_2$ = CH$_3$, R$_3$ = CH$_3$)

SL-3

Table 1
The composition (%, w/w) of best optimized membranes of different ligands.

Electrode type	Ionophore	PVC	Additives	Plasticizer	Working concentration range (M)	Detection limit (M)	Slope ($\pm$0.2 mV/ decade of activity)	Response time (s)
1	SL-1(4.5)	30.5	NaTPB(5.5)	o-NPOE(59.5)	5.4×10^{-8} to 1.0×10^{-2}	4.1×10^{-8}	19.4	10
2	SL-2(4.5)	30.5	NaTPB(5.5)	o-NPOE(59.5)	3.2×10^{-7} to 1.0×10^{-2}	2.1×10^{-7}	18.5	10
3	SL-3(4.5)	30.5	NaTPB(5.5)	o-NPOE(59.5)	2.1×10^{-6} to 1.0×10^{-2}	1.7×10^{-6}	17.8	11

added in terms of weight percentages. The homogeneous mixture was obtained after complete dissolution of all the components, concentrated by evaporating THF and it has been poured into poly-acrylate rings placed on a smooth glass plate. The viscosity of the solution and solvent evaporation was carefully controlled to obtain membranes with reproducible characteristics and uniform thickness otherwise the response of the membrane sensors have shown a significant variation. The membranes of 0.4 mm thickness were removed carefully from the glass plate and glued to one end of a "Pyrex" glass tube. It is known that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition and nature of plasticizer used [24]. Thus, the ratio of membrane ingredients, time of contact, concentration of equilibrating solution, etc. were optimized after a good deal of experimentation to provide membranes, which generate reproducible and stable potentials. The membranes having only PVC as membrane ingredient (dummy membranes) have also been prepared to observe whether any background potentials were being produced due to binding material or not. The potentials were not generated without the electroactive material in the membrane.

2.4. Conditioning of membranes and potential measurements

The membranes were equilibrated for 2 days in 0.01 M DyCl$_3$ solution. The potentials have been measured by varying the concentration of DyCl$_3$ in test solution in the range of 1.0×10^{-8} to 1.0×10^{-1} M. The standard DyCl$_3$ solutions of metal salt have been obtained by gradual dilution of 0.1 M DyCl$_3$ solution and pH adjusted (pH 5.2) using Tris–HCl buffer. The potential measurements were carried out at $25 \pm 1\,^{\circ}$C using saturated calomel electrodes (SCE) as reference electrodes with the following cell assembly:

Hg/Hg$_2$Cl$_2$|KCl (satd.)|1.0 M DyCl$_3$||PVC membrane||test solution|Hg/Hg$_2$Cl$_2$|KCl (satd.)

3. Result and discussion

3.1. Effect of internal solution

The proposed electrodes were also examined at different concentrations of inner reference solution (1.0×10^{-1} to 1.0×10^{-4} M) and potential response of the electrodes based on SL-1, SL-2 and SL-3 membranes have been observed. It was found that the best results in terms of slope and working concentration range has been obtained with internal solution of activity 1.0×10^{-1} M. Thus, 1.0×10^{-1} M concentration of the reference solution was quite appropriate for the smooth functioning of the proposed electrodes.

3.2. Optimization of membrane electrodes

Once the membrane electrodes based on different ligands (SL-1, SL-2 and SL-3) have been synthesized and as their responses were checked against different concentration of Dy^{3+}, further to get the best results, membrane compositions have been optimized using different concentration of anionic additives: NaTPB, OA, KTpClPB,

KBF4 and plasticizers: TEHP, DBP, o-NPOE, CN, DOP, PVC and it was observed that the best response in terms of detection limit, working range, response time and slope observed with electrode no. 1 having composition (%, w/w); (SL-1) (4.5%): PVC (30.5%): o-NPOE (59.5%): NaTPB (5.5%) (Table 1). Although the response time and slopes are almost similar, working range and detection limit are different. This effect can be explained on the basis of cavity effect (size of cavity) of different ligands as SL-2 has –CH$_3$ in place of –H of SL-1 that makes SL-1 more selective for Dy^{3+} compared to SL-2 and SL-3, as it can easily fit into the cavity. SL-3 has some larger cavity compared to both SL-1 and SL-2 that makes it less selective compared to both of them.

3.3. Determination of formation constant

Formation constant of the ion–ionophore complex within the membrane phase is a very important parameter that dictates the practical selectivity of the sensor. In this method, two membrane segments are fused together, with only one containing the ionophore, to give a concentration-polarized sandwich membrane. A membrane potential measurement of this transient condition reveals the ion activity ratio at both interfaces, which translates into the apparent binding constants of the ion–ionophore complex [25]. In this method, complex formation constants are obtained by neglecting ion pairing. As reported, the membrane potential E_M is determined by subtracting the cell potential for a membrane without ionophore from that for the sandwich membrane. The formation constant is then calculated from the following equation.

$$\beta_{ILn} = \left(L_T - \frac{nR_T}{Z_I}\right)^{-n} \exp\left(\frac{E_M z_I F}{RT}\right) \tag{1}$$

where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n

Table 2
The formation constants of macrocyclic ligands–metal complexes.

Cations	SL-1 Formation constant (log β_{ILn})^a $\pm$ S.D.	SL-2 Formation constant (log β_{ILn})^a $\pm$ S.D.	SL-3 Formation constant (log β_{ILn})^a $\pm$ S.D.
Na$^+$	0.42 $\pm$ 0.03	0.37 $\pm$ 0.02	0.34 $\pm$ 0.03
K$^+$	0.38 $\pm$ 0.04	0.32 $\pm$ 0.04	0.30 $\pm$ 0.04
Ag$^+$	1.46 $\pm$ 0.06	1.05 $\pm$ 0.05	1.04 $\pm$ 0.03
Cu^{2+}	3.21 $\pm$ 0.10	3.10 $\pm$ 0.23	3.09 $\pm$ 0.22
Pb^{2+}	3.58 $\pm$ 0.34	3.44 $\pm$ 0.03	3.41 $\pm$ 0.01
Cd^{2+}	3.52 $\pm$ 0.23	3.41 $\pm$ 0.21	3.39 $\pm$ 0.06
Zn^{2+}	3.40 $\pm$ 0.06	3.38 $\pm$ 0.23	3.35 $\pm$ 0.21
Co^{2+}	3.15 $\pm$ 0.22	3.10 $\pm$ 0.11	3.09 $\pm$ 0.12
Cr^{3+}	4.52 $\pm$ 0.40	4.48 $\pm$ 0.07	4.45 $\pm$ 0.21
Ce^{3+}	5.15 $\pm$ 0.21	5.10 $\pm$ 0.16	5.07 $\pm$ 0.08
Nd^{3+}	5.21 $\pm$ 0.32	5.18 $\pm$ 0.30	5.13 $\pm$ 0.04
Sm^{3+}	5.33 $\pm$ 0.23	5.29 $\pm$ 0.23	5.25 $\pm$ 0.19
Eu^{3+}	5.34 $\pm$ 0.21	5.33 $\pm$ 0.19	5.31 $\pm$ 0.23
Gd^{3+}	5.40 $\pm$ 0.23	5.38 $\pm$ 0.21	5.36 $\pm$ 0.18
Tb^{3+}	5.45 $\pm$ 0.33	5.43 $\pm$ 0.05	5.40 $\pm$ 0.12
Dy^{3+}	8.86 $\pm$ 0.01	7.83 $\pm$ 0.04	6.86 $\pm$ 0.08
Ho^{3+}	5.43 $\pm$ 0.15	5.40 $\pm$ 0.05	5.36 $\pm$ 0.13
Er^{3+}	5.51 $\pm$ 0.31	5.49 $\pm$ 0.12	5.47 $\pm$ 0.21

^{a} Mean value $\pm$ standard deviation (four measurements).

Table 3
Selectivity coefficient (log $_{Dy^{3+},B}^{pot}$) values observed for best Dy(III) selective electrodes as calculated by fixed interference method.

Interfering ion (B)	Selectivity coefficient (log $_{Dy^{3+},B}^{pot}$) by FIM[a]		
	Sensor no. 1	Sensor no. 2	Sensor no. 3
Na$^+$	−4.24	−4.39	−4.73
K$^+$	−4.34	−4.53	−4.82
Ag^{3+}	−4.22	−4.34	−4.68
Co^{2+}	−3.91	−3.95	−3.97
Zn^{2+}	−3.88	−3.89	−3.90
Cd^{2+}	−3.64	−3.68	−3.75
Pb^{2+}	−3.54	−3.61	−3.63
Cr^{3+}	−3.44	−3.47	−3.50
Ce^{3+}	−3.34	−3.38	−3.41
Nd^{3+}	−3.21	−3.28	−3.31
Sm^{3+}	−3.10	−3.16	−3.21
Eu^{3+}	−3.05	−3.11	−3.18
Gd^{3+}	−2.93	−2.96	−2.98
Ho^{3+}	−2.91	−2.93	−2.95
Tb^{3+}	−2.85	−2.87	−2.89
Er^{3+}	−2.79	−2.84	−2.87

[a] Fixed interference method.

is the ion–ionophore complex stoichiometry, and *R*, *T* and *F* are the gas constant, the absolute temperature, and the Faraday constant, respectively. The ion I carries a charge of z_I. The determined formation constants (log β_{ILn}) for the examined different complexes were recorded in Table 2. The elapsed time between sandwich fusion and exposure to electrolyte was typically <1 min. The potential was recorded as the mean of the last minute of a 5 min measurement period in the appropriate salt solution. The potential of such sandwich membranes remains free of diffusion-induced potential drifts for about 20 min. Standard deviations were obtained based on the measurements of sets of at least three replicate membrane disks that were made from the same parent membrane. A careful analysis of the data in Table 2, reveals that Dy^{3+} ion has significant cation-binding characteristics.

3.4. Potentiometric selectivity

To investigate the selectivity of the proposed membrane electrodes, a fixed interfering ion method (FIM) was used [26–31]. The emf of a cell comprising an ion-selective electrode and a reference electrode (SCE cell) was measured for solutions of constant activity of the interfering ion (0.01 M), *a*B, and varying activity of the primary ion, *a*A. The emf values obtained are plotted versus the logarithm of the activity of the interfering ion. The intersection of the extrapolated linear portions of this plot indicates the value of *a*A that is used to calculate $K_{Dy^{3+},B}^{pot}$

$$K_{Dy^{3+},B}^{pot} = \frac{aDy^{3+}}{(aB)^{zA/zB}} \quad (2)$$

where *a*Dy3+ is the activity of the primary ion (Dy^{3+}) at the lower detection limit in the presence of interfering ion B with activity of *a*B, having *z*A and *z*B their respective charges. The values of selectivity coefficient so determined for best responsive membrane electrodes of SL-1, Sl-2 and SL-3, obtained results were compiled in Table 3. It was observed that the selectivity of electrode no. 1, towards Dy^{3+} is higher over most of the reported membrane electrodes (Table 4) in terms of detection limit, working range and response time. Next all studies were carried out with best responsive membrane electrode no. 1.

3.5. Response study of sensor no. 1 with different metal ions

In this study various PVC-membrane ion-selective electrodes with the synthesized Schiff's base were prepared, having identi-
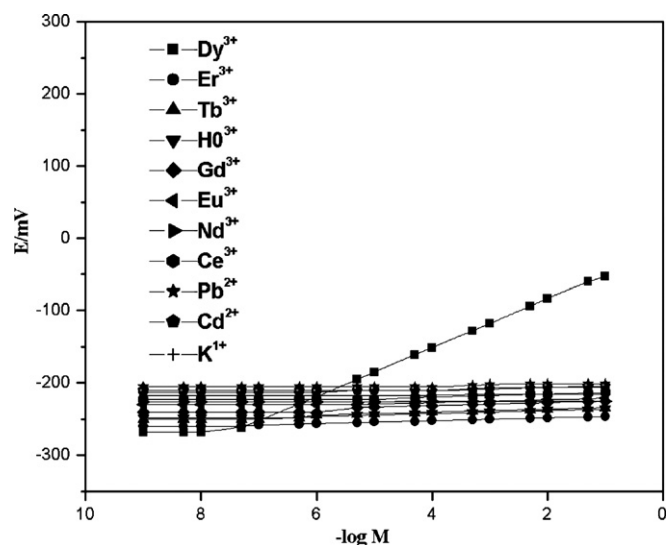

Fig. 2. The response study of best responsive sensor no. 1 with different metal ions.

cal composition (SL-1) (4.5%): PVC (30.5%): *o*-NPOE (59.5%): NaTPB (5.5%) and tested for different cations. The potential response of the electrodes based on SL-1for different cations are shown in Fig. 2.

3.6. pH and non-aqueous effect

The pH dependence response of the sensor no. 1 has been tested in the range of 1.5–8.0 at two Dy^{3+} concentrations of 1.0×10^{-3} and 1.0×10^{-4} M. The pH was adjusted with dilute nitric acid or sodium hydroxide solutions. The potential of the sensor was determined as a function of pH and the results are shown in Fig. 3. The potential remains constant over the pH range of 2.8–7.2, which may be taken as the working pH range of the sensor assembly. The performance of the sensor no. 1 was further assessed in partial non-aqueous media, i.e. methanol–water, ethanol–water and acetonitrile–water mixture. The results obtained are compiled in Table 5 and show that up to 20% non-aqueous content no significant change occurs in the slope and working concentration of the
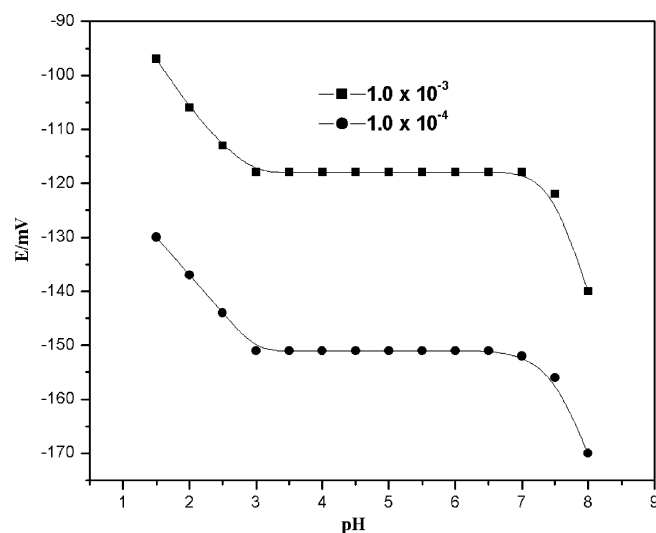

Fig. 3. pH response of sensor no. 1 at two concentrations (1.0×10^{-3} and 1.0×10^{-4} M).

Table 4
Comparative study of best responsive membrane electrode no. 1, with reported literature.

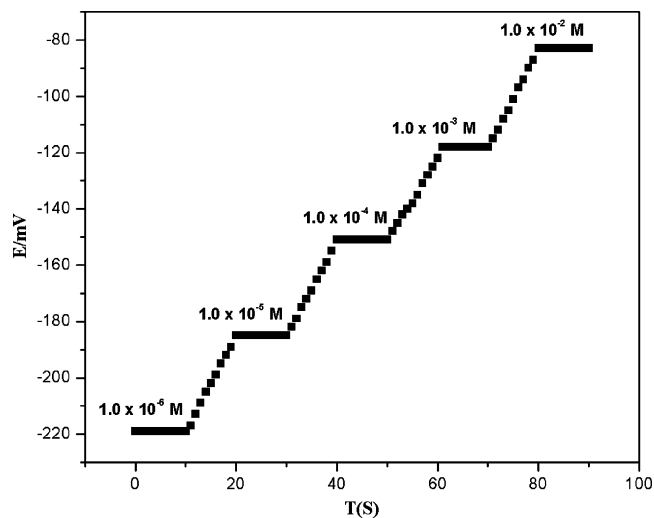| Reference	Inophore	Working range (M)	Dectection limit (M)	Slope (mV/decade of activity)	Response time (s)
[16]	N,N-bis(pyrrolidene)benzne-1,2-diamine	1.0×10^{-5} to 1.0×10^{-1}	6.0×10^{-6}	20.6 ± 0.2	<20
[2]	[(E)-N-(2 hydroxybenzylidene)benzohydraide]	1.0×10^{-6} to 1.0×10^{-2}	8.0×10^{-7}	20.1 ± 0.8	<20
[17]	Procaine	1.0×10^{-6} to 1.0×10^{-1}	7.9×10^{-7}	20.1 ± 0.1	<10
[18]	6-Hydrazino-1,5-diphenyl-6,7-dihydropyrazolo[3,4-d]pyrimidine-4(5H)-imine	8.0×10^{-7} to 1.0×10^{-1}	4.2×10^{-7}	19.6 ± 0.3	<10
[19]	Benzoxazoleguanidine (BG)	1.0×10^{-6} to 1.0×10^{-1}	4.7×10^{-7}	19.5 ± 0.4	<10
[This work]	Derivative of bis(5-bromo-2-thienyl)methane, SL-1	5.4×10^{-8} to 1.0×10^{-2}	4.1×10^{-8}	19.4 ± 0.2	10

sensor. However, above 20% non-aqueous content, the working concentration of the sensor is significantly reduced, and thus the sensor can only be utilized in mixtures containing up to 20% non-aqueous content.

3.7. Dynamic response time and life time

The critical response characteristics of the proposed Dy^{3+} selective electrode were investigated according to IUPAC recommendations [27–29], and the result thus obtained was 10 s (for reaching >95% of its equilibrium potential). This is most probably due to the fast exchange kinetics of complexation–decomplexation of Dy^{3+} ions with SL-1 at the test solution–membrane interface. The corresponding emf versus time plot was finally used for the evaluation of the practical response time of the electrode. The practical reversibility required for the Dy^{3+} sensor, to reach a potential within ± 1 mV of the final equilibrium value, after successive immersion of a series of nickel ion solutions, each having a 10-fold difference in concentration, was measured (Fig. 4). The sensing behavior of the membrane remained unchanged when the potentials were recorded either from low to high concentrations or vice versa. The life time of best responsive sensor no. 1 was found to be 1.5 months after which ingredients start leaching out of the membrane and finally result in the destruction of membrane.

Table 5
The performance of sensor no. 1 in partially non-aqueous media.

Non-aqueous content (%, v/v)	Working concentration range (M)	Slope (± 0.2 mV/decade of activity)
0	5.4×10^{-8} to 1.0×10^{-2}	19.4
Methanol		
10	5.4×10^{-8} to 1.0×10^{-2}	19.4
15	5.5×10^{-8} to 1.0×10^{-2}	19.4
20	5.5×10^{-8} to 1.0×10^{-2}	19.4
25	7.6×10^{-7} to 1.0×10^{-2}	18.5
30	4.4×10^{-6} to 1.0×10^{-2}	17.5
Ethanol		
10	5.4×10^{-8} to 1.0×10^{-2}	19.4
15	5.4×10^{-8} to 1.0×10^{-2}	19.4
20	5.5×10^{-8} to 1.0×10^{-2}	19.4
25	6.8×10^{-7} to 1.0×10^{-2}	18.4
30	4.2×10^{-6} to 1.0×10^{-2}	17.8
Acetonitrile		
10	5.4×10^{-8} to 1.0×10^{-2}	19.4
15	5.5×10^{-8} to 1.0×10^{-2}	19.4
20	5.5×10^{-8} to 1.0×10^{-2}	19.4
25	5.6×10^{-7} to 1.0×10^{-2}	19.1
30	7.1×10^{-6} to 1.0×10^{-2}	17.6

Fig. 4. Dynamic response study of sensor no. 1 at concentration range of 1.0×10^{-2} to 1.0×10^{-6} M.

Table 6
Determination of dysprosium in soil samples.

Sample no.	Proposed sensor (ppm $\pm$ S.D.)[a]	Arsenazo method (ppm $\pm$ S.D.)[a]
1	68.3 ± 0.3	64.7 ± 0.4
2	54.3 ± 0.5	53.2 ± 0.3
3	34.8 ± 0.3	31.6 ± 0.4
4	23.4 ± 0.4	21.4 ± 0.3
5	31.5 ± 0.3	29.5 ± 0.4

[a] Triplicate measurement.

4. Analytical application

4.1. Determination of Dy^{3+} in soil samples

The analytical application of proposed sensor was utilized to assess the Dy^{3+} concentration in soil samples as determined by reported method [17]. 1.0 g sample was weighed into a PTFE beaker, and 5 ml of 70% $HClO_4$ and 10 ml of 48% HF were added. The sample was heated in sand bath to incipient dryness. The acid attack with $HClO_4$ and HF (1 + 2) was repeated three times to complete digestion of the silicate matrix. Then the samples were transferred into flasks and diluted with 5 ml of NaOH 5% and distilled water to 50 ml (pH ~5.4) and the Dy^{3+} ion concentration in the samples was determined. The result, derived from triplicate measurements with the same sensor, was found to be in satisfactory agreement with that determined by Arsenazo method (Marczenko 1986), as it can be seen from Table 6.

5. Conclusion

Three different derivatives of macrocyclic tetraimine Schiff's base have been synthesized and explored for comparative analysis of best Dy^{3+} selective response and it was observed that sensor no. 1 is good selective compare to sensor no. 2 and 3. In this way author explain the cavity effect of all the proposed sensors and proved that sensor no. 1 has best suited cavity effect for selective response against Dy^{3+}.

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