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Comparative studies of neodymium (III)-selective PVC membrane sensors

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ABSTRACT

Sensors based on two neutral ionophores, N,N′-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine (**L_1**) and 3,3′-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl)pyridine-2-ol) (**L_2**) are described for quantification of neodymium (III). Effect of various plasticizers; 2-nitrophenyloctylether (*o*-NPOE), dibutyl butylphosphonate (DBBP), tri-n-butyl phosphates (TBP), dioctylpthalate (DOP) and chloronapthalen (CN) and anion excluder, sodiumtetraphenylborate (NaTPB) has been studied. The membrane composition of PVC:*o*-NPOE:ionophore (**L_1**):NaTPB (w/w; mg) of 150:300:5:5 exhibited best performance. The sensor with ionophore (**L_1**) exhibits significantly enhanced selectivity towards neodymium (III) in the concentration range 5.0×10^{-7} to 1.0×10^{-2} M with a detection limit of 1.0×10^{-7} M and a Nernstian compliance (19.8 ± 0.3 mV decade^{-1} of activity) within pH range 4.0–8.0. The response time of sensor was found as 10 s. The influence of the membrane composition and possible interfering ions has also been investigated on the response properties of the electrode. The fast and stable response, good reproducibility and long-term stability of the sensor are observed. The sensor has been found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of methanol, ethanol or acetonitrile and could be used for a period of 3 months. The selectivity coefficients determined by using fixed interference method (FIM) indicate high selectivity for neodymium. The proposed electrode shows fairly good discrimination of neodymium (III) from other cations. The application of prepared sensor has been demonstrated in the determination of neodymium (III) in spiked water samples.

1. Introduction

Neodymium is the second most abundant rare earth element. Naturally it is found in minerals such as monazite and bastnasite. The amount of neodymium present in human system is quite small and, although the metal has no biological role, it can affect the parts of the system. Neodymium dust and salts are irritating to eyes and are considered as a threat to the liver when it accumulates in the human body. Neodymium is used in the formation of permanent magnets that is used in microphones, professional loudspeakers, headphones and computer hard disks [1]. It is used for coloring glass to make welders and glass blowers goggles. It enters in an environment by dumping waste of petrol industries, by thrown away house hold equipment and gradually accumulates in soil and water and eventually leads to increasing concentrations in human beings and animals. Hence, monitoring neodymium concentration is the subject of interest in the last decade. A number of methods have been reported to determine trace amount of neodymium in different samples such as ICP-MS [2], ICP-AES [3], gravimetric determination [4], isotope dilution mass spectroscopy [5,6], absorption spectra of 4f electron transitions [7] and finally, design and preparation of electrochemical sensors for neodymium (III) [8–11]. Most of these methods are time consuming and require expertise and costly instrumentations. In addition the sensors reported have low detection limit and interference from other ions. Thus, a quick, convenient, fast method is required to monitor neodymium in large number of environmental samples. Recently many papers for lanthanide ions have been reported La [12–14], Ce [15–21], Pr [22], Sm [23], Tb [24], Ho [25] and Yb [26] ions.

The aim of this work is the development and comparative study of a neodymium (III) PVC membrane electrodes based on N,N′-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine (**L_1**, Fig. 1) and 3,3′-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl) pyridine-2-ol) (**L_2**, Fig. 2). The values of formation constants show that **L_1** form stronger complex with neodymium (III) than **L_2** and weaker complex with other metal ions.

2. Experimental

2.1. Reagent and solution

1,2-Cyclohexadiamine, pyrrole-2-carboxaldehyde and pyridoxalhydrochloride were purchased from Sigma–Aldrich and used as

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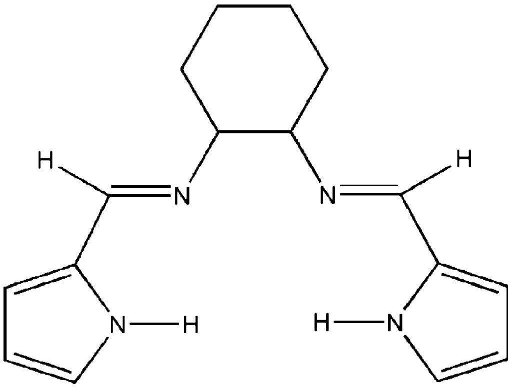

Fig. 1. Structure of ionophore N,N′-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine (**L$_1$**).

received. Analytical grade *o*-nitrophenyloctylether (*o*-NPOE), sodiumtriphenylborate and high molecular weight polyvinyl chloride (PVC) were purchased from Fluka and used as received. Chloronaphthalene (CN) and tri-n-butylphosphate (TBP) were obtained from Highmedia Laboratories (Mumbai, MH, India); dioctylpthalate (DOP) and dibutyl butylphosphonate (DBBP) were obtained from SD-Fine Chem. Limited (Mumbai, MH, India). Neodymium (III) nitrate (Sigma–Aldrich) was used without further purification. Doubly distilled water was used for the preparation of metal salt solutions of different concentrations by diluting stock solution (0.01 M).

2.2. Synthesis of ionophores

Schiff base N,N′-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine (**L$_1$**) was prepared by interaction of pyrrole-2-carbaldehyde with 1,2-cyclohexanediamine according to the literature [27] and 3,3′-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl) pyridine-2-ol) (**L$_2$**) was prepared by interaction of pyridoxalhydrochloride with 1,2-cyclohexanediamine as by reported procedure [28].

2.3. Development of PVC membranes and sandwich PVC membranes

The PVC based membranes were fabricated by dissolving appropriate amounts of ionophores (**L$_1$** or **L$_2$**), cation excluder (NaTBP), plasticizers (CN, DOP, DBBP, TBP or *o*-NOPE) and PVC in tetrahydrofuran (15 mL). The homogeneous mixture obtained was concentrated by evaporation of THF. The oily viscous mixture obtained was poured into polyacrylate rings placed on a smooth glass plate and was covered by glass plate. The solution was then allowed to evaporate for 24 h at room temperature. Transparent membranes of about ∼0.5 mm thickness were obtained, which were then cut to desired size and glued to one end of a 1.5 cm diameter pyrex glass tube with araldite. The molar ratio of membrane components, contact time and concentration of equilibrating solution were optimized so that the potential recorded was reproducible and stable within the standard deviation. The membrane that gave best performance and reproducible results was selected for detailed studies.

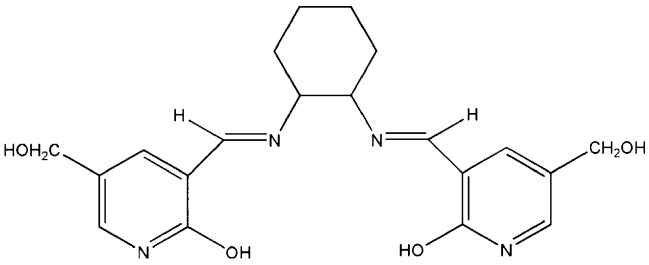

Fig. 2. Structure of ionophore 3,3′-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl)pyridine-2-ol) (**L$_2$**).

The sandwich membrane was prepared by pressing two dry individual membranes (ordinarily one without ionophore and one with the same components and an additional ionophore) together. The obtained sandwich membrane was visibly checked for air bubbles before mounting on electrode body with the ionophore containing segment facing the sample solution. The combined segmented membrane was then rapidly mounted on to the electrode body for further equilibration and potential measurements.

2.4. Conditioning of membranes and potential measurements

The prepared membranes were equilibrated for 2 days in different concentrations of outer (2.0×10^{-1} to 3.0×10^{-3} M) with side by side inner solution of different concentration range (1.0×10^{-2} to 1.0×10^{-3} M) neodymium nitrate solution. The potentials were measured by varying the concentration of neodymium (III) in test solution in the range of 5.0×10^{-9} to 1.0×10^{-2} M. The standard neodymium (III) solutions were obtained by the gradual dilution of 0.1 M neodymium (III) stock solution. The best results were obtained when the concentration of inner electrolyte was 0.001 M $Nd^{3+} + 5.0 \times 10^{-1}$ M Na_2EDTA. This may be due to the decreasing zero-current ion fluxes from the membrane into the sample due to the presence of Na_2EDTA as reported in the literature [29,30]. The potential measurements were carried out at room temperature using the saturated calomel electrodes (SCE) as reference electrode with the following assembly:

SCE|test solution|PVC membrane|10^{-3} M $NdCl_3 + 5.0 \times 10^{-1}$ M Na_2EDTA|SCE

The activities of neodymium (III) were calculated according to the Debye–Huckel procedure, using the following equation [31]:

$$\mathrm{Log}\,\gamma = -0.511\,z^2\left[\frac{\mu^{\frac{1}{2}}}{1+1.5\mu^{\frac{1}{2}}} - 0.2\mu\right], \qquad (1)$$

where μ is the ionic strength and z the valency.

3. Results and discussion

3.1. Membrane composition

The composition of PVC membrane was found to affect the selectivity, linearity and sensitivity of the ionophore; hence, it was optimized by varying the ratio of ionophore, plasticizer and additive used. The potentials of membrane of two Schiff bases **L$_1$** and **L$_2$** are determined as a function of neodymium (III) ion concentration and the results obtained are presented in Table 1. It was observed that the membranes incorporating the ingredients with composition:ionophore (**L$_1$** or **L$_2$**):NaTBP:plasticizer:PVC as (w/w; mg) of 5:5:300:150, exhibited the linear potential response for neodymium (III). This indicates that synergism between lipophilicity and polarity, exist at the composition used and the best result of detection limit was obtained when these properties reach an intermediate value [32–34].

3.2. Effect of plasticizer

The nature of plasticizer has been found to improve the sensitivity and stability of sensors due to characteristics such as lipophilicity, high molecular weight, low vapor pressure and high

Table 1
Optimization of membrane composition of neodymium sensors.

Sensor no.	Composition (w/w, mg)				Slope (mV decade^{-1} of activity)	Linear working range (M)	Detection limit (M)	Response time(s)	Life time (months)
	Ionophore	NATBP	Plasticizer	PVC					
1	$\mathbf{L_1}$, 5	5	300, CN	150	18.1 ± 0.3	1.0×10^{-5} to 1.0×10^{-2}	5.0×10^{-6}	30	2.5
2	$\mathbf{L_1}$, 5	5	300, TBP	150	19.1 ± 0.2	1.0×10^{-6} to 1.0×10^{-2}	3.1×10^{-7}	15	3.0
3	$\mathbf{L_1}$, 3	5	300, DBBP	150	18.5 ± 0.2	3.1×10^{-6} to 1.0×10^{-2}	1.0×10^{-6}	20	3.0
4	$\mathbf{L_1}$, 5	5	300, DOP	150	17.3 ± 0.1	1.0×10^{-5} to 1.0×10^{-2}	1.7×10^{-6}	23	2.5
5	$\mathbf{L_1}$, 5	5	300, *o*-NOPE	150	19.8 ± 0.3	5.0×10^{-7} to 1.0×10^{-2}	1.0×10^{-7}	10	3.0
6	$\mathbf{L_2}$, 5	5	300, CN	150	17.0 ± 0.4	5.0×10^{-5} to 1.0×10^{-2}	3.1×10^{-5}	32	1.7
7	$\mathbf{L_2}$, 5	5	300, TBP	150	19.2 ± 0.2	1.0×10^{-5} to 1.0×10^{-2}	5.0×10^{-6}	18	1.2
8	$\mathbf{L_2}$, 5	5	300, DBBP	150	16.0 ± 0.3	1.6×10^{-5} to 1.0×10^{-2}	4.4×10^{-6}	20	1.0
9	$\mathbf{L_2}$, 5	5	300, DOP	150	16.7 ± 0.2	5.0×10^{-5} to 1.0×10^{-2}	2.2×10^{-5}	23	1.5
10	$\mathbf{L_2}$, 5	5	300, *o*-NPOE	150	19.3 ± 0.1	3.1×10^{-6} to 1.0×10^{-2}	1.0×10^{-6}	14	1.5

capacity to dissolve the substrate and other additives present in the polymeric membrane [35]. Hence, several membranes of varying compositions and different plasticizers CN, DOP, DBBP, TBP and *o*-NPOE in PVC matrix were prepared. The best results obtained are shown in Figs. 3 and 4. It is clear from Table 1 and Figs. 3 and 4 that the best results are obtained with the sensors prepared by using *o*-NPOE as plasticizer. The values of detection limit obtained, with respect to ionophore $\mathbf{L_1}$ and different plasticizers has followed the order: *o*-NPOE (1.0×10^{-7} M) > TBP (3.1×10^{-7} M) > DBBP (1.0×10^{-6} M) > DOP (1.7×10^{-6} M) > CN (5.0×10^{-6} M) for ionophore $\mathbf{L_2}$ and order of detection limit was: *o*-NPOE (1.0×10^{-6} M) > TBP (5.0×10^{-6} M) > (4.4×10^{-6} M) > DOP (2.2×10^{-5} M) > CN (3.1×10^{-5} M). The observed results clearly indicate that as the value of dielectric constant of plasticizers decreases, the detection limit of sensors also decreases.

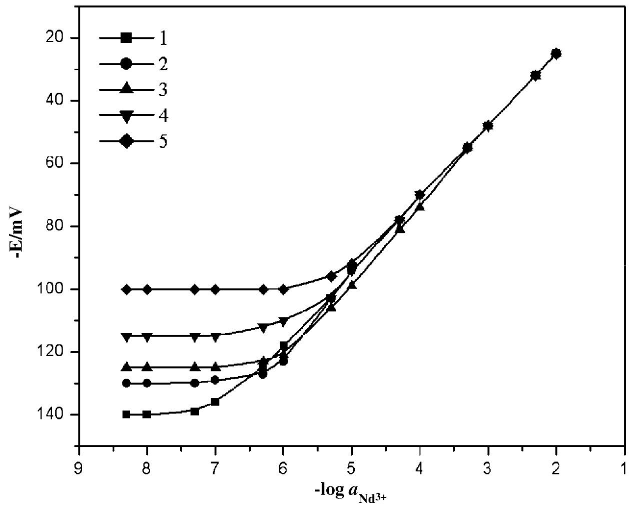

Fig. 3. Variation of membrane potential with activity of neodymium (III) ions, of PVC based membranes of $\mathbf{L_1}$ with plasticizers: (1) *o*-NPOE, (2) TBP, (3) DBBP, (4) DOP, (5) CN.

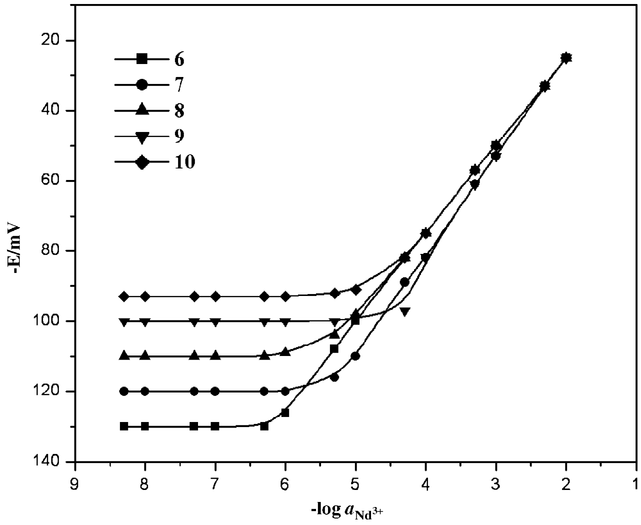

Fig. 4. Variation of membrane potential with activity of neodymium (III) ions, of PVC based membranes of $\mathbf{L_2}$ with plasticizers: (6) *o*-NPOE, (7) TBP, (8) DBBP, (9) CN, (10) DOP.

3.3. *Working concentration range and slope*

The results presented in Table 1 and Fig. 5, indicate that the best electrode (no. 5) based on $\mathbf{L_1}$ exhibits Nernstian slope of 19.8 ± 0.3 mV decade^{-1} of activity, over a wide concentration range of 5.0×10^{-7} to 1.0×10^{-2} M with detection limit 1.0×10^{-7} M while electrode (no. 10) based on $\mathbf{L_2}$ exhibits a Nernstian slope of 19.3 ± 0.1 mV decade^{-1} of activity in the concentration range 3.1×10^{-6} to 1.0×10^{-2} M with a limit of detection 1.0×10^{-6} M. These values of slopes correspond to those expected by Nernst for trivalent cation. The most sensible values of slope and working concentration range correspond to sensors constructed by using *o*-NPOE. This indicates that the solvent medium of *o*-NPOE is probably providing the best complexation environment between neodymium ions and their respective carriers.

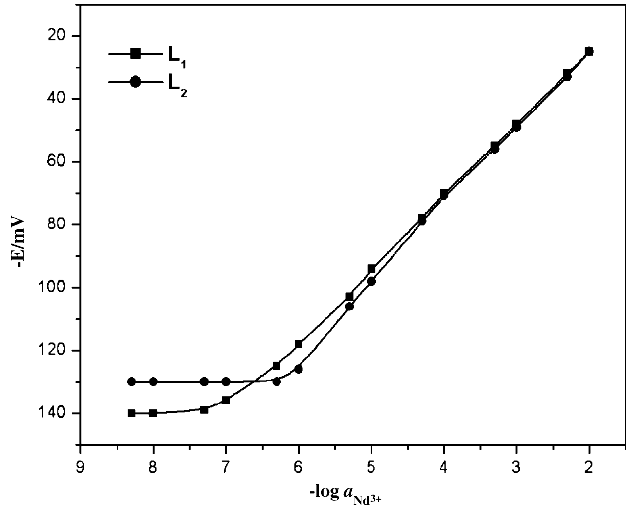

Fig. 5. Calibration plot of the neodymium ion-electrode with ionophores $\mathbf{L_1}$ and $\mathbf{L_2}$.

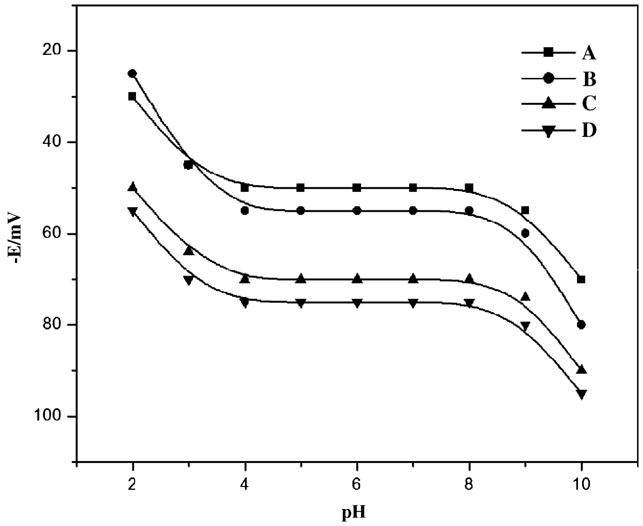

Fig. 6. Effect of pH on cell potential of sensor no. 5 at: (A) 1.0×10^{-3} M, (C) 1.0×10^{-4} M and sensor no. 10 at: (B) 1.0×10^{-3} M, (D) 1.0×10^{-4} M neodymium (III) solutions.

3.4. *Life time of proposed sensor*

The high lipophilicity of ionophore and plasticizer ensure stable potentials and longer life time [36] for the membrane. Among all the membranes prepared, the life time of membrane sensor based on *o*-NPOE and $\mathbf{L_1}$ (no. 5) found to be 3 months, and for sensor based on *o*-NPOE and $\mathbf{L_2}$ (no. 10) the life time was 1 month. Sensor no. 10 has been found to exhibit small life time as compared to sensor no. 5 most likely due to the reason that ionophore $\mathbf{L_2}$ leachs out from the membrane to solution. Table 1 presents the life time of various prepared using different composition of membranes. The best values were obtained for *o*-NPOE based sensors probably because of their greater polarity. It was noticed that during this period, the potentials were within the standard deviation (±0.2 mV). However, it is important to emphasize that the membranes were stored in a 0.01 M neodymium (III) solution when not in use.

3.5. *Effect of pH change and non-aqueous solvent*

The pH effect on the potential response of sensors was investigated in the pH range 2.0–10 for 1.0×10^{-3} and 1.0×10^{-4} M neodymium (III) solutions (Fig. 6). The pH of the solution was adjusted by the addition of nitric acid or sodium hydroxide. Fig. 6 indicates that the potential is independent of pH in the range 4.0–8.0 for sensor nos. 5 and 10, based on $\mathbf{L_1}$ and $\mathbf{L_2}$, respectively. Therefore, the pH range 4.0–8.0 was taken as the working pH range of the sensors assemblies. One of the reason for the change in potentials at higher pH (>8.0) may be hydrolysis of the neodymium (III) ion, while at lower pH, H^+ ion are likely to interfere in the chare transport of membrane.

The performance of the sensor no. 5 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 2 and indicate that up to 20% of non-aqueous content no significant change in the slope and working concentration range of the sensor is observed. At more than 20% non-aqueous medium the working range is significantly reduced, and thus the sensor can only be utilized in mixtures containing up to 20% non-aqueous content.

Table 2
Performance of sensor no. 5 in partially non-aqueous medium.

Non-aqueous content (%, v/v)	Working concentration range (M)	Slope (mV decade^{-1} activity)
0	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3
Methanol		
10	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3
20	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3
30	4.2×10^{-7} to 1.0×10^{-2}	17.1 ± 0.3
35	1.5×10^{-7} to 1.0×10^{-2}	15.1 ± 0.3
Ethanol		
10	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3
20	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3
30	3.8×10^{-7} to 1.0×10^{-2}	17.6 ± 0.4
35	5.2×10^{-6} to 1.0×10^{-2}	14.6 ± 0.3
Acetonitrile		
10	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3
20	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3
30	1.3×10^{-6} to 1.0×10^{-2}	18.3 ± 0.2
35	5.3×10^{-6} to 1.0×10^{-2}	15.3 ± 0.1

3.6. *Response time behavior of the proposed electrode*

Response time is an important factor for a sensor to become sensitive. In this study, the practical response time has been recorded (for sensor no. 5) by changing solutions with different neodymium ion concentrations. In the first case the measurement sequence was from the lower (1.0×10^{-6} M) to higher (1.0×10^{-3} M) concentration. After each measurement, the solution was rapidly changed. Such a change required nearly 8–10 s. The actual potential versus time curve is shown in Fig. 7 and it can be seen that the electrode reached the equilibrium response in a very short time of about 10 s. In the second case a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from (1.0×10^{-4} to $1.0 \times {}^{-5}$ M) sample concentrations. The results showed that, the potentiometric response of the sensor was reversible; although the time needed to reach equilibrium values was longer (~40 s) than that of low-to-high sample concentrations.

3.7. *Determination of binding constants*

The binding 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

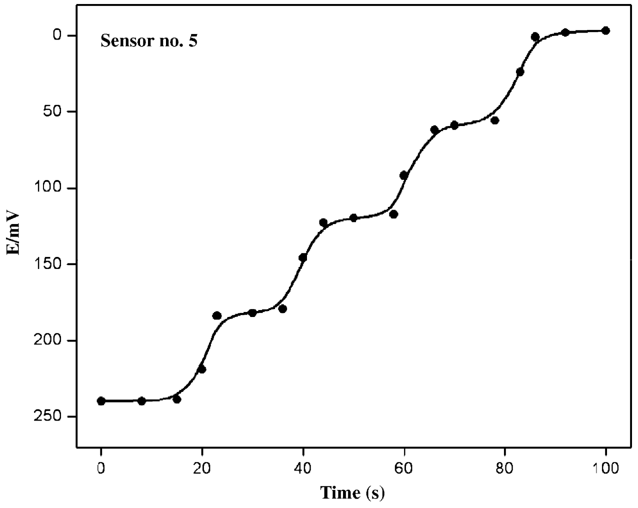

Fig. 7. Response time behavior of the membrane sensor (no. 5) based on, N,N′-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine ($\mathbf{L_1}$).

Table 3
Formation constants of Schiff base–metal complexes.

Metal ions	Formation constants (log β_{IL_n})[a]	
	Schiff base (**L$_1$**)	Schiff base (**L$_2$**)
Nd^{3+}	6.0	4.8
Dy^{3+}	3.1	2.8
Tb^{3+}	2.8	2.1
La^{3+}	2.4	1.8
Gd^{3+}	3.0	2.5
Sm^{3+}	2.9	2.4
Mn^{2+}	2.0	1.8
Co^{2+}	1.8	1.6
Yb^{3+}	2.5	2.1
Cu^{2+}	2.8	2.3
Hg^{2+}	1.7	1.4
Ni^{2+}	1.9	1.6
Zn^{2+}	2.2	2.0
Ca^{2+}	2.5	2.1
Fe^{3+}	2.7	1.6
Al^{3+}	2.5	1.4
Na^{+}	2.1	1.0
K^{+}	1.9	1.3

[a] $n = 5$, RSD% < 1.2.

Table 4
Selectivity coefficient values ($-\log K^{\mathrm{Pot}}_{Nd^{3+},B}$) of sensor nos. 5 and 10 of the membranes of **L$_1$** and **L$_2$**, respectively.

Interfering ions (B)	Selectivity coefficients [$-\log K^{\mathrm{Pot}}_{Nd^{3+},B}$][a] by FIM method	
	Sensor no. 5	Sensor no. 10
Dy^{3+}	4.50	4.10
Tb^{3+}	4.45	4.12
La^{3+}	3.80	3.50
Gd^{3+}	3.60	3.30
Sm^{3+}	3.78	3.47
Mn^{2+}	3.40	3.00
Co^{2+}	2.41	2.22
Yb^{3+}	3.20	2.80
Cu^{2+}	3.30	2.90
Hg^{2+}	1.62	1.30
Ni^{2+}	1.25	1.00
Zn^{2+}	2.15	1.95
Ca^{2+}	2.10	1.30
Fe^{3+}	2.30	2.28
Al^{3+}	2.80	2.50
Na^{+}	3.0	2.60
K^{+}	2.8	1.9

[a] $n = 5$, RSD% < 1.5.

reveals the ion activity ratio at both interfaces, which translates into the apparent binding constants of the ion–ionophore complex [37]. In this method complex formation constants are obtained by neglecting ion pairing. As mentioned earlier, 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 using equation:

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_I}\right)^{-n} \exp\left(\frac{E_M z_I F}{RT}\right) \qquad (2)$$

where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion–ionophore complex stoichiometry, and R, T and F are the gas constant, the absolute temperature, and the Faraday constant. The ion I carries a charge of z_I. The determined formation constants (log β_{IL_n}) for the examined different complexes are presented in Table 3. The elapsed time between sandwich fusion and exposure to electrolyte was typically <1 min. The potential was recorded as the mean of the last min 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 3 reveals that neodymium ion has significant cation-binding characteristics.

3.8. *Potentiometric selectivity*

The potentiometric selectivity of PVC sensors is one of the important parameters that determine the efficacy of sensor. Thus, the selectivity studies were carried out only for sensor nos. 5 and 10, which exhibit the best performance in terms of working concentration range, slope, response time and life time. Different methods of selectivity determination have been found in the literature. In the present study, the selectivity coefficients ($K^{\mathrm{Pot}}_{Nd^{3+},B}$) have been evaluated using modified form of fixed interference method [38] at 1.0×10^{-2} M concentration of interfering ions as per IUPAC rec-

Table 5
Comparison of the potentiometric parameters of the proposed neodymium sensor (sensor no 5) with the literature reported neodymium-selective sensors.

Ref. no.	Ionophore name	Linear range (M)	Slope (mV decade^{-1} of activity)	pH range	Selectivity coefficients ($-\log K^{Pot}_{Nd^{3+},B}$)	Response time (s)
[Proposed sensor no. 5]	N,N-bis(pyrrole-2-yl) methylenecyclohexane-1,2-diamine (**L$_1$**)	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3	4.0 to 8.0	Dy^{3+} (4.50), Tb^{3+} (4.55), La^{3+} (3.80), Gd^{3+} (3.60), Sm^{3+} (3.78), Mn^{2+} (3.40), Co^{2+} (2.41), Yb^{3+} (3.20), Cu^{2+} (3.30), Hg^{2+} (1.62), Ni^{2+} (1.25), Zn^{2+} (2.15), Ca^{2+} (2.10), Fe^{3+} (2.30), Al^{3+} (2.80), Na^{+} (3.0), K^{+} (2.8). By FIM method.	<10
[9]	2-{[(6-Amino pyridin-2-yl) imino]-methyl} phenol [9]	1.0×10^{-5} to 1.0×10^{-2}	19.8 ± 0.3	3.5 to 8.5	Na^{+} (2.67), K^{+} (2.67), Mg^{2+} (2.53), Ca2+ (2.49), Cu^{2+} (2.05), La^{3+} (1.60), Gd^{3+} (1.8), Sm^{3+} (1.50), Dy^{3+} (2.14), Yb^{3+} (2.14), Yb^{3+} (2.23), Al^{3+} (2.56), Cr^{3+} (2.14), Ce^{3+} (1.56) and Fe^{3+} (2.23). By MPM method.	<10
[10]	Benzyl bisthio semicarbazone	1.0×10^{-6} to 1.0×10^{-2}	19.7 ± 0.4	3.7 to 8.3	Sm^{3+} (3.04), La^{3+} (2.10), Gd^{3+} (3.08), Tb^{3+} (2.92), Dy^{3+} (3.08), Cr^{3+} (3.30), Na^{+} (3.0), Ca^{2+} (3.50), Pb^{2+} (3.17), Hg^{2+} (2.36), Ag^{2+} (2.25), Ni^{2+} (2.92), Cd^{2+} (2.95), Zn^{2+} (3.08), Co^{2+} (3.30), Cu^{2+} (3.16). By MPM method.	<10

Table 6
Determination of neodymium in spiked water samples using proposed sensor no. 5.

Sample	Added (μg L^{-1})	Found by proposed sensor (μg L^{-1})	Found by AAS (μg L^{-1})	Recovery ±SD (%)[a]
Roorkee City	8	8.05	8.86	100 ± 0.2
	100	101.05	99.52	99.9 ± 0.1
	400	402.0	400.32	100 ± 0.1

[a] $n = 5$, RSD% < 1.2.

ommendation. In this method, the electromotive force (emf) values were measured for solutions of constant activity of the interfering ion, a_B and varying activity of the primary ion, a_A in a cell comprising of an ion-selective electrode and a reference electrode. The emf values obtained were plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of the plot indicates the value of a_A that is to be used to calculate $K^{\text{Pot}}_{\text{Nd}^{3+},B}$ from the following equation:

$$K^{\text{pot}}_{A,B} = \frac{a_A}{(a_B)^{Z_A/Z_B}} \tag{3}$$

where both Z_A and Z_B have the positive charges of both ions.

It is seen from Table 4 that the selectivity coefficients values determined are much smaller than 1.0. Thus, both electrodes are substantially selective to neodymium (III) ions over the all interfering ions studied. Thus, it is clear from the values of selectivity coefficients that it is possible to determine neodymium (III) in the presence of interfering ions at a concentration level smaller or slightly higher than the neodymium (III) concentration. Of the two sensors, the selectivity of the sensor no. 5 is found to be better. The selectivity of proposed sensor towards neodymium is better for most of the cations as compared to reported sensors as shown in Table 5 and thus it is superior.

3.9. Analytical application

Using ion-selective sensor is very convenient for the analysis of samples having difficult matrices, such as soil and industrial waste water. The present membrane sensor was successfully used in the potentiometric determination of neodymium in spiked water samples. Three water samples were prepared by the addition of 8, 100 and 400 μg L^{-1} neodymium in tap water of Roorkee city and analysis was done after adjusting pH to 5.0. The data presented in Table 6, shows that the results obtained by sensor are comparable with atomic absorption spectrometer and recovery is 99.9–100.

4. Conclusion

PVC based membranes of two Schiff bases **L$_1$** and **L$_2$** have been investigated and are used as selective sensors for neodymium (III) ions. The sensor (no. 5) based on N,N-bis(pyrrole-2-yl)methylenecyclohexane-1,2-diamine (**L$_1$**), having membrane composition PVC:*o*-NPOE:ionophore (**L$_1$**):NaTPB ratio (w/w, %) of 150:300:5:5 is found to give the best performance. It responded linearly to neodymium (III) over a wider working concentration range 5.0×10^{-7} to 1.0×10^{-2} M, with Nernstian slope 19.8 ± 0.3 mV decade^{-1} of activity, lower detection limit 1.0×10^{-7} M and fast response time <10 s. The electrode was found to perform satisfactory over the pH range 4.0–8.0 and even in the presence of 20% non-aqueous content. Comparison of this electrode and reported electrodes in Table 5 indicates that sensor no. 5 is superior in terms of wider concentration range, lower detection limit and fast response time. However, the electrode based on ionophore (**L$_2$**) is selective for neodymium ion but shows narrow concentration range and higher detection limit.

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