



Comparative studies of praseodymium(III) selective sensors based on newly synthesized Schiff's bases

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ABSTRACT

Praseodymium ion selective polyvinyl chloride (PVC) membrane sensors, based on two new Schiff's bases 1,3-diphenylpropane-1,3-diylidenebis(azan-1-ylidene)diphenol (**M**₁) and N,N'-bis(pyridoxylideneiminato) ethylene (**M**₂) have been developed and studied. The sensor having membrane composition of PVC: *o*-NPOE: ionophore (**M**₁): NaTPB (w/w; mg) of 150: 300: 8: 5 showed best performances in comparison to **M**₂ based membranes. The sensor based on (**M**₁) exhibits the working concentration range 1.0×10^{-8} to 1.0×10^{-2} M with a detection limit of 5.0×10^{-9} M and a Nernstian slope 20.0 ± 0.3 mV decade⁻¹ of activity. It exhibited a quick response time as <8 s and its potential responses were pH independent across the range of 3.5–8.5. The influence of the membrane composition and possible interfering ions have also been investigated on the response properties of the electrode. The sensor has been found to work satisfactorily in partially non-aqueous media up to 15% (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 praseodymium(III) ions over wide variety of other cations. To assess its analytical applicability the prepared sensor was successfully applied for determination of praseodymium(III) in spiked water samples.

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1. Introduction

Praseodymium a soft silvery metal having anticorrosion property, is used in the aircrafts engines as an alloying agent with magnesium to impart high strength metal. It is also used as a coloring agent in glasses and enamels to produces an intense clean yellow color [1]. Praseodymium–germanium (silicon) alloys are used as superconductor [2]. Now a day, number of methods has been reported for the determination of praseodymium in real sample analysis, such as, absorption spectra of 4d electron transitions, derivative spectroscopy, and some other spectroscopic method. However, these techniques require expertise and infrastructure backup; hence, a simple and low cost method needs to be developed for the analysis of praseodymium in large number of environmental samples. A literature survey reveals that only two sensors [3,4] have been reported to determine praseodymium(III) concentration in real samples, but they two have limitations of narrow working concentration range and interference to various metal cations. Thus, a good sensor for praseodymium still needs to be developed.

Schiff's bases (SB) have been found to act as ion carriers in the polymeric membrane. The geometric and cavity control of host–guest complexation and modulation of lipophilicity in SBs provide remarkable selectivity [5], sensitivity and stability for specific ion. Thus, SB have attracted increasing attention for determining rare earth metals such as Gd³⁺ [6], Tb³⁺ [7], Ce³⁺ [8,10], Nd³⁺ [9], La³⁺ [11], Cr³⁺ [12], EU³⁺ [13]. The 1,3-diphenylpropane-1,3-diylidenebis(azan-1-ylidene) diphenol (DPDBD) is a newly synthesized Schiff base and is known to form complex with Praseodymium. This paper presents the comparative result of sensors based on DPDBD and N,N'-bis(pyridoxylideneiminato) NBPB as a ionophore. The sensor based on DPDBD gives better performance than sensor based on NBPB.

2. Experiment

2.1. Reagent and solution

Dibenzoylmethane and 2-aminophenol were obtained from E. Merck and used as received. For membrane preparation, high molecular weight polyvinyl chloride (PVC), *o*-nitrophenyloctylether (*o*-NPOE), dibutylphthalate (DBP), tributylphosphate (TBP), diethylphthalate (DEP), chloronaphthalene (CN), dioctylphthalate (DOP), cetyltrimethylammonium-bromide

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(CTAB), and tetrahydrofuran (THF) were used as received from Fluka. Reagent grade praseodymium(III) chloride was purchased from Loba Chemie India. HPLC-grade n-hexane and methanol were obtained from Ranbaxy India. All potentiometric measurements were performed at room temperature using Thermo Orion 4 star pH meter with PVC membrane based DPDBD electrode in conjunction with a SCE reference electrode.

2.2. Synthesis of ionophores

Ionophore is a key in component determining the membrane selectivity. Ideally, it forms reversible and relatively strong complex with targeted ion and does not complex with other ions. In order to keep the membrane composition constant, the ionophore must retain within the membrane; therefore, aside from the binding centre it must contain numerous lipophilic groups.

The ionophore 1,3-diphenylpropane-1,3-diylidenebis(azan-1-ylidene) diphenol (**M₁**, **I**) was synthesized by refluxing 0.025 mol of dibenzoylmethane and 0.05 mol of 2-aminophenol in ethanol for 12 on a water bath. On cooling the reaction mixture a yellow color solution was obtained. The ionophore was extracted using n-hexane (2 × 10 mL) and the solution extractant was left overnight. Wine red color crystals were obtained. The compound obtained was recrystallized in n-hexane. The compound was stable at room temperature. Anal. Cal. for [C₂₇H₂₂N₂O₂]: C, 78.78, H, 5.46, N, 6.89, O, 7.87%. Found: C, 78.65, H, 5.50, N, 6.85, O, 7.89. Melting point: 54 °C. IR (KBr) cm⁻¹: 3050(Phenolic OH), 1535(C=N), 2900(-CH). The ¹H NMR (CDCl₃) exhibited signals at: δ (ppm): 8.17–8.18(m, 8H), 7.64–7.67 (m, 4H), 7.56–7.59 (m, 6H), 7.57 (2H, 1s), 7.358 (2H, 1s).

The ionophore N,N'-bis (pyridoxylideneiminato) ethylene (**M₂**, **II**) was derived by the condensation of pyridoxal with ethylenediamine according to method reported in literature [14]. Anal. Cal. for [C₁₈H₂₂N₄O₄]: C, 60.32, H, 6.19, N, 15.63. Found: C, 60.5, H, 6.4, N, 15.7. IR (KBr) cm⁻¹: 3100(Phenolic OH), 1623(C=N), 2900(-CH₃), 1580(C=N, pyridine). ¹H NMR (D₂O) exhibited signals at: δ (ppm): 2.41 (s, 6H; CH₃), 3.21(s, 4H, CH₂-OH), 5.10 (dd, 4H, -CH₂CH₂-), 6.50 (s, 2H, CH=N), 7.50 (s, 2H, CH_{aromatic}).

2.3. Development of electrode

The PVC membranes were prepared by mixing various components (ionophore, anion excluder, plasticizer and PVC) in tetrahydrofuran. Varying amounts of the ionophore and anion excluder were dissolved together with an appropriate amount of PVC in 10 mL THF. To these, plasticizers viz. CN, DOP, DBBP, TBP or o-NPOE were added to get membranes of different compositions. The mixture was dissolved by a vigorous stirring with a glass rod. When the solution became homogenous and viscous it was poured in acrylic ring placed on smooth glass plate. The THF was then allowed to evaporate overnight at room temperature. A light yellow colored membrane of ~0.4 thickness was obtained, which was then cut to optimum size and glued to one end of Pyrex glass tube with araldite.

2.4. Equilibration of membranes and potential measurements

The prepared membranes were equilibrated for three days in 0.01 M praseodymium(III) solution. The potentials were measured by varying the concentration of Pr³⁺ in the test solution in the range 1.0 × 10⁻¹⁰ to 1.0 × 10⁻² M using a buffer solution Tris-HCl (pH 4.0) with a digital potentiometer (model 5652 A, ECIL, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrode.

2.5. SCE | test solution || PVC membrane || 0.1 M Na₂S₂O₃ + 0.01 M PrCl₃ | SCE

The activity of Pr³⁺ ions was calculated using modified form of the Debye-Huckel equation [15].

3. Result and discussion

3.1. Determination of binding constant

The ionophore-complex formation constant was determined by a potentiometric method. In this method, the potential of sandwich membranes were measured, where only one side sandwich membrane contains the ionophore. If both membrane segments have the same ionic strength, it is convenient to assume that the activity coefficients for the complexed and uncomplexed ions are approximately equal. In that case, they can be omitted and the complex formation constant is related to the potential as follows [16]

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_1} \right)^{-n} \exp \left(\frac{E_M Z_1 F}{RT} \right) \quad (1)$$

where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion-ionophore complexes 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_1 . This relationship allows for the convenient determination of formation constants of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurements on two-layer sandwich membranes can be if ion pairing neglected.

The resulting formation constants for Schiff base **M₁** and **M₂** are summarized in Table 1. It is clear from Table 1 that the values of binding constant are greater for praseodymium ion than other metal cations. Hence, the ionophore **M₁** and **M₂** exhibits significant cation-binding characteristics with praseodymium ion.

3.2. Calibration curves

The optimum response of the **M₁** and **M₂** based sensors were evaluated and presented in Table 2 and Fig. 1. The potential response of the sensor no. 5 based on **M₁** exhibited a linear working concentration range from 1.0 × 10⁻⁸ to 1.0 × 10⁻² M. Furthermore, it was observed that the slope of calibration curve was 20.0 ± 0.3 mV decade⁻¹ of activity of the praseodymium ion

Table 1
Formation constants of different Schiff base-metal complexes.

Metal ion	Formation constant (log β _{IL_n}) ^a	
	Schiff base (M₁)	Schiff base (M₂)
Pr ³⁺	6.03	4.50
Lu ³⁺	2.40	2.00
Er ³⁺	2.46	2.10
Yb ³⁺	3.12	2.75
Sm ³⁺	2.50	2.15
Eu ³⁺	2.21	1.92
Ce ³⁺	2.05	1.75
Gd ³⁺	2.18	1.60
La ³⁺	2.85	2.20
Nd ³⁺	2.96	2.75
Ho ³⁺	2.60	2.30
Tm ³⁺	2.10	1.80
Cr ³⁺	1.98	1.50
Pb ²⁺	2.40	2.15
Zn ²⁺	4.50	3.10
K ⁺	1.30	1.20
Na ⁺	1.50	1.35

^a n = 3, RSD < 1.3.

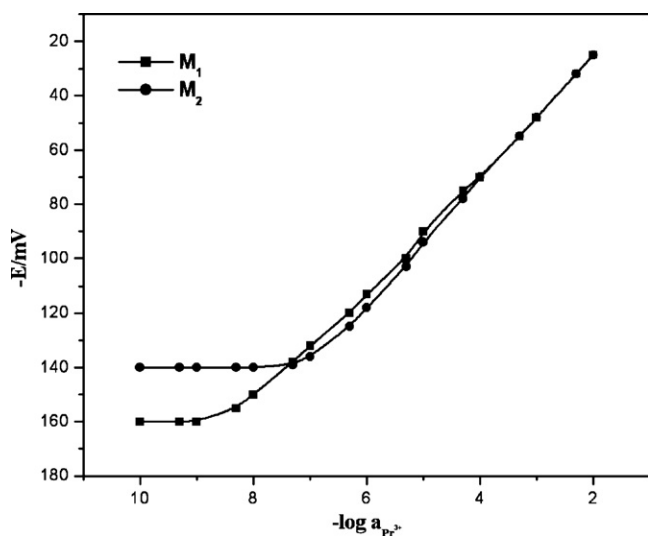


Fig. 1. Calibration plot of the praseodymium ion-electrode with ionophore M_1 and M_2 .

concentration. The detection limit of the electrode was determined from the intersection of the extrapolated segments of the calibration graph and was estimated to be 5.0×10^{-9} M. The electrode (no. 10) based on M_2 exhibits a Nernstian slope of 19.3 ± 0.1 mV decade $^{-1}$ of activity in the concentration range 1.0×10^{-7} to 1.0×10^{-2} M with a limit of detection 5.0×10^{-8} M. Both the membrane sensors show best compatible results with *o*-NPOE.

3.3. Life time of proposed sensor

Lipophilicity of the ionophore and dielectric constant of plasticizer has been found to affect the potential response and life time [17] of the PVC membrane. The membranes were prepared using different plasticizer, among them the membrane sensor based on *o*-NPOE and M_1 (no. 5) exhibited life time of three months, and sensor based on *o*-NPOE and M_2 (no. 10) showed life time of one month. Thus, it is clear that the sensor no. 10 exhibits small life time as compared to sensor no.5. One of the reasons for small life time for the sensor no. 10 is that the M_2 is partially soluble in water therefore, M_2 may leach out from the membrane to solution. The life time of different membrane of different compositions calculated are listed in Table 2. The best values were obtained for *o*-NPOE based sensors probably because of their greater polarity and dielectric constant

3.4. Effect of pH and non-aqueous solvent

In order to evaluate the pH effect on sensor performance, the potentials were determined in the pH range 2.0–10 using different

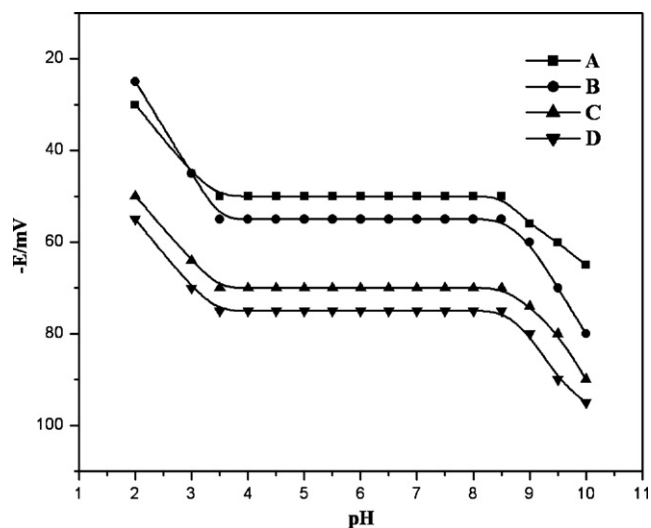


Fig. 2. Effect of pH on cell potential of sensor no. 5 (A) 1.0×10^{-3} M, (C) 1.0×10^{-4} M and sensor no.10 at (B) 1.0×10^{-3} M, (D) 1.0×10^{-4} M Pr^{3+} solutions.

pH Tris–HCl buffers for 1.0×10^{-3} M and 1.0×10^{-4} M Pr^{3+} solutions. The pH of the solution was adjusted by the addition of dilute solution of hydrochloric acid or sodium hydroxide. The respective results are depicted in Fig. 2, where the potentials remained constant from the pH range 3.5–8.5 for sensors no. 5 and 10. Beyond this range, a gradual change in potential was observed. Therefore, the pH range 3.5–8.5 was taken as the working pH range of the sensor. The potential increase at higher pH (>8.5) may be due to formation of some Pr^{3+} hydroxyl complexes in the solution. The potential decrease indicates at pH < 3.5 that the membrane sensor responds to H^+ ion.

The effect of partially non-aqueous medium using methanol–water; ethanol–water and acetonitrile–water mixture was also monitored on the functioning of the sensor no. 5 and the obtained results are presented in Table 3. It is observed that the values of slope and working concentration range remain constant up to 15% non-aqueous content at higher percentage of non-aqueous content the slope decreased. Therefore, the sensor can be satisfactorily used for the determination of praseodymium in mixtures up to 15% percentage of non-aqueous content.

3.5. Response time behavior of the proposed electrode

Response time of the sensor (no. 5) was investigated by dipping method [18–21] and was measured at various concentrations (1.0×10^{-2} to 1.0×10^{-6} M) of the test solution. The respective results are presented in Fig. 3. In all concentrations electrode reaches its equilibrium response quickly (<8 s). To evaluate the

Table 2
Optimization of membrane composition of praseodymium 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	M_1 , 8	5	300, CN	150	18.1 ± 0.3	1.0×10^{-5} to 1.0×10^{-2}	5.5×10^{-6}	25	2.5
2	M_1 , 8	5	300, TBP	150	19.1 ± 0.2	1.0×10^{-6} to 1.0×10^{-2}	4.0×10^{-7}	15	3.0
3	M_1 , 8	5	300, DBBP	150	18.5 ± 0.2	3.1×10^{-6} to 1.0×10^{-2}	1.2×10^{-6}	20	3.0
4	M_1 , 8	5	300, DOP	150	17.3 ± 0.1	1.0×10^{-5} to 1.0×10^{-2}	1.5×10^{-6}	23	2.5
5	M_1 , 8	5	300, <i>o</i> -NOPE	150	20.0 ± 0.3	1.0×10^{-8} to 1.0×10^{-2}	5.0×10^{-9}	<8	3.0
6	M_2 , 8	5	300, CN	150	17.0 ± 0.4	5.0×10^{-5} to 1.0×10^{-2}	3.0×10^{-5}	30	1.7
7	M_2 , 8	5	300, TBP	150	19.2 ± 0.2	1.0×10^{-5} to 1.0×10^{-2}	5.2×10^{-6}	18	1.2
8	M_2 , 8	5	300, DBBP	150	16.0 ± 0.3	1.6×10^{-5} to 1.0×10^{-2}	4.0×10^{-6}	20	1.0
9	M_2 , 8	5	300, DOP	150	16.7 ± 0.2	5.0×10^{-5} to 1.0×10^{-2}	2.5×10^{-5}	23	1.5
10	M_2 , 8	5	300, <i>o</i> -NPOE	150	19.8 ± 0.3	3.1×10^{-6} to 1.0×10^{-2}	5.0×10^{-8}	12	1.0

Table 3
Performance of the membrane sensor no. 5 in partially non-aqueous media.

Non-aqueous content (% v/v)	Working concentration range (M)	Slope (mV decade ⁻¹ activity)
0	1.0×10^{-8} – 1.0×10^{-2}	20.0×0.1
Methanol		
10	1.0×10^{-8} – 1.0×10^{-2}	20.0×0.1
15	1.0×10^{-8} – 1.0×10^{-2}	20.3×0.1
20	1.2×10^{-7} – 1.0×10^{-2}	17.5×0.3
Ethanol		
10	1.0×10^{-8} – 1.0×10^{-2}	20.0×0.1
15	1.0×10^{-8} – 1.0×10^{-2}	20.3×0.1
20	1.5×10^{-7} – 1.0×10^{-2}	18.0×0.5
Acetonitrile		
10	1.0×10^{-8} – 1.0×10^{-2}	20.0×0.1
15	1.0×10^{-8} – 1.0×10^{-2}	20.3×0.1
20	1.3×10^{-7} – 1.0×10^{-2}	17.3×0.1
Acetone		
10	1.0×10^{-8} – 1.0×10^{-2}	20.0×0.1
15	1.0×10^{-8} – 1.0×10^{-2}	20.3×0.1
20	1.4×10^{-7} – 1.0×10^{-2}	17.8×0.2

reversibility of the electrode, a similar procedure with opposite direction was adapted and it was found that same curve was traced back.

3.6. Potential response of membrane

The ionophore, membrane composition, nature of plasticizer and additive used affect the potential response of PVC membrane [15,22–24] which is the function of praseodymium ion free concentration. The measured potentials were plotted against active concentration of Pr(III) and shown in Figs. 4 and 5. From these plots the working concentration range, the slope and the response time have been evaluated and are given in Table 2 along with response of each sensor. It is clear from Table 2 that the best results are obtained when the PVC membrane have ingredients with composition: Ionophore (M_1 or M_2): NaTPB: Plasticizer: PVC as (w/w; mg) of 8:5:300:150.

3.7. Potentiometric selectivity

The selectivity coefficients of the prepared electrodes were determined by the fixed interference method [25]. In this method,

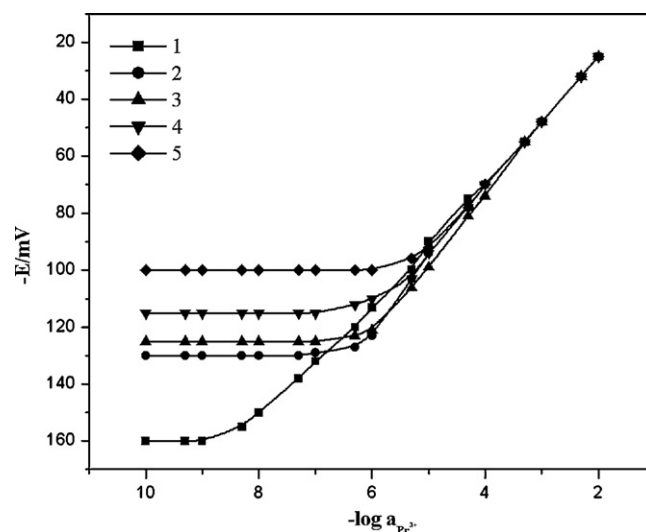


Fig. 4. Variation of membrane potential with activity of Pr^{3+} ions, of PVC based membranes of M_1 with plasticizers (1) *o*-NPOE, (2) TBP, (3) DBBP, (4) DOP, (5) CN.

the potentials of electrode were measured at constant activity of interference ion a_B and varying the activity of primary ion, a_A . The potentials 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 $K_{Pr^{3+},B}^{Pot}$ from the following equation:

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{Z_A/Z_B}} \quad (2)$$

where Z_A and Z_B are the positive charges of respective ions.

The selectivity coefficients values for different interfering ions have been studied using Tris–HCl (pH 4) buffer and result obtained for sensor no. 5 and 10 are presented in Table 4. The selectivity coefficients data indicate that the sensor no. 5 is selective towards praseodymium ions including the transition metal ion or lanthanides metal ions. However, zinc (II) may cause some interference as selectivity coefficients for zinc (II) is slightly higher. To have an actual idea of the levels of interference caused by zinc (II) ions, some mixed run studies were performed. Fig. 6 shows that in the presence of 1.0×10^{-5} M zinc (II) ions the sensor can be used to

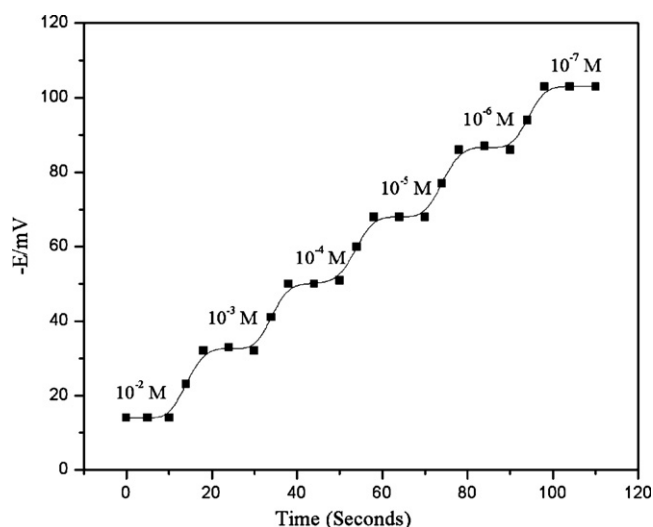


Fig. 3. Response time behavior of the membrane sensor (no. 5) based on, 1,3-diphenylpropane-1,3-diylidenebis(azan-1-ylidene) diphenol (M_1).

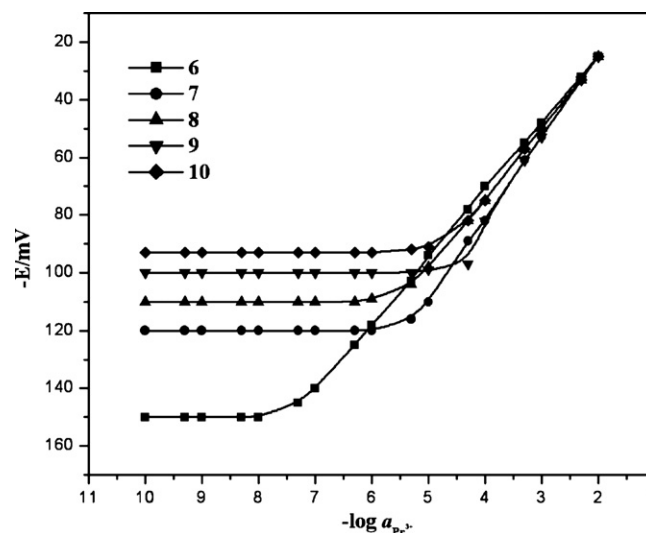


Fig. 5. Variation of membrane potential with activity of Pr^{3+} ions, of PVC based membranes of M_2 with plasticizers (6) *o*-NPOE, (7) TBP, (8) DBBP, (9) CN, (12) DOP.

Table 4
Selectivity coefficient values ($-\log K_{Pr^{3+},B}^{Pot}$) for praseodymium(III) selective sensor by fixed interference method.

Interfering ion (B)	Selectivity coefficients [$-\log K_{Pr^{3+},B}^{Pot}$] ^a by FIM method.	
	Sensor no. 5	Sensor no. 10
Lu ³⁺	3.80	3.20
Er ³⁺	3.38	2.75
Sm ³⁺	4.05	3.60
Yb ³⁺	4.85	4.30
Eu ³⁺	4.02	3.50
Ce ³⁺	4.18	3.40
Gd ³⁺	4.20	3.90
La ³⁺	3.84	3.15
Nd ³⁺	4.50	4.10
Ho ³⁺	4.76	4.25
Tm ³⁺	3.57	3.12
Cr ³⁺	2.52	2.10
Al ³⁺	2.79	2.23
Pb ²⁺	4.30	3.50
Zn ²⁺	1.91	2.65
Na ⁺	3.40	2.12
K ⁺	3.85	3.46

^a $n=5$, RSD% < 1.

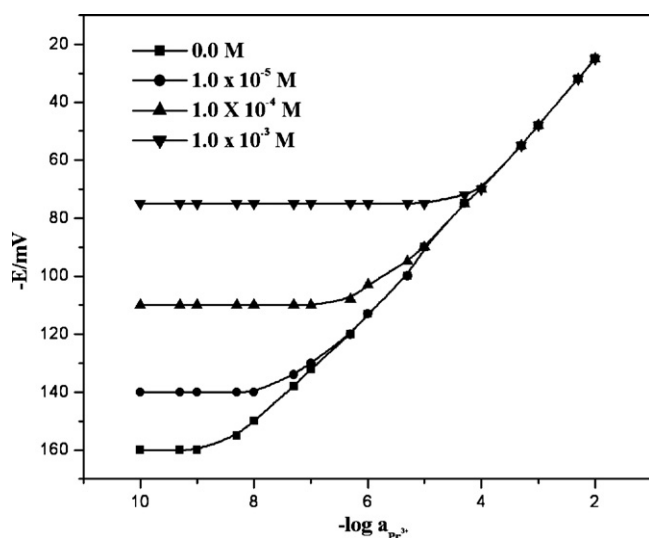


Fig. 6. Variation of membrane potential as a function of praseodymium(III) ion concentration in the presence of different concentration of zinc (II) ions.

Table 5
Comparison of the proposed praseodymium(III) selective electrode with the reported electrode.

Ref. no.	Ionophore name	Working concentration range (M)	Detection limit (M)	Slope (mV decade ⁻¹ of activity)	pH range	Selectivity coefficients ($-\log K_{Pr^{3+},B}^{Pot}$)	Response time (s)
[3]	N'-(pyridin-2-ylmethylene) benzohydrazide (PBH)	1.0×10^{-3} to 1.0×10^{-8}	7.0×10^{-9}	19.8 ± 0.3	3.5–8.5	Yb ³⁺ (3.82), Sm ³⁺ (3.45), Lu ³⁺ (3.52), Eu ³⁺ (4.60), Ce ³⁺ (4.0), Gd ³⁺ (3.52), La ³⁺ (4.60), Nd ³⁺ (4.39), Dy ³⁺ (3.45), Ho ³⁺ (4.67), Tm ³⁺ (3.34), Pb ²⁺ (4.34), Mg ²⁺ (4.18) K ⁺ (3.82), Na ⁺ (3.38). By MPM method.	<10
[4]	N,N-bis(α-methyl salicylidene)diethylenetriamine	1.0×10^{-2} to 1.6×10^{-6}	6.0×10^{-2}	19.8 ± 0.2	3.0–8.4	K ⁺ (2.30), Sr ²⁺ (3.22), La ³⁺ (3.0), Gd ³⁺ (3.45), Sm ³⁺ (2.88), Eu ³⁺ (3.01), Nd ³⁺ (3.09), Dy ³⁺ (3.11), Cr ³⁺ (2.42), Fe ³⁺ (2.65), Al ³⁺ (2.76). By FPM method	<5
[This work]	1,3-diphenyl propane-1,3-diylidenebis(azan-1-ylidene) diphenol	1.0×10^{-2} to 2.0×10^{-8}	5.0×10^{-9}	20 ± 0.1	3.5–8.0	Yb ³⁺ (4.05), Sm ³⁺ (3.16), Lu ³⁺ (3.80), Eu ³⁺ (4.85), Ce ³⁺ (4.18), Gd ³⁺ (4.20), La ³⁺ (3.84), Nd ³⁺ (4.50), Ho ³⁺ (4.76), Tm ³⁺ (3.57), Pb ²⁺ (4.30), Zn ²⁺ (1.91) K ⁺ (3.85), Na ⁺ (3.40). By FIM method.	<8

Table 6
Comparison of the results from the proposed sensor and AAS.

Sample	Added (μg L ⁻¹)	Found by proposed sensor (μg L ⁻¹)	Found by AAS (μg L ⁻¹)	Recovery ± SD (%)
Roorkee City	16	16.05	16.86	100 ± 0.2
	100	101.05	99.52	99.9 ± 0.1
	500	502.0	500.32	500 ± 0.1

Mean ± SD, $n=3$, RSD% < 1.2.

determine praseodymium in the concentration range 5.5×10^{-8} M. The sensor no. 5 has smaller values of selectivity coefficient than sensor no. 10. Therefore, sensor no.5 based on ligand **M₁** exhibited better performance in presence of interfering ions as compared to sensor no. 10. Table 5 compares the selectivity coefficient values, detection limit, linear range, working pH range and response time of the proposed electrode with those of the best previously reported praseodymium sensors. It is clear that the selectivity coefficients of this electrode for all tested cations and detection limit are superior to those of the formerly stated praseodymium sensors.

3.8. Analytical application

The prepared sensor was effectively employed for the determination of praseodymium in spiked water samples. Three water samples were prepared by addition of 16, 100 and 500 μg praseodymium L⁻¹ 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 the proposed sensor are comparable with Atomic Absorption spectrometer and recovery is 99.9–100.

4. Conclusion

A PVC based ion selective electrode was constructed by a simple procedure and applied for the determination of praseodymium at low concentrations. The use of new Schiff base **M₁** has been investigated and incorporated in membranes having composition PVC: *o*-NPOE: Ionophore (**M₁**): NaTPB ratio (w/w, %) of 150:300:8:5 is found to give the best performance. The recommended sensor displayed a linear working range of 1.0×10^{-8} to 1.0×10^{-2} M, with Nernstian slope 20.0 ± 0.3 mV decade⁻¹ of activity, lower detection limit 5.0×10^{-9} M. It exhibited a quick response time <8 s and its potential responses were pH independent across the range of 3.5–8.5. It also worked satisfactorily upto 15% non-aqueous content. Moreover, it was successfully

applied to the determination of praseodymium ions in spiked water samples.

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