Use of (2*e*)-2-Benzylidene-*N*-Phenylhydrazine Carbothioamide as an Ionophore in Fabrication of a Polymeric Membrane Sensor for Determination of Pr³⁺ IONS

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Abstract

In this work, we report as new Pr^{3+}-PVC membrane electrode containing 2% (2E)-2-benzylidene-N-phenylhydrazinecarbothioamide as an ion carrier, 1% sodium tetraphenyl borate (NaTPB) as an anionic additive, 67% dibutylphthalate (DBP), as solvent mediator and 30% poly(vinyl chloride) as binder. The proposed sensor exhibits a Nernstian slope of 19.7 ± 0.4 mV per decade over the wide linear dynamic range from 1.0×10^{-6} to 1.0×10^{-2} M, and a low detection limit of 5.6×10^{-7} M in the pH range of 2.6–9.0. It has a very short response time of about 10 seconds, in the whole concentration range. The proposed sensor shows a good selectivity for Pr^{3+} ions over other tested cations i.e. alkali, alkaline earth, transition and heavy metal ions. The proposed sensor was used as an indicator electrode in the potentiometric titration of Pr^{3+} ions with EDTA and was used for the determination of Pr^{3+} in various water samples.

Keywords: *Sensor, PVC membrane, Ion-selective electrode, Potentiometry, Sensor*

Introduction

Lanthanides are found throughout the earth's crust in very low concentration. All these elements have various applications, some of the elements are used in optical glass, glass fibers for optical purposes, gasoline-cracking catalysts, polishing compounds and carbon arcs [1]. Praseodymium is a soft, silvery, malleable and ductile lanthanide metal. The metal is highly important due to its magnetic, electrical and optical properties. Praseodymium generally occurs naturally together with the other rare-earth metals. Due to high importance, the selective determination of metal is a considered to be very important [2,3]. The available methods for low-level determination of lanthanide ions in solution include spectrophotometry, ICP-MS and ICP-AES [4,5]. Isotope dilution mass spectrometry, neutron activation analysis, X-ray fluorescence spectrometry, etc, are also used in some

laboratories [6-9]. These techniques are either time consuming, involve multiple sample manipulations, or are too expensive for most analytical laboratories [10]. Potentiometric membrane sensors have shown to be very effective tools for analysis of a wide variety of metal ions [11]. They are very simple, fast, inexpensive, and capable of reliable response in wide concentration ranges.

Recently various praseodymium selective electrode has been constructed by different researchers [12-17] most of the have either high detection limit, narrow working concentration range, high detection limit and serious interference of other ions. In present work a new Pr³⁺ selective electrode based on (2*E*)-2-benzylidene-*N*-phenylhydrazine carbothioamide as electroactive material have been constructed and used for the selective determination of Pr³⁺ ion.
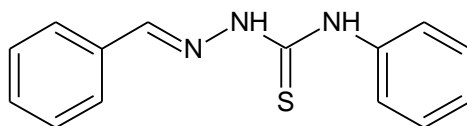

Figure 1. (2*E*)-2-benzylidene-*N*-phenylhydrazinecarbothioamide (Ionophore)

Experimental
Reagents and materials
Reagent grade (2*E*)-2-benzylidene-*N*-phenylhydrazinecarbothioamide, dibutylphthalate (DBP), benzylacetate (BA), high-molecular weight polyvinylchloride (PVC), prseodymium chloride (PrCl₃), ethanol, acetone, tetrahydrofuran (THF) and sodium tetraphenyl borate (NaTPB) were obtained from Sigma-Aldrich (Munich, Germany). Nitrobenzene (NB), acetophenon (AP), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck. All metal nitrates were also brought from Merck. Doubly distilled deionized water was used throughout. Stock solution of metal nitrates of 10^{-1} M concentration was obtained by dissolving weighed amounts of corresponding salt in double distilled water.

Ionophore:
The analytical grade ionophore (2*E*)-2-benzylidene-*N*-phenylhydrazinecarbothioamide was brought from Sigma-Aldrich and used without further purification (Figure. 1)

EMF measurements
All emf measurements were carried out with the following assembly:
Ag–AgCl| 1.0×10^{-3} M HoCl₃ | PVC membrane: test solution of Pr^{3+} ion | Ag, AgCl, KCl (satd). All the potential measurements were measured with digital potentiometer (Equiptronics EQ-602, India) and ECIL India double junction Ag/AgCl was used as reference electrode containing 10% (w/w) KNO₃ solution in outer compartment. Activities were calculated according to the Debye–Huckel procedure [18].

The membrane preparation
The general procedure to prepare the PVC membrane was as followed: 2% ionophore, 30% of powdered PVC, 67%, DBP and 1% of NaTPB were dissolved in 5 mL tetrahydrofuran (THF). The solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter, and the solvent was evaporated slowly until an oily concentrated mixture remained. In order to obtained a homogenous membrane a pyrex tube was dipped into the mixture for about 10 s [19-25].

At the end, the tube was removed from the solution, kept at room temperature for 12 h and filled with an internal filling solution $(1.0 \times 10^{-3}$ M PrCl₃). The electrode was conditioned for 24 h by soaking in a 1.0×10^{-3} M PrCl₃ solution. As an internal reference electrode, a silver/silver chloride coated wire was used.

Results and Discussion
Optimizing the membrane composition
To test the selectivity of the proposed ionophore various electrode based on PVC as binder were prepared and used for the potentiometric determination of various mono-, di- and tri-valent metal ions. The experimental evidence revealed that the proposed electrode based on (2*E*)-2-benzylidene-*N*-phenylhydrazinecarbothioamide as an ionophore has highest selectivity towards Pr^{3+} ion, which may be due to fast exchange of ions at membrane solution interface.

The potentiometric response of membrane electrode highly depends on the properties of the plasticizer used, the plasticizer/PVC ratio, the nature and the amount of the ionophore, the nature and the amount of the anionic additives used [26-29]. In general, the presence of lipophilic anions in cationic-selective membrane electrodes not only diminishes the ohmic resistance, but also increases the sensitivity of the membrane electrodes [30-33]. To investigate the effect of membrane components various electrode based on (2*E*)-2-benzylidene-*N*-phenylhydrazinecarbothioamide as an ionophore were tested for the determination of Pr^{3+} ion Table 1. The data presented in Table 1 clearly indicates that the sensor slope in the absence of NaTPB as anionic additive is lower than the expected Nernstian value (membranes no. 5). Nevertheless, the addition of 1 % NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a Nernstian behavior (membrane no. 4). However, the membranes with the composition of 30% PVC, 2% ionophore, 2% NaTPB and 67% DBP exhibit a Nernstian potential response. Table 1 shows that the optimum amount of ionophore was 2% (Membrane No. 4). To evaluate the best plasticizer

to be used in the sensor four commonly used compounds (i.e. benzylacetate (BA), nitrobenzene (NB), dibutylphthalate (DBP), Methoxyethty sterate (MES) were used in the construction of the sensor (Nos. 1-4, Table 1). Among the different plasticizers tested, we found that the electrode based on DBP as plasticizer exhibits superior response as compared to other plasticizers. This is due to high polarity of the DBP as compared to other tested plasticizers.

Table 1. Optimization of the membrane ingredients.

| Sensor No.	Composition (wt %)				Concentration range (M)	Slope (mV/decade)
	PVC	Plasticizer	NaTPB	Ionophore		
1	30	NB, 66	2	2	1.0×10^{-2}-1.0×10^{-5}	26.3 ± 0.3
2	30	BA, 66	2	2	1.0×10^{-2}-1.0×10^{-5}	16.4 ± 0.5
3	30	MES, 66	2	2	1.0×10^{-2}-1.0×10^{-5}	15.6 ± 0.3
4	30	DBP, 67	1	2	1.0×10^{-2}-1.0×10^{-6}	19.7 ± 0.4
5	30	DBP, 68	0	2	1.0×10^{-2}-1.0×10^{-5}	15.7 ± 0.2
6	30	DBP, 66	2	2	1.0×10^{-2}-1.0×10^{-5}	21.2 ± 0.5
7	30	DBP, 65	3	2	1.0×10^{-2}-1.0×10^{-6}	18.7 ± 0.4
8	30	DBP, 67	2	1	1.0×10^{-2}-1.0×10^{-5}	18.5 ± 0.6
9	30	DBP, 65	2	3	1.0×10^{-2}-1.0×10^{-6}	17.9 ± 0.2
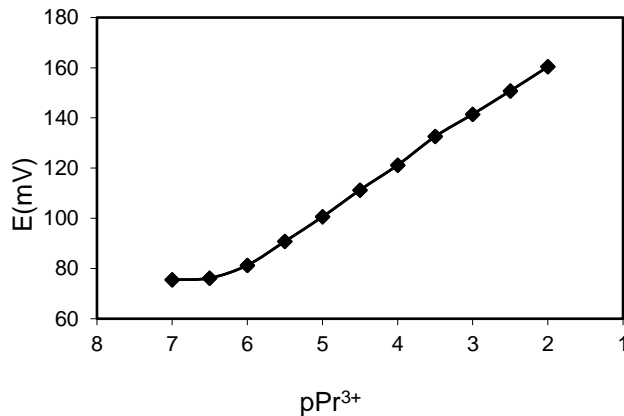
Figure 2. Calibration curves of the Pr³⁺ sensor based proposed ionophore.

Effect of pH

The potential response of proposed electrode was recorded in the pH range of 1.5-11.0 (the pH was adjusted with the use of concentrated NaOH and HCl Solution (Fig. 3). The figure 3 reveled that the potential response of the membrane electrode remains constant in the pH range of 2.7-9.0. At pH values lower than 2.7, a potential increase was observed which is due to the protonation of ionophore while significant decrease in potential response was observed at at higher pH (>9) this is due to formation of complex and competition kinetics of hydroxyl ion with ionophore.

Response time

The dynamic response time of the membrane was measured for whole concentration range of the Pr^{3+} ion solutions and results are shown in Figure 4. As can be seen from Figure 4, in the whole concentration range the electrode reaches its equilibrium response in a very short time of about 10 s.
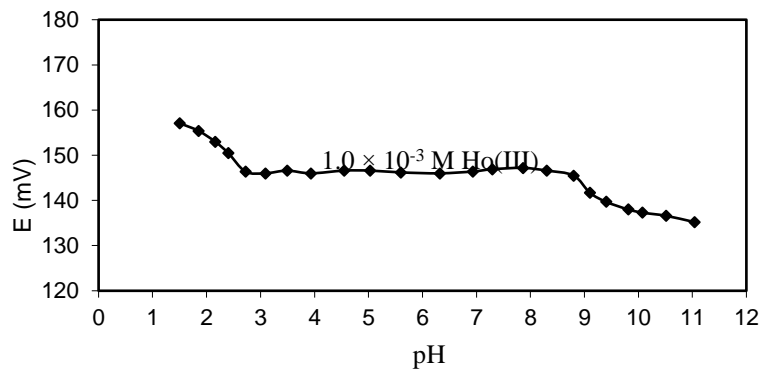

Figure 3. Effect of pH of the test solution (0.001 M of Pr^{3+}) of the Pr^{3+}Electrode based on (2*E*)-2-benzylidene-*N*-phenylhydrazinecarbothioamide.
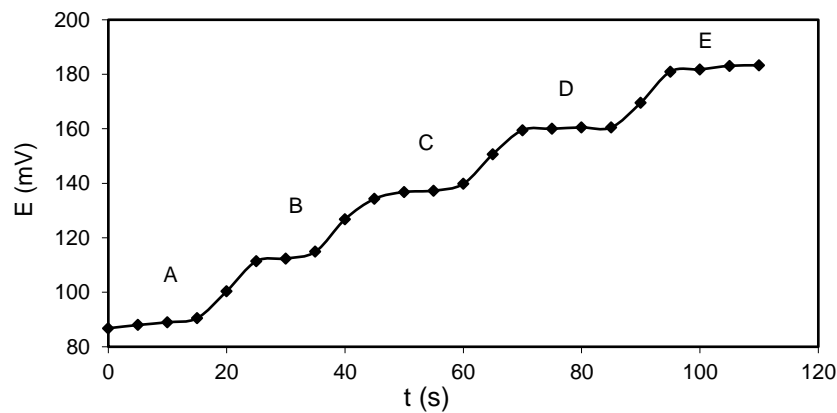

Figure 4. Dynamic response time of proposed electrode based on(2*E*)-2-benzylidene-*N*-phenylhydrazinecarbothioamide for step changes in the Pr^{3+} concentration: A) 1.0×10^{-6} M,   B) 1.0×10^{-5} M,   C) 1.0×10^{-4} M,   D) 1.0×10^{-3} M,   E) 1.0×10^{-2} M.

Selectivity of Proposed Pr^{3+} selective electrode

In this research, the potential responses of the recommended Pr^{3+} membrane sensor to a wide variety of cations were investigated through the matched potential method (MPM) [34-36]. According to this method, a specified activity of the primary ion (A) is added to a reference solution and the potential is measured. In a separate experiment, an interfering ion (B) is successively added to an identical reference solution (containing the primary ion), until the measured potential matches the one obtained with the primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to the interfering ion activity ratio, $K^{MPM} = a_A/a_B$. The results are listed in Table 2. The selectivity coefficients for the all mono, divalent and trivalent metal cations are smaller than 4.6×10^{-3} and they

can not disturb the functioning of the proposed Pr^{3+} membrane electrode.

Analytical application

The electrode was found to work well under the laboratory conditions and the proposed Pr^{3+} sensor was used as an indicator electrode in the titration of a 1.0×10^{-4} M Pr^{3+} ion solution with a standard 1.0×10^{-2} M EDTA. The resulting titration curve is shown in Figure 5. Clearly, the amount of Pr^{3+} ions in the solution can be effectively determined with the electrode.

The optimized sensor was successfully applied to the determination of Pr^{3+} ions in tap water and river water samples. The results of triplicate measurements are summarized in Table 4. As can be seen from Table 4, the amounts of the Pr^{3+} ions, which were added to the water sample solutions (0.25-0.5 mg/mL), could be determined by the sensor with relatively good accuracy.

Table 2. Selectivity coefficients of various interfering ions (B).

Interfering ion (B)	$K^{MPM}_{Ho,B}$
Dy^{3+}	3.4×10^{-3}
Yb^{3+}	4.2×10^{-3}
Tb^{3+}	4.6×10^{-3}
Er^{3+}	1.0×10^{-3}
Ho^{3+}	2.7×10^{-3}
Cr^{3+}	7.6×10^{-4}
Fe^{3+}	8.3×10^{-4}
Na^+	3.7×10^{-4}
K^+	5.6×10^{-4}
Ca^{2+}	6.4×10^{-4}
Mg^{2+}	5.5×10^{-4}
Cu^{2+}	7.2×10^{-4}
Cd^{2+}	8.4×10^{-4}
Ni^{2+}	8.7×10^{-4}
Pb^{2+}	8.8×10^{-4}
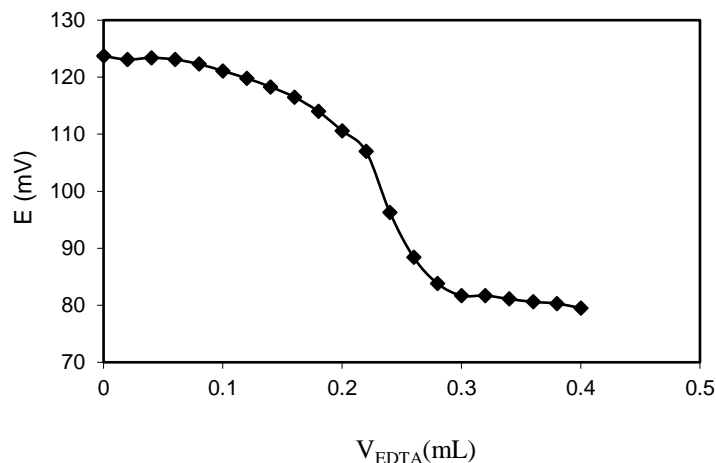
Figure 5. Potential titration curves of 25.0 mL 1.0×10^{-4} M Pr^{3+} solution with 1.0×10^{-2} M of EDTA.

Table 4. Determination of Pr^{3+} in different water samples

Sample	Pr^{3+} added (mg/mL)	Found (mg/mL)	Recovery (%)
River water	0.25 0.5	$(0.26^a \pm 0.03)$ (0.56 ± 0.02)	104 112
Tap water	0.25 0.5	(0.27 ± 0.02) (0.53 ± 0.04)	108 106

Results are based on three measurements

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