



Potentiometric Sensors for Pr(III) Based on *N-N'*-Phenylene-bis(salicylideneimine) Using Epoxy Resin and PVC as Binding Materials

K. SHARMA HARISH ^{§*}, VERMA NEHA [§] and J. K. KAPOOR

[§]PG Department of Chemistry
M.M. University, Mullana (Ambala), Haryana, India
Department of Chemistry, NIT, Kurukshetra, Haryana, India
shr.harish@gmail.com

Received 21 March 2011; Accepted 6 June 2011

Abstract: Praseodymium(III) ion selective electrodes have been prepared using *N-N'*-phenylene-bis(salicylideneimine) as a suitable electro-active material. Several membranes comprising of varying compositions of electro-active material with epoxy resin and polyvinylchloride (PVC) as binding materials were prepared. However the one with composition 50% Schiff's base and 50% binder was found to exhibit best performance. The sensor with epoxy resin as binder presents a linear dynamic range of 1.0×10^{-6} to 1.0×10^{-1} M with a Nernstian slope of 19.9 mV/decade. The sensor has a quick response time. (less than 10 s). The reproducibility of the electrode is about 6 months without any considerable, noticeable potential divergence. The sensor is effective in pH range of 3.00-8.62. In case of PVC as binding material; the results are compared for same composition of electro-active material. The sensor presents a linear dynamic range of 1.0×10^{-6} to 1.0×10^{-1} M with a slope of 14.0 mV/decade. The response time of the sensor is found to be 20s with a reproducibility of 4 months. The sensor is effective in pH range of 2.97-8.90. Effect of internal solution was studied and both the electrodes could satisfactorily be used in partially non-aqueous medium. Selectivity coefficients for both the electrodes have been determined by FIM (fixed interference method) with respect to many rare earth metal ions, alkali & alkaline earth metal ions and some transition metal ions. Both the electrodes were successfully employed as indicator electrode in the potentiometric titration of Pr(III) ions with oxalic acid and EDTA.

Keywords: Potentiometric sensor, ISE, FIM, *N-N'*-Phenylene-bis(salicylideneimine), Indicator electrode

Introduction

The applications of rare-earths are numerous. For instance they are being applied in agriculture as microelement fertilizer in China because of their ability to improve the yield

and quality of crops¹. They are also used in the production of optical glasses, the preparation of glass fibres for optical purposes, gasoline cracking catalysts, carbon arcs *etc.* They also find application in iron and steel industries to remove sulfur, carbon and other electronegative elements from iron and steel².

Praseodymium is an important member of lanthanides family. It is one of the rare chemicals that can be found in house equipment; such as color televisions, fluorescent lamps and glasses. Its primary use is as an alloying agent with magnesium to create high strength metals that are used in aircraft engine. Praseodymium also makes up about 5% of misch metal, a material that is used to make flints for lighters. Praseodymium forms the core of carbon arc lights which are used in the motion picture industry for studio lightening and projector lights. Praseodymium is also a component of didymium glass, which is used to make certain types of welder's and glass blower's goggles³. This element is mostly dangerous in the working atmosphere, due to the fact that fumes and gases can be inhaled with air. Moreover, it will gradually accumulate in soils and water and this phenomenon will eventually lead to increasing concentrations in humans, animals and soil particles. This may damage the cell walls and have negative effects on reproduction and functions of nervous system. In humans, it can damage the liver. Along with rejection from household equipments, it is also discarded to the environment mainly by petrol-producing industries.

Praseodymium alloyed with nickel (PrNi_5) has a strong magneto caloric effect, which has allowed scientists to approach within one thousandth of a degree of absolute zero⁴. Praseodymium oxide is also used to color glass and ceramics yellow⁵. Praseodymium oxide in solid solution with ceria, or with ceria-zirconia, has been used as oxidation catalysts⁵. Silicate glass doped with praseodymium ions are used to slow a light pulse down to a few hundred meters per second. These are also used as an alloying agent with magnesium to create high strength metals used in aircraft engine^{6,7}. Doping praseodymium in fluoride glass enables it to be used as a single mode fiber optical amplifier⁸.

REEs are not rare nor are they earths. The rare earths are a moderately abundant group of 17 metallic elements that includes the 15 lanthanides, yttrium and scandium. They exist together *i.e.* in one and the same mineral, mostly as phosphates and silicates. However, the selective determination of these metal ions is complicated by the similarity of their chemical properties and the fact that they all exist primarily as trivalent cations in solutions⁹. Available methods for low level determination of rare earth metal ions in solution include spectrophotometry, inductive coupled plasma-atomic emission spectroscopy, isotope dilution mass spectroscopy, neutron activator analysis, x-ray fluorescence spectrophotometry¹⁰⁻¹⁴. These methods are either time consuming, involving multiple analysis or too expensive for most of the analytical laboratories.

Potentiometric sensors offer an inexpensive and convenient method for analysis of rare earth metal ions in solutions¹⁵ and provide acceptable sensitivity and selectivity. They also provide several advantages such as ease of preparations and procedures, simple instrumentations, relatively fast responses, very low detection limit, reasonable selectivity and low costs. Large numbers of ion-selective electrodes based on natural or synthetic ionophore, which form selective complexes with the ions of interest, have been reported over the last three decades¹⁶⁻¹⁹. There has been an increasing interest in the preparation of molecular carriers possessing electrical neutrality. The Schiff's bases derived from salicylaldehyde are among the polydentate ligands that form very stable complexes with different cations²⁰⁻²².

There are only a limited number of reports on the development of microsensors for Pr³⁺ ions. In this paper, we report a highly selective and sensitive Pr(III) micro sensor based on schiff's base, *N-N'*-o-Phenylene-bis(salicylideneimine).

Experimental

Praseodymium(III) nitrate and other rare earth nitrates were obtained from CDH chemicals, India. All the chemicals were of analytical grade and hence, were used as such. A solution of praseodymium(III) nitrate was standardized against EDTA solution using xylenol orange as an indicator. Double-distilled deionized water was used throughout the experiments.

Instrument

EMF measurements were made using potentiometer (Microsil EQ/602, India) with an accuracy of 0.1 mV.

Preparation of exchanger

Etherial solution of salicylaldehyde and *o*-phenylenediamine was mixed in the ratio 2:1. Mixture was refluxed for one hour; precipitates of *N-N'*-*o*-phenylene bis (salicylideneimine) were formed. These were washed and dried at 40 °C for 30 minutes.

Preparation of epoxy membrane

A number of membranes were prepared using varying amount of epoxy resin as a binding material. Desired amount of finely powdered exchanger was mixed thoroughly with araldite in varying amounts (w/w) to make a near homogeneous paste, which was then, spread between the folds of butter paper. Glass plates were kept below and above the paper folds as supports. A pressure of 2.0 kg/cm² was applied over the glass plates for 24 h and left to dry. The sheet of membrane, thus obtained was then, dipped in distilled water to remove the paper from the membrane surface.

Preparation of PVC membrane

The procedure to prepare the PVC membrane was to mix the powered PVC and electro active material in 50% ratio. The contents were dissolved in 5 mL of THF as solvent and transferred into a glass dish of 2.5 cm diameter. The solvent was evaporated slowly at room temperature to get a sensing membrane of proposed composition.

Storage of electrodes

Electrodes were stored in distilled water when not in use for more than one day. These were activated by keeping immersed in the 0.1 M Pr³⁺ ion solution for two hours, to compensate for any loss of metal ions in the membrane phase that might have taken place due to a long storage in distilled water. Electrodes were then washed thoroughly with distilled water before use.

Distribution studies

Distribution coefficients (K_d) for different metal ions such as La³⁺, Ce³⁺, Sm³⁺, Nd³⁺ and Pr³⁺ were determined in aqueous solutions by keeping 20 mL of distilled water and 0.2 g of synthesized exchanger, overnight in a titration flask. Meanwhile intermittent shaking was done to attain the equilibrium. The strength of the exchanged metal ion solution was obtained by titrating against 0.1 M EDTA (standardized with PbNO₃). Then the distribution coefficient was determined by using the formula-

$$K_d = (I - F) / F \cdot V / W$$

Where, I & F= Volume of EDTA consumed by cations before and after equilibrium V is the initial volume of the metal ion solution for analysis and W is the initial dry mass of ion exchanger.

EMF measurements

The membrane was fixed to one end of glass tube 1.8 cm (internal dia.) using epoxy resin. These were then equilibrated with 0.1 M Pr³⁺ ion solution for 24 h. The tube was filled with a solution of praseodymium nitrate (0.1 M) and immersed in a beaker containing test solutions of varying concentrations, keeping the level of inner solution higher than the level of outer solution to avoid any reverse diffusion of electrolyte. All the EMF measurements were carried out by using cell assembly:



A digital potentiometer (Microsil EQ/602, India) was used for the potential measurements at 25±0.1 °C. Activities were calculated according to Debye-Huckel equation²³. Test solutions of Pr³⁺ were obtained by gradual dilution of 0.1 M solution and their potential measurements were made in un-buffered solution.

Results and Discussion

On the basis of distribution studies, the most promising property of *N-N'*-phenylene bis (salicylideneimine) was found to be high selectivity towards Pr³⁺ metal ion. The distribution coefficient (K_d) values are given in Table 1.

Table 1. Distribution coefficient values for various metal ions

Sensor	<i>N-N'</i> -Phenylene bis(salicylideneimine)				
Metal ions	Pr(III)	La(III)	Ce(III)	Nd(III)	Sm(III)
Distribution coefficient (K _d)	42.36	19.05	25.00	8.70	21.95

Optimization of different binder membranes

The effect of membrane composition on the response of the electrode was studied. For this purpose, the performance parameters, like slope of the calibration curve, measurement range and the response time were compared for prepared electrodes. The results are given in Table 2. Results show that the epoxy binder based electrode shows excellent response in the concentration range of 1×10⁻⁶-1×10⁻¹ M Pr(III) ion with a Nernstian slope of 19.9 mV decade⁻¹. It has a response time of less than 10 s. In case of PVC as binder, best performance is exhibited by the electrode in the concentration range of 1×10⁻⁶-1×10⁻¹ M Pr(III) ion with a Nernstian slope of 14.0 mV decade⁻¹. It has a response time of 20 s. So these two electrodes are selected for further studies.

Table 2. Optimization of different binder membranes

Electro-active material	% of electro-active material	Binder	Slope, mV/decade	Measuring Range, M	Response Time, s
<i>N-N'</i> -Phenylene bis(salicylideneimine)	50, %	Epoxy	19.9	1.0×10 ⁻⁶ -10 ⁻¹	<10
	50, %	PVC	14.0	1.0×10 ⁻⁶ -10 ⁻¹	15-20

Potential measurements were made on the selected electrode for different concentrations of Pr³⁺ ion solutions. EMFs were plotted against log of activities of the Praseodymium ion. Experiment was repeated five times to check the reproducibility of the electrode system. A standard deviation of ±1.0 mV was observed for epoxy and PVC-binder based electrode. A representative calibration curve is shown in Figure 1 and 2. Detection limit was calculated according to IUPAC recommendation²⁴ from the intersection of the two extrapolated linear portions of the curve.

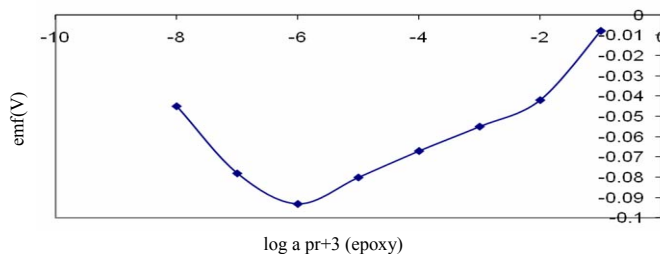


Figure 1. Calibration curve for Pr^{3+} selective electrode based on epoxy binder

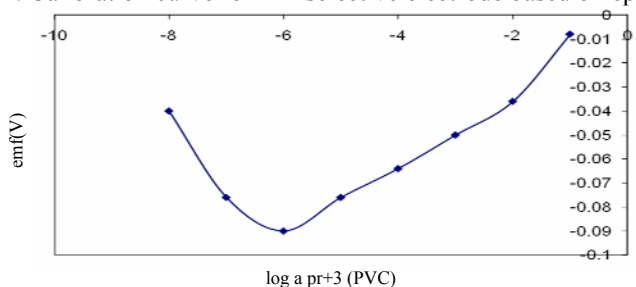


Figure 2. Calibration curve for Pr^{3+} selective electrode based on PVC binder

The non-nerstian behavior of the electrode may also be due to a possible discrepancy between the ions activities in the bulk and at the phase boundary, *i.e.* the uptake of the ions by the membranes results in a depletion zone of the analyte ion from the nearest diffusion layer. This is supported by earlier reports²⁵. Response time for epoxy binder electrode was 10 s while that for PVC binder electrode was 15-20 s. The sensing behavior of the membranes remain unchanged when the potentials are measured either from low to high or from high to low concentration. The electrode was stored in 0.1 M Pr^{3+} ion solution when not in use to avoid any change in the concentration in membrane phase.

Effects of internal solution concentration

The effect of internal solution on the response of the proposed sensor for Pr^{3+} ion was studied by using 10^{-1} M to 10^{-3} M internal solution concentration for epoxy as well as PVC binder based electrodes, the results are given in Figures 3 and 4 respectively. The results show that a variation in concentration of the internal solution does not have any significant effect on the response of the electrode except for an expected change in the intercept of the curves as observed by Ganjali *et al.*²⁵ and Mittal *et al.*²⁶.

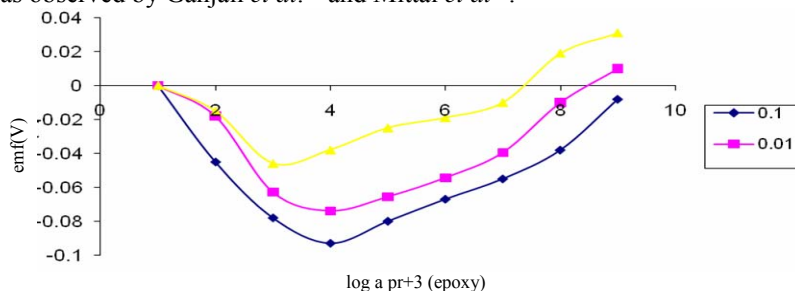


Figure 3. Effect of internal solution on the potential response of the Pr^{3+} selective electrode based on epoxy binder

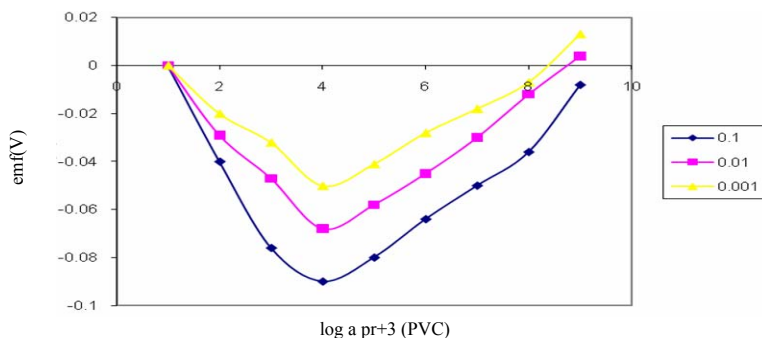


Figure 4. Effect of internal solution on the potential response of the Pr³⁺ selective electrode based on PVC binder

Effect of pH

The influence of pH on the potential response of the electrode was studied at 2×10^{-2} M and 2×10^{-3} M over a pH range of 2.0- 12.0 for the epoxy as well as PVC based binder electrodes. The results are shown in Figure 5 and 6 respectively. pH was adjusted by introducing small drops of HCl (0.1 M) or NaOH (0.1 M) as per requirement. The potential is independent of the pH range 3.00-8.62 and 2.97-8.90 for the epoxy and PVC-binder based electrodes, respectively. Hence, this pH range may be chosen as the working pH range for the electrode assembly. The variation above and below this pH range may be due to the formation of Pr(OH)₃ and protonation nitrogen atoms of exchangers, respectively.

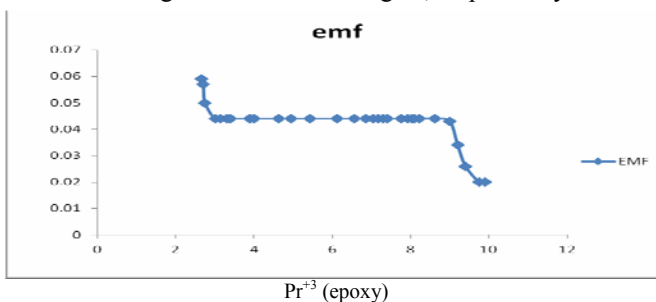


Figure 5. Effect of pH on the response of the Pr³⁺ selective electrode based on epoxy binder

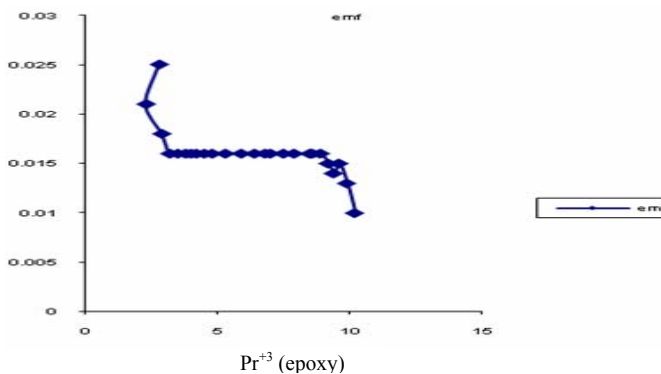


Figure 6. Effect of pH on the response of the Pr³⁺ selective electrode based on PVC binder

Selectivity coefficient and analytical properties of Pr³⁺ selective electrode

Selectivity is one of the most important characteristics of electrode, which defines the nature of the device and extent to which it may be employed in the determination of a particular ion in the presence of other interfering ions. Potentiometric selectivity coefficients of the Pr³⁺ membrane electrodes were evaluated by the fixed interference method (FIM)²⁴ at 1.0×10⁻³ M and 1.0×10⁻⁴ M interfering ion concentrations. According to this method, a calibration curve is drawn for the primary ion with a constant interfering ion background. The linear portion of the curve is extrapolated until it intersects with the second linear part of the curve in the low concentration region. The selectivity coefficients are calculated from these two segments of the calibration curve by using formula:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}}$$

Where, a_A is the activity of the primary ion and a_B the activity of the interfering ion. z_A and z_B are their respective charges. The results given in Table 3 and 4, show potentiometric selectivity coefficients of epoxy and PVC binder based sensors. Results are obvious that the electrode has a reasonably good selectivity with respect to rare earth metal ions, considering the fact that all rare have identical sizes and properties. It also has a good selectivity over some common alkali, alkaline earth and transition metal ions.

Table 3. Selectivity coefficient values for Pr³⁺ selective electrode base for various interfering ions by FIM (10⁻³ M)

Interfering ion(B)	Selectivity coefficient values $K_{A,B}$	
	With epoxy binder	With PVC binder
Nd(III)	0.5×10 ⁻³	0.5×10 ⁻⁴
Sm(III)	2.5×10 ⁻⁴	1.99×10 ⁻⁴
Eu(III)	1.0×10 ⁻⁴	0.5×10 ⁻⁴
Ce(III)	0.5×10 ⁻³	0.99×10 ⁻³
Fe(III)	0.5×10 ⁻³	0.5×10 ⁻³
La(III)	0.5×10 ⁻³	-
Al(III)	7.9×10 ⁻⁵	0.5×10 ⁻³
Ca(II)	1.5×10 ⁻⁴	1.1×10 ⁻⁴
Na (I)	4.5×10 ⁻³	1.5×10 ⁻³

Table 4. Selectivity coefficient values for Pr³⁺ selective electrode for various interfering ions by FIM (10⁻⁴ M)

Interfering ion (B)	Selectivity coefficient values $K_{A,B}$	
	With epoxy binder	With PVC binder
Nd(III)	2.0×10 ⁻²	3.97×10 ⁻³
Sm(III)	5.0×10 ⁻²	0.99×10 ⁻²
Eu(III)	0.5×10 ⁻²	0.5×10 ⁻²
Ce(III)	4.0×10 ⁻²	0.5×10 ⁻²
Fe(III)	1.3×10 ⁻²	0.5×10 ⁻²
La(III)	0.5×10 ⁻²	-
Al(III)	0.5×10 ⁻²	0.99×10 ⁻²
Ca(II)	0.5×10 ⁻³	2.5×10 ⁻⁴
Na (I)	1.3×10 ⁻²	4.5×10 ⁻³

Effect of partially non-aqueous medium on the working of Pr³⁺ selective electrodes

Both the electrodes were investigated in partially non-aqueous media using acetone, ethanol and methanol. The slope remains unaltered with the addition of non-aqueous solvents. Hence, the proposed sensor can be used in partially non-aqueous solvents. The results of the effect of various non-aqueous solvents on the functioning of epoxy and PVC binder based electrodes are given in the Table 5 and 6.

Table 5. Effect of partially non –aqueous media on the working of Pr³⁺ selective electrode based on epoxy binder

Solvent	Percentage, v/v	Slope, mV/decade	Measuring range, M
Acetone	30%	18.0	1.0x10 ⁻⁶
	20%	16.0	1.0x10 ⁻⁶
	10%	18.0	1.0x10 ⁻⁶
	30%	20.0	1.25x10 ⁻⁶
Ethanol	20%	18.0	1.25x10 ⁻⁶
	10%	20.0	1.0x10 ⁻⁶
	30%	15.0	1.25x10 ⁻⁶
Methanol	20%	20.0	1.0x10 ⁻⁶
	10%	18.0	1.0x10 ⁻⁶

Table 6. Effect of partially non –aqueous media on the working of Pr³⁺ selective electrode based on PVC binder

Solvent	Percentage, v/v	Slope, mV/decade	Measuring range, M
Acetone	30%	13.0	5.01x10 ⁻⁷
	20%	9.0	1.0x10 ⁻⁶
	10%	13.0	5.01x10 ⁻⁷
Ethanol	30%	11.0	1.0x10 ⁻⁷
	20%	9.0	1.25x10 ⁻⁵
	10%	11.0	1.99x10 ⁻⁷
Methanol	30%	9.0	1.0x10 ⁻⁶
	20%	11.0	5.01x10 ⁻⁷
	10%	13.0	5.01x10 ⁻⁷

Potentiometric titration

The practical utility of epoxy as well as PVC binder membrane sensors were tested by their use as indicator electrodes for the titration of 20 mL of 10⁻³ M Pr³⁺ ions vs. 5.0x10⁻³ M EDTA and oxalic acid. The emf data was plotted against volume of EDTA and oxalic acid added. The titration curve for epoxy binder sensor is shown in Figure7. Figure 8 shows the results of 20 mL of 10⁻³ M Pr³⁺ ions vs. 5.0x10⁻³ M EDTA titration for PVC binder based sensor electrode. The curves show a sharp inflection point at the titrant volume corresponding to the end point, which corresponds to 1:1 complexation between Pr³⁺ and EDTA. The sharp inflection point shows that these electrodes can be used for the determination of Pr³⁺ ion potentiometrically.

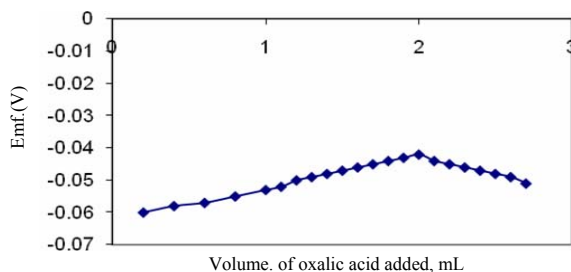


Figure 7. Potentiometric titration curve using proposed epoxy binder sensor as an indicator electrode

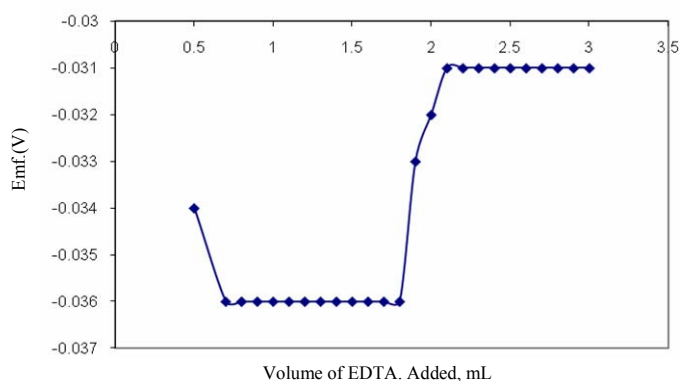


Figure 8. Potentiometric titration curve using proposed PVC binder sensor as an indicator electrode

Conclusion

Epoxy resin and PVC can both be successfully used as binders for making a Pr^{3+} selective membrane electrode. The electrodes have reasonably good lifetime, detection limit, pH range, selectivity coefficient and can be successfully used in partially non aqueous mediums. They can also be used as indicator electrodes. However on comparing the performance of the two sensors, it can be concluded that the one based on epoxy binder is better in terms of better response time, Nernstian response.

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