

A POLY (VINYL CHLORIDE) BASED MEMBRANE ELECTRODE FOR THE SELECTIVE DETERMINATION OF ZR(IV)

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ABSTRACT

A new Schiff base chelating ligand 1-(1H-indol-1-yl)-N-(thiophen-2-ylmethyl) ethanimine have been synthesized and used as electroactive material for the selective determination of Zr(IV). The membrane electrode has a wide linear concentration range of 2.0×10^{-8} M to 1.0×10^{-1} M with a fast response time of about 5s and could be used in a pH range of 3.5 -7.6 without divergence in response characters. The membrane electrode was used for the determination of Zr(IV) in various samples and the values were also compared with those obtained by AAS and ICP-MS.

Keywords: Chelating ligand, ion-selective electrode, potentiometry, Schiff base, Zirconium.

INTRODUCTION

Ion-selective electrodes are the devices used for the selective determination of various ionic species in solutions. The sensing surface of these electrodes is comprised of a homogeneous polymeric matrix containing an organic ion-exchanger selective to a particular ion. The organic ion-exchanger containing sufficient lipophilic groups acts as sensing material of the membrane. This sensing material exchanges only one type of ion between the two phases and generates a potential difference between the phases. Thus the use of highly sensitive ion-exchanger makes these devices a good analytical method for the determination of target ion in presence of other interfering ions [1-9].

Zirconium is used to make special parts of chemical apparatus, such as extrusion jets, nozzles, pumps, stirrers, pipes, evaporators and heat exchangers. It is also used in nuclear

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applications since it does not readily absorb neutrons [10, 11]. Due to these applications the selective determination of zirconium is important and is a matter of scientific significance. Therefore, the main objective of current research is to find and develop a suitable ion-selective electrode based on polymeric membrane for the determination of Zr(IV) ion on an industrial scale.

EXPERIMENTAL SECTION:

Material and apparatus used

The reagents *viz.*, N-acetylindol, 1-(thiophen-2-yl)methanamine and tetrahydrofuran (THF) were bought from Sigma-Aldrich and were used without further purification. Acetone, ethanol, dioctylphthalate (DOP), tris(2-ethylhexyl)phosphate (TEP), dioctylsebacate (DOS), oleic acid (OA), sodium tetraphenyl borate (NaTPB) and polyvinyl chloride (PVC) were obtained from SD-Fine Chem. Limited (Mumbai, India). All metal nitrates were bought from Sisco Research Lab (Mumbai, India) and the stock solution of metal nitrates was obtained by dissolving weighed amounts of corresponding salt in double distilled water. Double distilled water was used throughout the investigation.

All potentiometric measurements were made at $25 \pm 1^\circ$ C with a digital potentiometer manufactured at ECIL, Hyderabad, India (Model pH 5662) using Zr(IV) selective membrane electrode in conjunction with double junction Ag/AgCl reference electrode.

Synthesis of chelating ligand

The chelating ligand 1-(1*H*-indol-1-yl)-*N*-(thiophen-2-ylmethyl)ethanimine(L) was synthesized by condensation reaction of N-acetylindole and 1-(thiophen-2-yl) methanamine as follows (Scheme -1) [12].

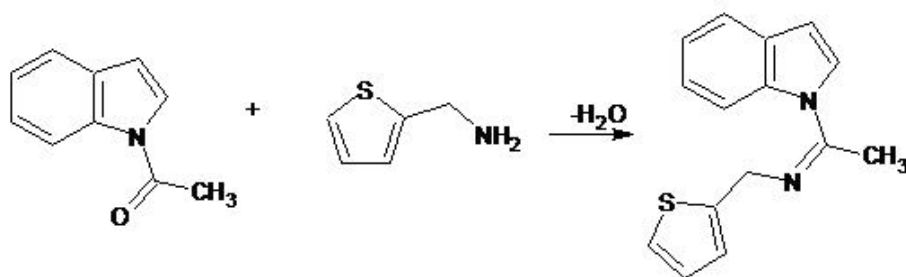
A solution of N-acetylindole (1.50 mmol in 20 mL THF) was vigorously stirred with 1-(thiophen-2-yl)methanamine (1.75 mmol in 20 mL THF) at 30°C to get a yellow crystalline solid. The solid was filtered off and washed with water to remove impurities or unused chemicals associated with the ligand. The crystalline substance then re-crystallized by absolute ethanol and acetone solution (2:1, v/v) in Erlenmeyer flask. The H-NMR and C-NMR studies of the compound were carried out to prove the structure of the compound.

The analytical and physical data of the ligand are given below:

Molecular formula: $\text{C}_{15}\text{H}_{14}\text{N}_2\text{S}$, Yield: 72%.

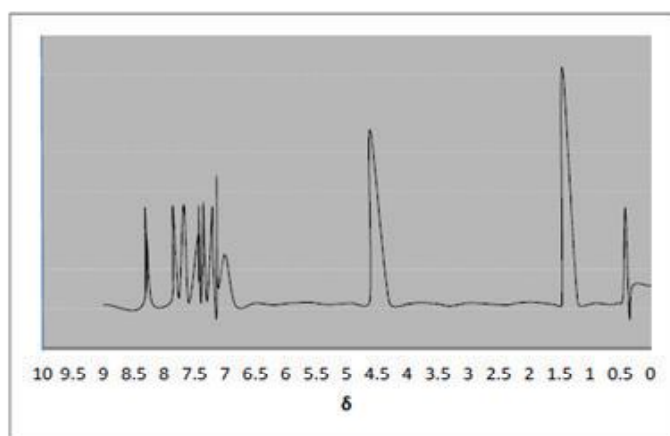
Analysis: **$^1\text{H-NMR}$** (CDCl_3 , ppm): $\delta = 8.32$ (d, 2H, ArH), 7.86 (d, 2H, ArH), 7.68 (t, 1H, ArH), 7.43 (d, 1H, ArH), 7.36 (d, 1H, ArH), 7.21 (d, 1H, OH), 7.14 (t, 1H, ArH), 4.62 (s, 2H, N- CH_2 Ar), 1.46 (s, 4H, $-\text{CH}_3$).

$^{13}\text{C NMR}$ (CD_3CN , ppm): $\delta =$ (12 C aromatic); 182.40, 182.32, 181.28, 181.13, 179.67, 179.14, 178.60, 178.46, 177.38, 177.12, 176.10, 175.65. (3 C aliphatic); 85.5, 36.68, 28.45.



1-(1H-indol-1-yl)-N-(thiophen-2-ylmethyl) ethanamine (L)

Scheme 1

Figure 1: ¹H-NMR Spectra of ligand

Calculation of formation constant

The stability of complex of ligand with different metal ion was calculated with the help of formation constant (K_f) of complexation kinetics of ligand and metal ions, by using molar conductance ratio (Equation 1 and 2) in acetone solution at $25 \pm 2^\circ\text{C}$. The complex formation constants, K_f , and the molar conductance of complex, Λ_{obs} , were obtained by using a nonlinear least squares program KINFIT [13].

$$K_f = \frac{[M^+]}{[M^+][L]} \times \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_M)[L]} \quad (1)$$

where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (2)$$

where, Λ_M = the molar conductance of the cation before addition of ligand.

Λ_{ML} = the molar conductance of the complex.

Λ_{obs} = the molar conductance of the solution during titration

C_L = the analytical concentration of the ionophore added, and C_M the analytical concentration of the cation.

The data presented in the Table 1 indicates that the chelating ligand 1-(1*H*-indol-1-yl)-*N*-(thiophen-2-ylmethyl)ethanimine (L) forms most stable complex with Zr(IV) as compared to other tested cations. Therefore the said ligand could be used for the selective determination of Zr(IV) .

Table 1: Formation constants of Ligands (L) metal complexation

Metal ions	Formation constants (log K_f)
	(L_f)
Zr(IV)	4.20
Hf(IV)	3.42
La(III)	2.85
Ce(III)	2.68
Pr(III)	2.65
Nd(III)	2.62
Sm(III)	2.59
Eu(III)	2.59
Gd(III)	2.57
Tb(III)	2.56
Dy(III)	2.53
Y(III)	2.0
Nb(III)	2.3
Ti(III)	2.2
Al(III)	2.2
Li(I)	2.13
Na(I)	2.10

Fabrication of electrodes

The polymeric membrane of the chelating ligand has been fabricated as suggested by Craggs et. al. [14]. The PVC-based membranes of various compositions have been prepared by dissolving appropriate amounts of ligand (L), anionic additive NaTPB, plasticizers i.e. DOP, TEP, DOS, OA and PVC powder in 15 mL THF. The components were added in terms of weight percentage. The components were carefully stirred to obtain a homogenous mixture. The mixture then poured into a flat petri dish kept for 24 hours to evaporate the solvent (THF). The Membranes of 0.5 mm diameter were removed carefully from the glass plate and glued to the one end of the "Pyrex" glass tube with araldite. A saturated silver electrode was inserted in the tube for electrical contact and another saturated silver electrode was used as an external reference electrode.

The EMF measurements were carried out with the cell assembly given below:

Internal reference Silver electrode	Internal reference solution (0.01 M Zr(IV))	Zr(IV) ion Selective Membrane	Test Solution	External Reference Silver electrode
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RESULTS AND DISCUSSION:*Optimization of membrane composition*

The response mechanism of membrane electrode is highly dependent on nature and composition of additional membrane components [15]. To find the optimum composition of membrane, the membranes of different compositions were prepared and their response characters were investigated. The data presented in Table 2 indicated that the membrane with composition of L : NaTPB: Plasticizer: PVC of 4: 2: 57: 37 (w/w, %) gives the best possible response in terms of linear concentration range, detection limit, response time, and life time.

Table 2: Composition of the different membranes of Zr(IV) selective electrode

E. No.	Membrane Composition (% w/w)				Linear working range (M) ^a	Slope (mV/dec. of activity) ^a	Response Time (sec)
	PVC	Additive	Plasti-cizer	Iono-phore			
1	37	2, NaTPB	57, DOP	4, (L)	2×10^{-8} - 1×10^{-1}	59.40 ± 0.3	08
2	37	2, NaTPB	57, TEP	4, (L)	6×10^{-6} - 1×10^{-1}	48.80 ± 0.3	16
3	37	2, NaTPB	57, DOS	4, (L)	5×10^{-5} - 1×10^{-1}	54.28 ± 0.3	20
4	36	2, NaTPB	57, OA	4, (L)	3×10^{-5} - 1×10^{-1}	53.46 ± 0.3	18
5	37	6, NaTPB	57, DOS	0	2×10^{-2} - 1×10^{-1}	19.40 ± 0.3	26
6	37	2, NaTPB	57, DOS	5, (L)	3×10^{-8} - 1×10^{-1}	59.10 ± 0.3	08
7	35	2, NaTPB	59, DOS	4, (L)	2.5×10^{-8} - 1×10^{-1}	59.30 ± 0.3	08

The membrane without ionophore responds to a very small extent towards Zr(IV). This is probably due to reaction of either anionic additive or plasticizer with metal ion. However the membrane with composition of ionophore : NaTPB: DOS : PVC of 4: 2: 57: 37 (w/w, %) has a lower detection limit of 1.0×10^{-8} M in a linear concentration range of 2.0×10^{-8} – 1.0×10^{-1} M for Zr(IV) ion (Figure 2). The amount of ionophore with more than 4% (w/w) does not significantly affect the response characters of the membrane electrode. The anionic additive as membrane components significantly affects the response mechanism because it diminish the ohmic resistant at solution membrane interface. The 2% (w/w) anionic additive is sufficient for the best response of the membrane electrode. More than 2% of anionic additive is not suitable since anionic additive as membrane component may compete with the ionophore during the complexation reaction.

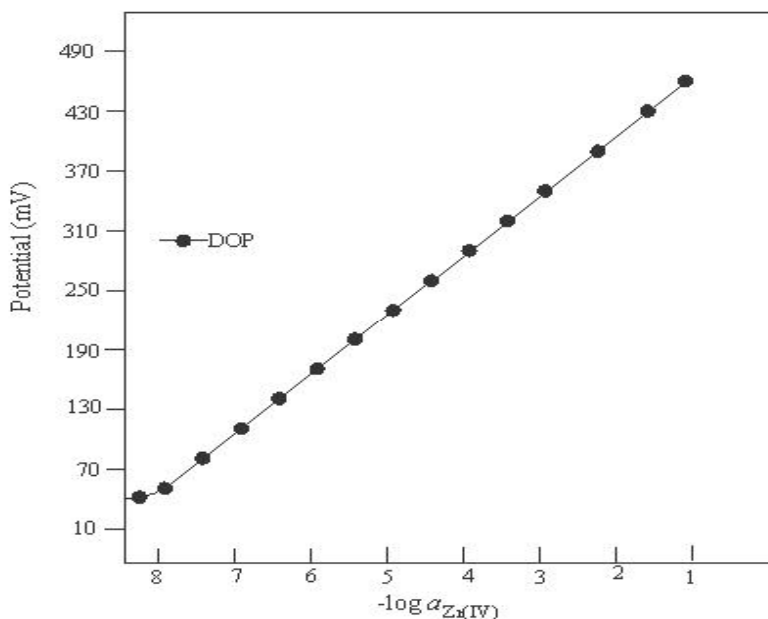


Figure 2: Calibration curve of Electrode No. 1

Potentiometric selectivity of Zr(IV) selective electrodes

The practical utility of membrane electrode was investigated in terms of selectivity coefficient ($\log K_{Zr^{4+}, M^{n+}}^{POT}$). The selectivity coefficients were calculated by fixed interference method by using modified Nikolsky equation (Eq. 3) [16, 17].

$$K_{Zr^{4+}, M^{n+}}^{POT} = \frac{a_{Zr^{4+}}}{a_{M^{n+}}^{z_{Zr^{4+}}/z_{M^{n+}}}} \quad (3)$$

Where $a_{Zr^{4+}}$ is the activity of the primary ion and $a_{M^{n+}}$ is the activity of other metal ions $z_{Zr^{4+}}$ and $z_{M^{n+}}$ are their respective charges.

The selectivity coefficients were calculated for fixed concentration of Zr(IV) (0.001 M) and varying concentration of interfering ions. The selectivity coefficient values presented in Table 3 indicates that the presence of interfering ions does not have any effect on response characters of membrane Electrode No. 1.

Table 3: Selectivity coefficient calculated by FIM method

Metal ions	Selectivity Coefficient, $\left[\log K_{Nd^{3+}, M^{n+}}^{Pot} \right]$
	<i>Electrode No. 1</i>
Hf(IV)	2.21
La(III)	3.42
Ce(III)	3.41
Pr(III)	3.23
Nd(III)	3.40
Sm(III)	3.32
Eu(III)	3.62
Gd(III)	3.32
Tb(III)	3.30
Dy(III)	3.30
Y(III)	3.37
Nb(III)	3.12
Ti(III)	3.40
Al(III)	3.60
Li(I)	3.82
Na(I)	2.78

Effect of pH and static response time

The presence of hydrogen ion or hydroxide ion in the solution may affect the binding ability of the ligand as well as the solubility of metal ion. Thus the effect of pH on the response characters of the electrode assembly was investigated in the range of 0 – 9.0. It was observed that the potential response of membrane electrode remains same in the pH range of 1.5 – 7.6. Thus this pH range was taken as the optimum pH range of the electrode assembly. The significant potential drift was observed at pH less than 1.5 and at pH more than 7.6, due to interference caused by H⁺ and OH⁻ respectively. The pH of the test solution was adjusted by adding HCl (0.01M) and NaOH solution (0.01M).

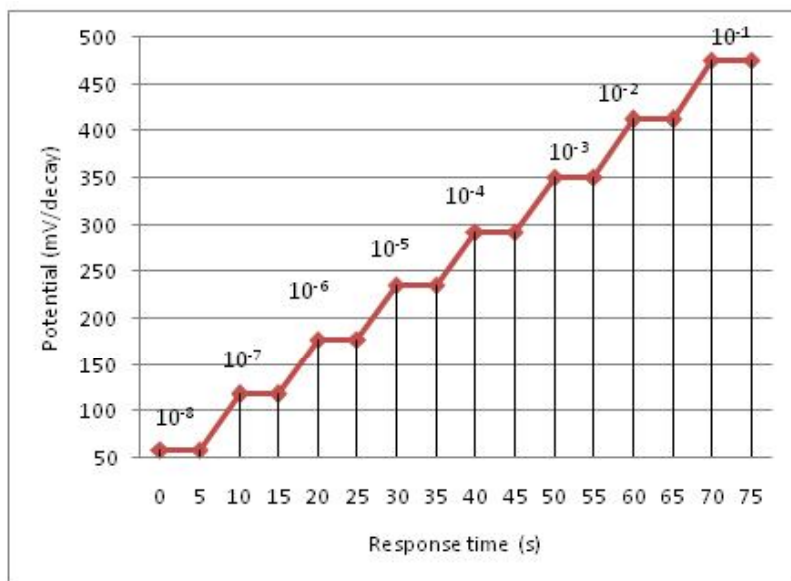


Figure 3: Response time of membrane Electrode No. 1

The time at which membrane electrode reached the optimum potential is called response time of the electrode assembly. In the present study, the response time of the electrode no. 1 was calculated for different concentration sequences i.e. from lower to higher and then higher to lower. It was observed that average response time for both the sequences was 5 second. However the response time for higher concentration is slightly more than lower concentration (Fig. 3).

Life time

The lipophilic nature of ionophore and plasticizer ensure a longer life time of membrane electrode. In present study, the life time of membrane electrode was calculated in terms of slope of calibration curve and lower detection limit. The data presented in Table 4 indicates that the slope and lower detection limit of membrane Electrode No. 1 remains almost same for a period of 8 weeks. After this time period, the ionophore and plasticizers leached out significantly from the membrane, thus the significant variation of slope and detection limit was observed. The response characters proposed electrode was also compared with the previously reported electrode and the data are summarized in Table 4.

Table 4: The lifetime of Zr(IV) membrane Electrode No. 1

S. No.	Week	Slope (mV/decade)	Detection Limit (mol/L)
1	First	59.40 ± 0.3	1.0 × 10 ⁻⁸
2	Third	59.4 ± 0.3	1.0 × 10 ⁻⁸
3	Fifth	59.32 ± 0.3	1.0 × 10 ⁻⁸
4	Sixth	59.00 ± 0.3	1.1 × 10 ⁻⁸
5	Seventh	58.85 ± 0.3	1.2 × 10 ⁻⁸
6	Eighth	58.79 ± 0.3	1.2 × 10 ⁻⁸
7	Ninth	47.08 ± 0.3	5.6 × 10 ⁻⁶
8	Tenth	35.57 ± 0.3	1.3 × 10 ⁻⁵

Table 5: Comparative analysis of proposed Electrode No. 1 with the reported Electrode

Ionophore	Working Conc. range (M)	Slope (mV/decade of activity)	pH range	Re- sponse time (sec)	Detection limit (M)	Ref
1-(1 <i>H</i> -indol-1-yl)- <i>N</i> -(thiophen-2-ylmeth-yl)ethanimine	2 × 10 ⁻⁸ -1.0 × 10 ⁻²	59.40 ± 0.3	3.5 – 7.4	5	1.0 × 10 ⁻⁸	This work
bis (diphe-nylphosphino) ferrocene	1.0 × 10 ⁻⁷ -1.0 × 10 ⁻¹	59.70 ± 0.3	4.15-7.8	-	1.8 × 10 ⁻⁸	11

ANALYTICAL APPLICATIONS

The practical utility of membrane Electrode No. 1 has been investigated by its use for the determination of Zr(IV) in some alloy, tap water and waste water samples. The obtained values are in good agreement with the values obtained by AAS and ICP-MS (Table 6). The test sample of metal alloy was prepared by dissolving metal alloy in concentrated nitric acid. All the measurements were carried at constant pH (4.8) of test solution. The pH of test solution was adjusted by adding nitric acid (0.01 M) solution.

Table 6: Comparison of Test Results

Sample	Proposed Electrode (ppm)	AAS (ppm)	ICP-MS (ppm)
Alloy sample	0.053	0.053	0.054
Tap water	0.018	0.017	0.017
Industrial waste water (Ghaziabad)	0.026	0.025	0.026

CONCLUSION

1-(1*H*-indol-1-yl)-*N*-(thiophen-2-ylmethyl)ethanimine was used as electroactive material for the selective determination of Zr(IV) in various samples. The electrode with the composition (w/w) of ionophore: NaTPB: DOS: PVC of 4%: 2%: 57%: 37% has a lower detection limit of 1.0×10^{-8} M in a linear concentration range of 2.0×10^{-8} – 1.0×10^{-1} M with slope of calibration curve of 59.40 mV/decade of activity. The proposed Electrode No. 1 has a fast response time of 5s and could be used in a pH range of 3.5 – 7.6 for a period of 8 weeks.

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