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Research Article

A Zinc Selective Polymeric Membrane Electrode Based on *N*, *N*'-benzene-1, 2-diylbis[1-(pyridin-2-yl)ethanimine] as an Ionophore

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Abstract: A Schiff base *N*, *N'*-benzene-1, 2-diylbis [1-(pyridin-2-yl) ethanimine] was synthesized and used as ionophore for selective determination zinc ion in various samples. The proposed sensor show good selectivity for zinc (Zn^{2+}) ions over all alkali, alkaline earth, transition and rare earth metal cations. The electrode works satisfactorily in a wide concentration range (1.4 x 1 0^{-7} M to 1.0 x 1 0^{-1} M). It has a response time of about 8s and can be used for at least 2 months without any considerable divergence in potentials. The proposed membrane sensor revealed good selectivities for Zn^{2+} ion in a pH range 1.0-7.0.
Keywords: Zn^{2+}-selective electrode, PVC-membrane, Schiff base, Potentiometry.

INTRODUCTION

Zinc ion is an important divalent cation needed for the proper growth and maintenance of human body. It is found in several biological systems and play an important role in various biological reactions including gene transcription. The deficiency of zinc can leads to stunted growth, diarrhea, impotence, hair loss, eye and skin lesions, impaired appetite, and depressed immunity. Conversely, consuming too much zinc can lead to nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches in the short term, and can disrupt absorption of copper and iron in the long term [1-3]. The metal is most commonly used as an anti-corrosion agent and in manufacturing of alloys [4]. Thus the determination of zinc is very important in various scientific, biological and environmental areas.

The various analytical techniques such as UV spectroscopy [5, 6], atomic absorption spectroscopy [7] inductivity coupled plasma atomic emission spectroscopy [8] and fluorescence methods have been used for the determination of zinc in various samples. But these methods are rather expensive, required large infrastructure and time-consuming. Electro-analytical studies based on ion-selective electrodes are particularly suitable for the direct determination of free ions since they measure the activity instead of concentration [9 - 17]. In the present work a Schiff base *N*, *N'*-benzene-1, 2-diylbis [1-(pyridin-2-yl) ethanimine] was synthesized and used as an ionophore for constricting zinc selective membrane electrode.

EXPERIMENTAL SECTION

Reagents

The reagents and chemicals were of analytical grade and used without any further purification. High molecular weight Poly(Vinyl Chloride) (PVC), 1-chloronapthalene (CN), oleic acid (OA), dibutylbutyl phosphonate (DBBP), dioctylphthalate (DOP), dibutylphthalate (DBP), o-nitropheny octylether (o-NPOE), sodium tetraphenyl borate and (NaTPB), tetrahydrofuran (THF) were purchased from Merck. 1-(pyridin-2-yl)ethanone and 1,2-diamino benzene was purchased from Sigma Aldrich. All metal nitrates were also purchased from Fischer Scientific India. Doubly distilled deionized water was used throughout.

Synthesis of Ionophore

The ionophore *N*,*N*'-benzene-1,2-diylbis[1-(pyridin-2-yl)ethanimine] was synthesized by modified the procedure already available in literature [17] and the brief synthesis is given as below:

To a solution of 1-(pyridin-2-yl) ethanone (0.030 mole in 15 mL ethanol), 1,2-diamino benzene (0.030 mol in 15 mL ethanol) was and stirred and heated for 40 min at 45° C. A solid mass separated was collected and washed with diethylether. Crystalization was done with ethanol and then dried over $MgSO_4$. The pale yellow ligand was collected (yield, 80%).

Preparation of membrane

The zinc selective membranes were obtained by pouring a solution of the membrane components: PVC, plasticizer (DBBP, DBP, TEP, DOP, OA and CN respectively), NaTFPB, and ionophore (*L*) in THF (15 ml) at room temperature as per procedure of Craggs *et al*. [18]. The components were added in terms of weight percentage. The viscous solution obtained was poured in a glass ring of 30 mm diameter placed on a Pyrex glass plate. Solvent was allowed to evaporate slowly for about 24 hrs at room temperature. The membranes of 0.5 mm of thickness and 8 mm diameter were removed from the glass plate and glued to one end of a Pyrex glass tube with the help of araldite and M-seal. The membrane electrode was finally conditioned by soaking in a 0.001 M $Zn(NO_3)_2$ solution for 4 days. The potential responses were calculated by following cell assembly.

Ag / AgCl, 0.1M KCl)	Internal reference solution	Zn^{2+}ion Selective Membrane	Test solution of Zn^{2+} ion	1 M KCl, Ag / AgCl

Membrane Optimization

Effect of composition of membrane on the response characteristics of the electrode like slope of the calibration curve, measurement range and detection limit were studied. The six membranes of different composition were fabricated by using different type of plasticizers *i.e.* DOP, o-NPOE, DBBP, TEP, CN and OA keeping PVC, ionophore and NaTPB in fixed composition. The studies based of formation constant of ligand with various metal ions indicate that the ionophore forms most stable complex with Zn(II) ion. Thus the ionophore can be used for the direct determination of zinc ion various aqueous and nonaqueous samples.

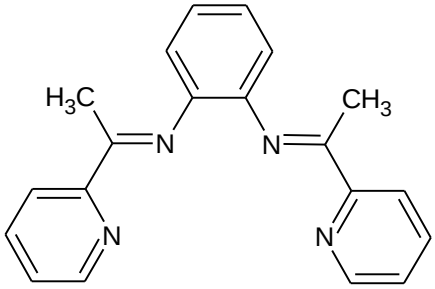

Fig. 1: *N,N'*-benzene-1,2-diylbis[1-(pyridin-2-yl)ethanimine]

RESULTS AND DISCUSSION

The complex formation constant (K_f), were evaluated by molar conductance mole ratio data **(Equation 1)** using Deby-Huckel limiting law of 1:1 electrolytes at 25 ± 1^0C in an acetonitrile solution. The complex formation constant (K_f), in term of the molar conductance can be expressed as [19]:

$$M^+ + L \overset{K_f}{\rightleftharpoons} ML^+$$

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

where

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

Here, Λ_M is 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 complex formation constants, K_f, and the molar conductance of complex, Λ_{obs}, were obtained by using a nonlinear least squares program KINFIT [20]. The logarithm of the formation constants ($\log K_f$) of 1:1 complexes for various metal cations is given in Table 1.

Table 1: Formation constant of metal ions-ligand complexation

Cation	Log K_f
Zn^{2+}	4.38 ± 0.18
Na^+	2.63 ± 0.11
Cd^{2+}	2.82 ± 0.11
Ag^+	2.23 ± 0.14
Mg^{2+}	1.72 ± 0.12
Ca^{2+}	1.93 ± 0.19
Cu^{2+}	1.87 ± 0.15
Sr^{2+}	1.76 ± 0.12
Co^{2+}	2.10 ± 0.16
Ni^{2+}	2.15 ± 0.13
Pb^{2+}	1.21 ± 0.17
Hg^{2+}	2.30 ± 0.09
Fe^{3+}	2.16 ± 0.11
Mn^{2+}	2.71± 0.15

Working concentration range, Response time, and slope of Calibration carve

The potential response of electrochemical cells with 10^{-2} M Zn^{2+} as internal solution was determined in the range of 1.0 x 1 0^{-7} M to 1.0 x 1 0^{-1} M Zn^{2+} solution and the calibration curve depicted in fig. 2. It has been clearly shown that membrane containing plasticizer DBP with the PVC, ionophore and NaTPB in 470:300:40:5 respectively shown Nernstian response (slope of 30.0 ± 1.0 mV/decade of activity) in the conc. range 1.4 x 1 0^{-7} M to 1.0 x 1 0^{-1} M Zn^{2+} ion (Table 2).

Table 2: Optimization of membrane components

Membrane No.	Membrane composition (mg)				Detection limit (M)	Working Concentration range (M)	Slope (mV/ decade)	Response Time(s)
	PVC	NaTPB	Plasticizer	Ionophore				
1	300	5	470(DBP)	40	$1.0 \times 1\ 0^{-7}$	$1.4 \times 1\ 0^{-7}$-$1 \times 1\ 0^{-1}$	30.05 ± 1.0	8
2	300	5	470(DBBP)	40	$1. \times 1\ 0^{-6}$	$2.1 \times 1\ 0^{-6}$-$1 \times 1\ 0^{-1}$	28.00 ± 1.0	14
3	300	5	470(TEP)	40	$4.0 \times 1\ 0^{-6}$	$6.2 \times 1\ 0^{-6}$-$1 \times 1\ 0^{-1}$	27.05 ± 1.0	18
4	300	5	470 (OA)	40	$1.6 \times 1\ 0^{-6}$	$3.8 \times 1\ 0^{-6}$-$1 \times 1\ 0^{-1}$	28.01 ± 1.0	20
5	300	5	470 (CN)	40	$3.0 \times 1\ 0^{-6}$	$4.1 \times 1\ 0^{-6}$-$1 \times 1\ 0^{-1}$	29.01 ± 1.0	16
6	300	5	470 (DOP)	120	$2.8 \times 1\ 0^{-5}$	$1.2 \times 1\ 0^{-4}$-$1 \times 1\ 0^{-1}$	21.40 ± 1.0	30

The static response time of the electrode was found to be 8 s over the entire concentration range. A sample emf *vs.* time plot is shown in figure 5. This is actually the average time required for the electrode to reach a potential with in ±1mV of the final equilibrium value after successive immersion of a series of Zn^{2+} ions, each having a tenfold difference in concentration.

The effect of pH (Fig. 3) of test solution on the potential response with the proposed membrane sensor was studied over the pH range of 1.0 – 8.0 in the 1.0 x 10^{-3} M $Zn(NO_3)_2$ solution and pH of test solution was adjusted by drop wise addition of 10^{-1} M solution of dil. HNO_3 and/or hexamine because direct addition of acid could influence the membrane. It was observed that the potential of sensor electrode remains constant in the pH range of 2.0 - 6.5**.**

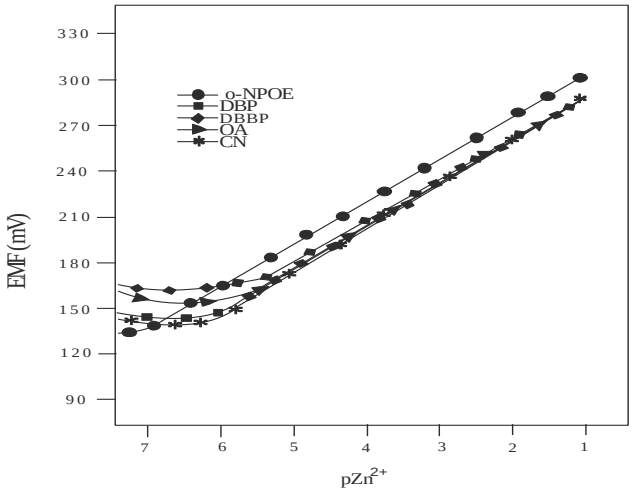

Fig. 2: Variation of membrane potential of PVC based membranes of Schiff base ionophore with varying concentrations of Zn^{2+} ion

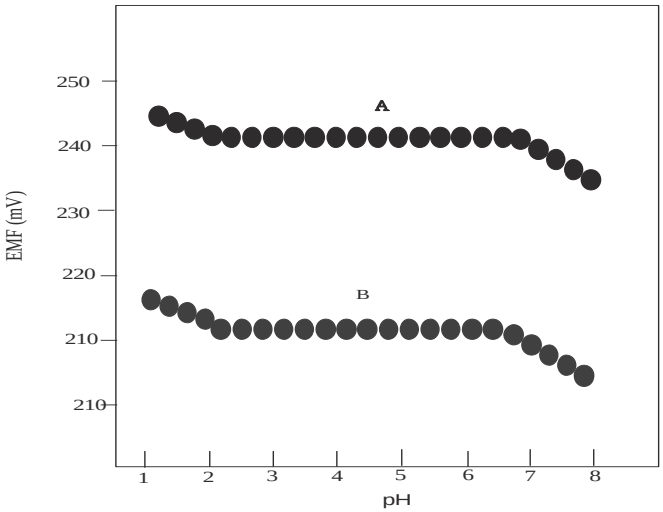

Fig. 3: Effect of pH of the test solution (A = 1.0 X 10^{-4} M and B = 1.0 X 10^{-3} M) on the response potential of the electrode.

It was observe that the proposed membrane works satisfactorily in a mixtures having up to 30 % v/v methanol or ethanol or acetone, no appreciable change in working concentration range, response time, and slope in Calibration carve were observe. But above 30 % of non-aqueous content, electrode sensor showed potential drift with time **(**Table 3).

Table 3: Effect of partially non-aqueous medium on the working of membrane (No.1)

Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Working Conc. Range (M)	Response time (Sec)
0	30.05 ± 1.0	$1.4 \times 1\ 0^{-7}$- 1.0×10^{-1}	8.00
Methanol			
10	30.10 ± 1.0	1.4×10^{-7}- 1.0×10^{-1}	8:00
20	30.08 ± 0.8	1.4×10^{-7}- 1.0×10^{-1}	8:00
30	30.03 ± 0.5	1.2×10^{-7}-1.0×10^{-1}	8:00
35	23.20 ± 0.5	3.2×10^{-5}- 1.0×10^{-1}	12:00
40	21.50 ± 0.5	5.4×10^{-5}- 1.0×10^{-1}	15:00
Ethanol			
10	30.12 ± 1.0	1.4×10^{-7}-1.0×10^{-1}	8:00
20	30.10 ± 0.8	1.32×10^{-7}-1.0×10^{-1}	8:00
30	30.05 ± 0.5	1.28×10^{-7}- 1.0×10^{-1}	8:00
35	22.10 ± 0.3	5.6×10^{-5}- 1.0×10^{-1}	11:00
40	21.40 ± 0.3	7.2×10^{-5}- 1.0×10^{-1}	15:00
Acetonitrile			
10	30.10 ± 1.0	1.4×10^{-7}- 1.0×10^{-1}	8:00
20	30.08 ± 0.8	1.15×10^{-7}- 1.0×10^{-1}	8:00
30	30.03 ± 0.5	$1.1.10 \times 10^{-7}$-1.0×10^{-1}	9:00
35	21.90 ± 0.3	2.0×10^{-5}- 1.0×10^{-1}	12:00
40	21.30 ± 0.3	5.0×10^{-5}- 1.0×10^{-1}	14:00

Selectivity Coefficient

Selectivity is the most important characteristic of any electrode, which defines nature of the device and the extent to which it may be employed in the determination of a particular ion in presence of other interfering ions. This is measured in terms of potentiometric selectivity coefficients **(**log $K_{M^{n+}}^{Zn^{2+}}$) which has been measured using Fixed Interference Method (FIM) at 1 x 10^{-3} M concentration of interfering ions using the following modified the Nicolsky equation (Equation 3) and neglected the power term from the equation for calculating the selectivity coefficients Saez de Viteri and Diamond [21].

$$K_{Cd^{2+},M^{n+}}^{POT} = \frac{a_{Cd^{2+}}}{a_{M^{n+}}^{z_{Cd^{2+}}/z_{M^{n+}}}} \quad \text{.....(3)}$$

Where a^{Zn2+} is the activity of the primary ion and $a_M{}^{n+}$ is the activity of interfering ion ${}^{z}{}_{Zn}{}^{2+}$and ${}^{z}{}_{M}{}^{n+}$ are their respective charges (table 4).

The response characters of the membrane electrode no. 1 was also compared with the previously reported electrodes [16, 22-26]. The data presented in table 5 indicates that the proposed membrane electrode no. 1 based on Schiff base *N*, *N*'-benzene-1,2-diylbis[1-(pyridin-2-yl)ethanimine] is superior in termes of selectivity and sensitivity.

Table 4: Calculation of selectivity coefficient by Fixed Interference Method

Interfering Ion	Selectivity Coefficient,($K_{M^{n+}}^{Zn^{2+}}$)
	Fixed Interference Method
Na^{+}	2.7×10^{-4}
Ag^{+}	4.2×10^{-4}
Ca^{2+}	2.4×10^{-4}
Cd^{2+}	2.8×10^{-4}
Cu^{2+}	3.2×10^{-4}
Sr^{2+}	4.0×10^{-4}
Co^{2+}	2.6×10^{-4}
Ni^{2+}	2.8×10^{-4}
Pb^{2+}	2.9×10^{-4}
Hg^{2+}	1.3×10^{-4}
Fe^{3+}	3.3×10^{-4}
Mg^{2+}	2.6×10^{-4}
Cs^{+}	3.4×10^{-4}

Table 5: Comparison of response characters of proposed electrode with those of the previously reported electrodes

Concentration range (M)	Detection limit (M)	Slope	Reference No.
1.4×10^{-7}- 1.0×10^{-1}	1.0×10^{-7}	30.05 ± 1.0	This work
1.0×10^{-6}- 1.0×10^{-1}	8.9×10^{-7}	30.00	22
5×10^{-5}- 1.0×10^{-1}	3.0×10^{-5}	22.00	23
2.8×10^{-6}- 1.0×10^{-1}	2.24×10^{-6}	28.50	24
6.2×10^{-6}- 1.0×10^{-1}		29.00	25
1.0×10^{-7}- 1.0×10^{-2}	8.5×10^{-7}	29.30	26
5.0×10^{-7}- 1.0×10^{-2}	2.6×10^{-7}	29.40	16

Analytical application

The concentration of cadmium ions in industrial wastewater and cigarettes samples were determined using proposed ion selective electrode. The obtained values are quite comparable to those obtained with AAS and ICP, thereby illustrating the utility of the sensor for determining the Zn^{2+} in real samples (Table 6).

Table 6: Determination of zinc in industrial waste water and cigarettes samples*.

Sample	$^{Zn2+}$-ISE[a] (µg/L)	AAS (µg/L)	ICP (µg/L)
Synthetic sample	2.2	2.0	2.1
Industrial waste water	11.6	11.5	11.6

*Average of three replicate measurements

CONCLUSION

The proposed electrode showed high selectivity and sensitivity to Zn^{2+} ion, wide dynamic range (1.4×10^{-7} – $1.0\ 10^{-1}$M), low detection limit (1.0×10^{-7}) and fast response time (8s). The electrode was successfully applied for the direct determination of Zn^{2+} ion in various samples in a pH range of 2.0 – 6.5.

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