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Potentiometric Based Membrane Sensor for Zinc Ion

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ABSTRACT: A PVC-based membrane of 12-crown-4 exhibits good response for Zn^{2+} in a wide concentration range (7.08×10^{-5}-1.00×10^{-1} M) with a non-nernstian slope of 20.5 mv per decade of concentration of Zn^{2+}. The response time of sensor is <10 s and the membrane can be used for more than 3 months without observing any divergence. In addition, the proposed sensor exhibits very good selectivity for Zn^{2+} over other cations and can be used in a pH range (4.0-7.0). The membrane worked satisfactorily in non-aqueous medium up to 40% (v/v) non-aqueous content. The electrode has been used as an indicator electrode to determine the end point in the potentiometric titration of Zn^{2+} with EDTA.

Keywords: crown ether, potentiometric sensor, waste analysis

I. INTRODUCTION

Ion Selective Electrodes are being widely used in the fields of environmental, industrial, agricultural and medicinal as they offer several advantages over other methods of analysis. The most attractive features of this technique are the speed with which samples can be analyzed portability of the device, sample non-destruction, online monitoring, cost effectiveness and large measuring range.

Some commercialized sensors for alkali and alkaline earth metals, halides, etc. are available; however more efforts are required to develop ion-selective electrodes of commercial standards for heavy metal ions, which are toxic beyond a certain concentration level.

Besides its carcinogens and mutagens nature the toxicity of zinc arises from its synergistic/antagonistic interaction with other heavy metals, particularly its homologue cadmium [1]. Its compounds are widely used in electroplating, pharmaceuticals, paint, rubber, dye, wood preservatives, ointments and batteries so the waste from these industries need to be frequently analyzed. Common zinc compounds found at hazardous waste sites include zinc chloride, zinc oxide, zinc sulfate and zinc sulfide. Besides, it is also present in high protein foods and its large doses can cause fever, chills, pulmonary manifestation, gastroenteritis, vomiting, nausea, anemia and renal failure. In view of its toxicity, the determination of zinc becomes important.

Macrocyclic compounds have the ability to form complexes with metal ions of compatible dimensions. Cyclic polyethers, such as crowns, have already been exploited for the fabrication of highly specific ion sensors [2-14]. The present paper deals with the membrane of 12-crown-4,used for the estimation of zinc(II) ions.

The proposed membrane electrode incorporating 12-crown-4 as an electroactive phase exhibits reasonably good selectivity, a short response time, and a fairly wide concentration range for the estimation of zinc ions.

II. EXPERIMENTAL

Reagents

12-crown-4 was obtained from Fluca and zinc chloride from BDH (Merck). All other chemicals used in these investigations were analytical grade reagents. Double distilled water used for preparing all solutions.

Electrode Preparation

The method reported by Craggs *et al* [15] was adopted for the preparation of membranes. A known amount of 12-crown-4, PVC and dibutyl phthalate was dissolved in tetrahydrofuran. After shaking the mixture vigorously for some time and removing all the air bubbles it was poured into a holder and the solvent was made to evaporate at room temperature. The resulting membrane was cut into size, attached to a Pyrex tube with the help of araldite and immersed in Zn^{2+} solution for equilibrium.

The ratios of the membrane ingredients, time and concentration of equilibrating solution were optimized first so that that the membrane developed reproducible potentials and remained stable for a long time. Satisfactory equilibration was achieved with 0.1M Zn^{2+} solution in a contact time of 36 h.

Potential Measurements

Potentials were measured at 25 ±1 ^{o}C with the help of ceramic junction calomel electrodes by setting up the following assembly.

- Internal reference electrode (SCE)
- Internal solution (0.1M Zn^{2+})
- Membrane
- Test solution
- External reference electrode (SCE)

A fixed concentration of Zn^{2+} solution was taken as internal solution (0.1M) and saturated calomel electrodes (SCE) were used as reference electrodes. All pH adjustments were made by appropriate acid or base. pH measurements were made on a digital pH meter (model pH 5652, ECIL, Hyderabad, India; Glass electrodes as pH electrode and calomel as reference electrode).

III. RESULTS AND DISCUSSION

Some important features of various fabrications having ingredients in different ratios are recorded in Table 1. Out of the six castings the membrane number 2 having crown, PVC and Dibutyl Phthalate in the ratio 1 : 10 : 2 exhibits a wide working concentration range (7.08×10^{-5} – 1.00×10^{-1} M) with a non-Nernstian slope of 20.5 mV decade^{-1} of Zn^{2+}solution.

Table 1. Optimization of membrane ingredients.

Membrane No.	Composition in ratio			Working Concentration range (M)	Slope (mV decade^{-1})
	Crown ether	PVC	Dibutyl Phthalate		
1	1	10	1.5	8.26×10^{-4} -1.00×10^{-1} M	19.5
2	1	10	2.0	7.08×10^{-5}-1.00×10^{-1} M	20.5
3	1	12	2.0	1.78×10^{-5}-1.00×10^{-1} M	29.0
4	1	12	2.5	5.00×10^{-5}-1.00×10^{-1} M	35.0
5	1	15	1.5	1.00×10^{-4}-1.00×10^{-1} M	23.0
6	1	15	2.0	9.00×10^{-5}-1.00×10^{-1} M	28.5

The PVC-based membrane of 12-crown-4 generates very stable potentials when placed in contact with $ZnCl_2$ solution. The e.m.f response of the membrane in presence of a wide concentration range of Zn^{2+} is shown in Fig. 1. The rectilinear range is 7.08×10^{-5}-1.00×10^{-1} M with a detection limit of the assembly down to 1.41×10^{-5} M.A near-nernstian slope of 20.5 mv per decade of Zn^{2+}concentration is also recorded for this assembly. Solutions of varying concentrations were tried as reference solution and its effect on the functioning of membrane sensor has also been tried. Fig. 2 depicts the potentials Vs [Zn^{2+}] plots obtained by using 5.0×10^{-2} and 1.0×10^{-2} M Zn^{2+} concentrations as reference solutions. It is observed that the best results are obtained when 0.1 M is used as reference solution whereas at other concentrations a decrease in detection limit is noticed.

Response and life time: The response time of the membrane sensor is <10 s over the entire concentration range. Potentials stay constant for more than 5 minutes, after which a very slow divergence is recorded. The standard deviation of 20 identical measurements is ±1.0 mV. A membrane can be used for a period of 3 months if properly stored and cross contamination is avoided.

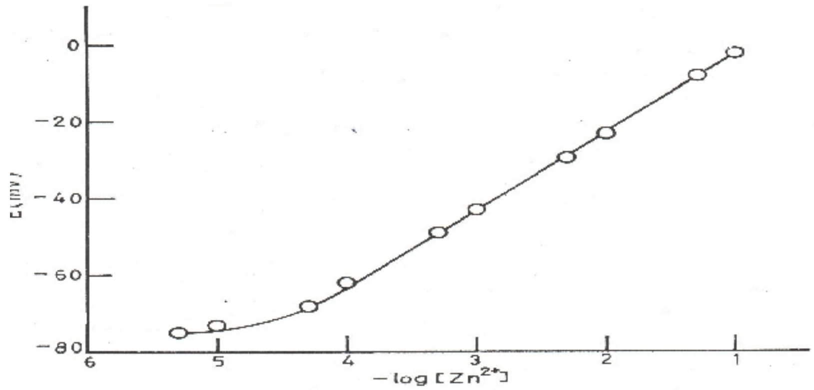

Figure 1. Plot of potential vs. −log [Zn^{2+}].

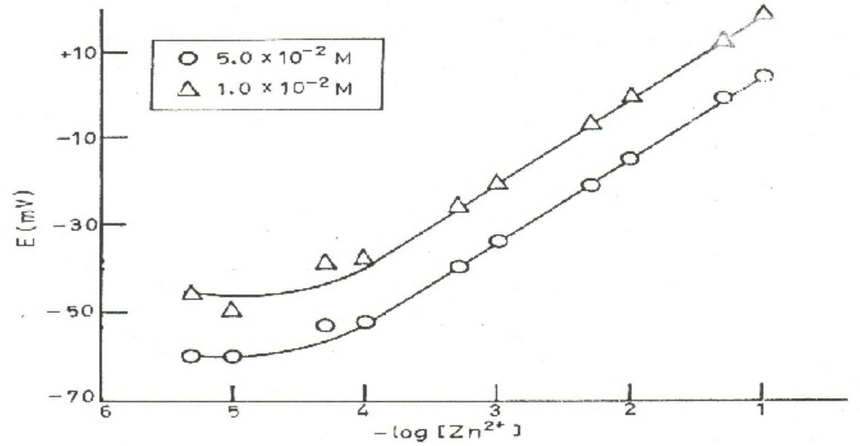

Figure 2. Plots of potential vs. −log [Zn^{2+}] at various concentrations of reference solution.

After 3 months, there was a slight change in both the slope and response time, and this could be corrected by equilibrating the membrane again with 1.0 M Zn^{2+} solution for 24 h.

Effect of pH: The working pH range of the proposed assembly has also been ascertained (Fig. 3). Potentials stay constant between pH 4.0 to 7.0 (1.0 × 10^{-3}M Zn^{2+}). Below this pH range divergence in potentials are observed.

Selectivity: The selectivity of the new membrane sensor is presented in terms of the potentiometric selectivity coefficient ($K^{pot}_{Zn,M}$), which has been calculated by fixed as well as mixed interference method [16]. In fixed interference method, the parameter has been obtained at relatively higher level of interference (1.0 × 10^{-2} M) while mixed interference method has been employed at 5.0 × 10^{-4} M concentration of primary ion and varying concentrations of interfering ions (Table 2 & 3).

The selectivity coefficient $K^{pot}_{Zn,M}$ for fixed interference method was obtained by the expression $K^{pot}_{Zn,M} = a_{Zn} / (a_M)^{Z_{Zn}/Z_M}$ and for mixed interference method it was obtained by the expression $K^{pot}_{Zn,M} = a_{Zn} [10^{(E_{Zn,M}-E_{Zn})/S} - 1] / (a_M)^{Z_{Zn}/Z_M}$. Where a_{Zn} and a_M are the activities of primary and interfering ions.

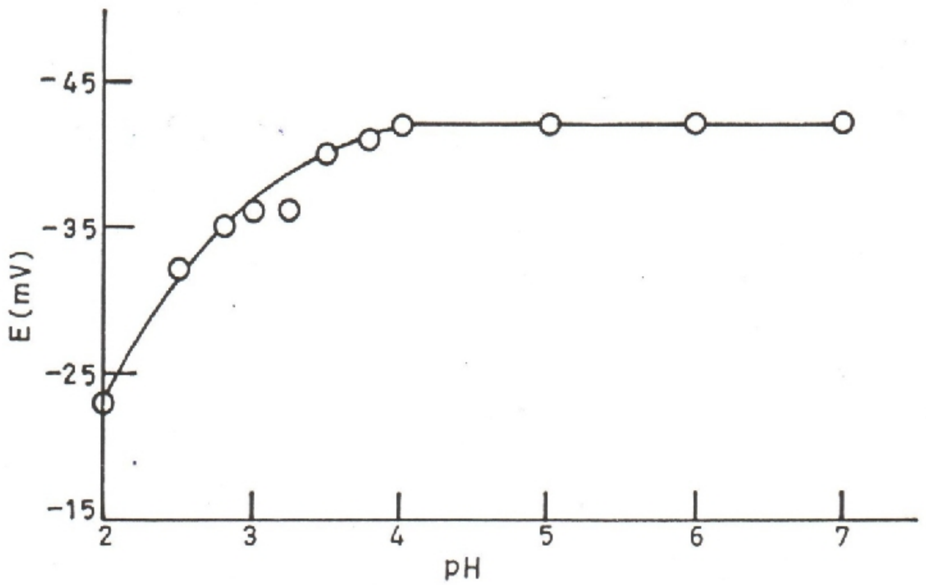

Figure 3. Plot of potential vs.pH: [Zn^{2+}]=1.0x10^{-3}M.

It has been observed that the equations for calculating the selectivity coefficient values are quite well suited when charges of primary and interfering ions are same ($Z_A=Z_B$) , however, when $Z_A \neq Z_B$ the expressions are not very well applicable due to the superscript on the concentration/activity term. So the selectivity coefficient values have been calculated by using the expressions with superscript (normal expressions) and also by excluding superscript and the values obtained are depicted in Table 2 & 3.

A marked difference can be noticed in the values of selectivity coefficient, when calculated by the expression using superscript in comparison to the expression without superscript when $Z_A \neq Z_B$.

TABLE 2

SELECTIVITY COEFFICIENT ($K^{pot}_{Zn^{2+},M^{n+}}$) VALUES OF OTHER INTERFERING IONS FOR 12-CROWN-4 AS OBTAINED BY FIXED INTERFERENCE METHOD (INTERFERRING ION CONCENTRATION IS 1.0X10^{-2} M) USING THE EXPRESSION WITH AND WITHOUT SUPERSCRIPT

Ion / $K^{Pot}_{Zn^{2+},M^{n+}}$	Na^+	K^+	NH_4^+	Li^+	Ca^{2+}	Cu^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Mg^{2+}	Cr^{3+}	Fe^{3+}
with superscript	7.94	7.94	7.94	8.91	1.78x10^{-1}	1.41x10^{-1}	1.58x10^{-1}	1.58x10^{-1}	1.58x10^{-1}	1.12x10^{-1}	1.00x10^{-1}	6.81x10^{-2}	4.30x10^{-2}
without superscript	7.94x10^{-2}	7.94x10^{-2}	7.94x10^{-2}	8.91x10^{-2}	1.78x10^{-1}	1.41x10^{-1}	1.58x10^{-1}	1.58x10^{-1}	1.58x10^{-1}	1.12x10^{-1}	1.00x10^{-1}	3.16x10^{-1}	1.99x10^{-1}

TABLE 3

SELECTIVITY COEFFICIENT ($K^{pot}_{Zn^{2+},M^{n+}}$) VALUES OF OTHER INTERFERING IONS FOR 12-CROWN-4 AS OBTAINED BY MIXED INTERFERENCE METHOD (PRIMARY ION CONCENTRATION IS 5.0X10^{-4} M) USING THE EXPRESSION WITH AND WITHOUT SUPERSCRIPT

Ion / $K^{Pot}_{Zn^{2+},M^{n+}}$	Na^+	K^+	NH_4^+	Li^+	Ca^{2+}	Cu^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Mg^{2+}	Cr^{3+}	Fe^{3+}
with superscript	1.25	1.25	2.37	2.37	6.08×10^{-1}	5.20×10^{-1}	4.02×10^{-1}	5.20×10^{-1}	6.41×10^{-1}	4.02×10^{-1}	4.35×10^{-1}	6.40×10^{-1}	5.73×10^{-1}
without superscript	1.20×10^{-1}	1.20×10^{-1}	2.86×10^{-1}	2.86×10^{-1}	6.08×10^{-1}	5.20×10^{-1}	4.02×10^{-1}	5.20×10^{-1}	6.41×10^{-1}	4.02×10^{-1}	4.35×10^{-1}	1.96	1.20

The selectivity pattern obtained by both the methods is almost same and it is observed that the monovalent cations interfere hundred times more when the values are calculated by the expression using the superscript and in case of trivalent cations the values are ten times higher.

The sensor does not appear to suffer with interference by other cations if the selectivity coefficient values obtained by the expression without superscript are considered. Thus the data is quite deceptive and in order to know the actual behaviour of the proposed electrode assembly, in presence of varying amounts of interfering ions, some mixed runs of primary plus interfering ions (Na^+, Ca^{2+} and Cr^{3+}) are made (Figs. 4 & 5).

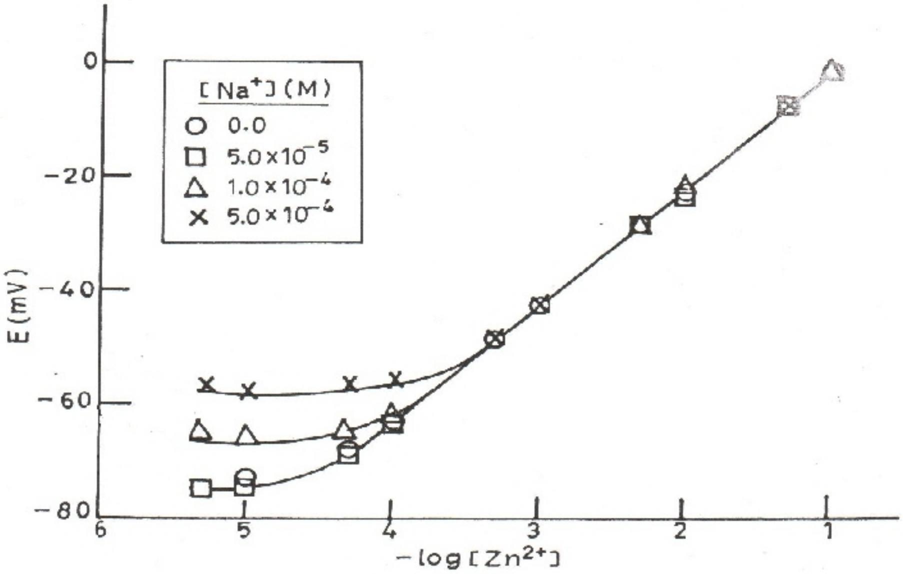

Figure .4. Plots of potential vs.−log [Zn^{2+}] in presence of Na^+ at varying concentrations.

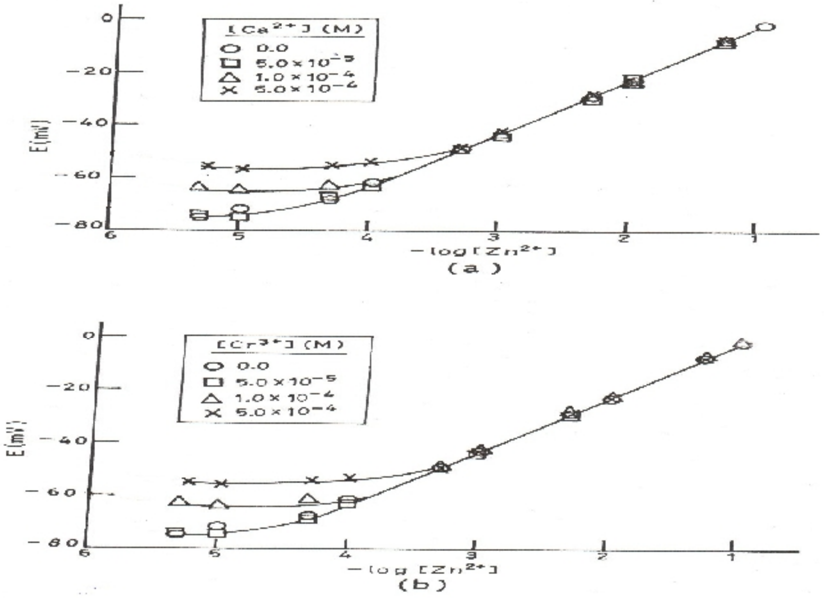

Figure .5. Plots of potential vs. −log [Zn^{2+}] in presence of (a) Ca^{2+} and (b) Cr^{3+} at varying concentrations.

It is apparent (from the plots) that none of the ions mentioned above interfere when the same are present upto a concentration level of ≤ 5.0×10^{-5} M. At higher concentration of interference, however, the linear portion of the plot (concentration Vs potential) as well as detection limit goes down. The effect of interference is more pronounced in case of Cr^{3+}than Ca^{2+} and is least for Na^{+}. This clearly indicates that the interference caused by monovalent ions is not as large as depicted by high values of selectivity coefficient when the same are calculated by using the expression with superscript. A perusal of data (Table 2 & 3) shows that the values obtained by fixed interference method using the expressions without superscript are more close to the observed behaviour of the membrane sensor.

Solvent effect: The utility of the electrode assembly is also examined in partially non-aqueous medium. The results of the membrane sensor in non-aqueous medium in terms of working concentration range and slope are depicted in Table 4. It is evident that the solutions having 25% (v/v) methanol or ethanol do not disturb the functioning of the proposed sensor whereas at higher non-aqueous content (35% or more) a divergence is recorded.

Table 4. Performance of the electrode system in 15, 25 and 35% (v/v) non-aqueous medium.

Non-aqueous content (%)	Working concentration range (M)	Slope(mV dacade^{-1})
00	7.08 × 10^{-5} 1.00 × 10^{-1}	20.5
Methanol		
15	7.08 × 10^{-5} 1.00 × 10^{-1}	20.5
25	7.08 × 10^{-5} 1.00 × 10^{-1}	20.5
35	8.25 × 10^{-5} 1.00 × 10^{-1}	16.2
Ethanol		
15	7.08 × 10^{-5} 1.00 × 10^{-1}	20.5
25	7.08 × 10^{-5} 1.00 × 10^{-1}	20.5
35	1.00 × 10^{-5} 1.00 × 10^{-1}	18.5

Titration: The sensor has also been used as an indicator electrode in the potentiometric titration of Zn^{2+} with EDTA. Fig. 6 shows the potential change of 1.0×10^{-2} M Zn^{2+} solution (10.0 mL) with the addition of 1.0×10^{-2} M EDTA. In spite of the small change in potentials, the inflection point is quite sharp and indicates perfect stoichiometry.

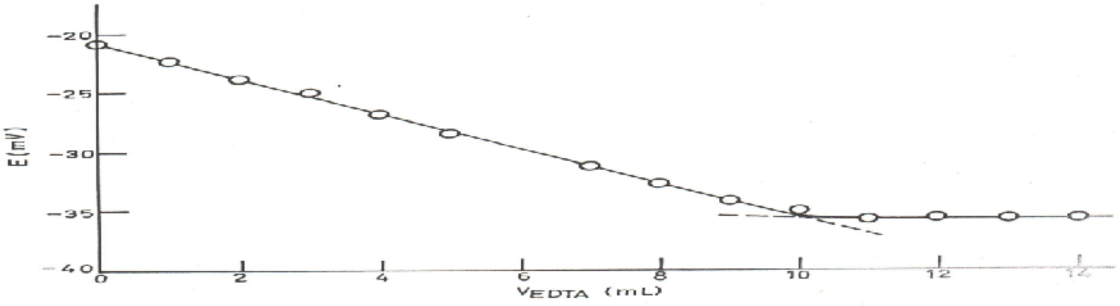

Figure .6.Titration plot of 10mLof 1.0×10^{-2}M Zn^{2+}solution with 1.0×10^{-2}M EDTA .

IV. CONCLUSION

In conclusion, the zinc ion–selective electrode based on 12-crown-4 exhibits good selectivity, sensitivity, stability and a very small response time (10s). Another characteristic feature of the electrode is much smaller equilibrium time in comparison with other similar sensors proposed for Zn^{2+}. The lifetime of the sensor is more than 3 months. The assembly has been used as an indicator electrode in potentiometric titration involving Zinc (II) ions.

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