

A PVC BASED ELECTROCHEMICAL SENSOR FOR COBALT (II) DETERMINATION

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PVC based membranes of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (TMOPP-Co) (I) as electroactive material with sodium tetra phenyl borate (NaTPB) as anion excluder and dibutyl phthalate (DBP), dioctyl phthalate (DOP), dibutyl butyl phosphonate (DBBP), tri-n-butyl phosphate (TBP), and 1-chloronaphthalene (CN) as plasticizing solvent mediators were prepared and investigated as Co²⁺ selective electrode. The PVC based membrane of I without plasticizer and having anion excluder, NaTPB in the ratio PVC: I: NaTPB (100: 2: 1) gave the best results in terms of working concentration range (1.9x10⁻⁵-1.0x10⁻¹M) with a slope (30.5 mV/decade of activity) over the pH range 1.9-5.8. The response time of this sensor is 20s and can be used for about 4 months in aqueous as well as in non-aqueous medium without showing considerable divergence in potentials. The selectivity coefficient values for mono-, di-, and trivalent cations indicate good selectivity for Co²⁺ over a large number of cations. It can be used to determine Co²⁺ in actual wastes as well as an indicator electrode in the potentiometric titration of Co²⁺.

Key Words : Poly Vinyl Chloride (PVC); Nernstian Slope; Cobalt Selective Electrode; Ion-Selective Electrode

Introduction

Ion-selective electrodes based on ionophore ligands are well established for many inorganic cations and anions¹⁻³. Among many ion-selective electrodes reported only a few have been found to be sufficiently selective to permit easy and reliable determination and the remaining ones need improvement with regard to selectivity, sensitivity and reproducibility. Among heavy metals, cobalt has received less attention in spite of its widespread occurrence in meteorites, sea and fresh waters, soils, plants and animals⁴. It is a vital trace element in animal nutrition. Cobalt deficiency in animals may lead to retarded growth, loss of appetite and anemia, and rapid recovery from these symptoms occurs upon feeding them with a cobalt-supplemented diet. Although cobalt is not highly toxic, but its acute and chronic poisoning give rise to symptoms such as pulmonary edema, nausea, allergy, gastro-intestinal tract disorders, diarrhoea and other disorders^{5,6}. It is thus obvious that monitoring of cobalt in environmental, biological and in various other samples, at trace and ultra trace levels, is necessary.

A survey of literature revealed that sensors for cobalt have been developed making use of organic

resins^{7,8}; chelates⁹; extractants¹⁰, macrocycles¹¹, and porphyrins¹² as sensor materials. However, these efforts have not been very fruitful as the developed electrodes have a narrow working concentration range, a near- or non- Nernstian response, exhibit high response times and suffer serious interference from various ions including iron and nickel, which have properties similar to those of cobalt.

With the availability of improved and highly selective materials, the possibility of developing specific sensors has opened up. The design and function of synthetic ionophores for ion-selective electrodes are based on such diverse parameters as the structure and cavity size of the ligand, the stability and selectivity of its metal ion complex, its solubility, and the ability to extract the metal ion into membrane phase. Macrocycles are a favoured class of compounds in this area as their complexes have high stability constants, lipophilicity to remain in the membrane phase and sufficient conformational flexibility for rapid ion-exchange¹³. The use of porphyrins as active constituents for membranes has been reported during the last few years¹⁴⁻¹⁶. Porphyrins are a class of naturally occurring macrocyclic compounds, which play an important role in the metabolism of living organisms. Almost all metals form complexes with porphyrin molecules. The porphyrin molecule consists of four pyrrolic units

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linked by four methine bridges. The chelation of metal ion by porphyrin involves the incorporation of the metal ion into the centre of the tetrapyrrole nucleus with the simultaneous displacement of two protons from the secondary nitrogen atoms. Preliminary studies showed that 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (TMOPP-Co) (I) tend to show affinity for cobalt. Thus, 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (TMOPP-Co) has been studied as an electroactive phase in PVC matrix for the fabrication of Co^{2+} -selective electrode and the results are presented in this paper. The present electrode shows good selectivity over other cations and is superior to the existing electrodes in many aspects.

Experimental

Reagents

Cobalt acetate was obtained from S.D. Fine Chem. (India). High molecular weight poly (vinyl) chloride (PVC) was obtained from Fluka, (Switzerland) and used as such. All other reagents used were of analytical grade purity (BDH, UK). Aqueous solutions were prepared in doubly distilled water. Anion excluder, sodium tetra phenyl borate (NaTPB) from BDH (England), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) from Reidal, India, dibutyl butylphosphonate (DBBP) from Mobil (USA) and chloro naphthalene (CN) and tri-n-butyl phosphate (TBP) from Merck (Germany) were used. Solutions of different concentration were prepared by diluting the stock solution of 0.1 M concentration.

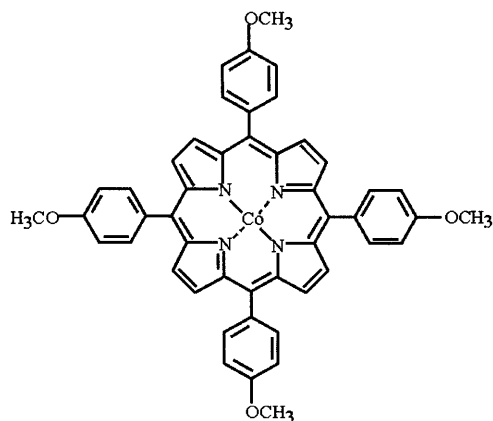
Apparatus

The potential measurements were carried out at 25 ± 0.1 °C on a PH 5652 digital pH meter/millivoltmeter (ECIL, Hyderabad, India) and CVM 301 Century microvoltmeter (Century Instruments, Chandigarh, India). 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).

Synthesis of 5,10,15,20-tetrakis (4-methoxyphenyl) Porphyrinatocobalt (TMOPP-Co) (I)

The 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinatocobalt (TMOPP-Co) was synthesized by the method of Dorough *et al.*¹⁷ by boiling a mixture of 50 ml of 2.5×10^{-4} M 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrin (TMOPP) and 1.25 g of cobalt acetate in 50 ml glacial acetic acid for about

5 min. The solution was then transferred to separator funnel with benzene. Water was then added to the separator funnel and the resulting benzene layer was washed several times with water to completely remove the reaction solvents and inorganic salts. The benzene layer was then dried over anhydrous sodium sulphate and after that it was evaporated to yield the final product, which was dried in a vacuum desiccator.



5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (I)

Membrane Preparation

The method reported by Craggs *et al.* was adopted for the preparation of membranes¹⁸. Varying amounts of the ion active phase 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinatocobalt (TMOPP-Co) and an appropriate amount of PVC were dissolved in a minimum amount of THF (~10ml). The anion excluder, NaTPB and solvent mediators; DBP, DOP, DBBP, TBP, and CN were also added to get membranes of different compositions. After complete dissolution of all the components and thorough mixing, the resulting solutions were poured into acrylic rings placed on a smooth glass plate and allowed to evaporate at room temperature. After 48 hours, transparent membranes of 0.5mm thickness were obtained. A 5mm-diameter piece was cut out and attached to one end of a Pyrex tube with Araldite (Ciba-Geigy, Bombay, India). The ratio of various membrane ingredients, time of contact and the concentration of equilibrating solution were optimized first so that the membranes develop reproducible, stable, and noiseless potentials. Membrane to membrane and batch-to-batch reproducibility was assured by carefully following the optimum condition of fabrication.

Potential Measurements

The membranes were equilibrated for 3 days in 0.5 M Co^{2+} solution. Potentials were measured by direct potentiometry at 25 ± 0.1 °C with the help of ceramic

junction calomel electrodes and the cell setup was the same as reported earlier¹⁹. The 1.0×10^{-1} M cobalt nitrate was taken as inner reference solution and saturated calomel electrodes (SCE) were used as reference electrodes. All pH adjustments were made with appropriate acid or base.

Results and Discussion

Membrane Characteristics

A number of PVC based membranes were prepared incorporating (I) as electroactive material and equilibrated in different concentrations of Co^{2+} solutions for different periods of time. Investigation revealed that proper equilibration of the membranes was achieved when these were dipped in a solution of 0.5 M Co^{2+} for three days. Of the various membranes prepared, one having PVC and I in the ratio 100:2 (w/w) gave satisfactory results.

Effect of Plasticizer

The effect of addition of anion excluder, sodium tetra phenyl borate (NaTPB) and plasticizers, viz., dibutyl phthalate (DBP), dioctyl phthalate (DOP), dibutyl butylphosphonate (DBBP), tri-n-butyl phosphate (TBP) and chloronaphthalene (CN) was also studied for optimizing the composition of the membranes for obtaining best response characteristics and the same are listed in Table I.

Working Concentration Range and Slope

The potential response of the sensor with 0.1 M Co^{2+} as internal solution was determined as a function of Co^{2+} concentration in the range of 1.0×10^{-6} – 1.0×10^{-1} M. It was observed that membrane, which contained only I in PVC matrix, exhibited a narrow working concentration range of 6.2×10^{-4} – 1.0×10^{-1} M of Co^{2+} . The membrane having anion excluder, NaTPB but with no plasticizer (Membrane No. 1) proved to be best in

terms of working concentration range 1.9×10^{-5} – 1.0×10^{-1} M with a slope of 30.5 mV/decade of activity (Table I). Addition of plasticizers deteriorated the performance of the sensor with regard to working concentration range in all cases (Fig. 1). It is clear from Table I that with the use of plasticizers, the slopes were affected adversely. In some cases, super-Nernstian and in other non-Nernstian slopes were noticed. Thus, addition of plasticizers did not improve the response characteristics as has earlier been observed by other workers also^{12,20}. So Membrane No. 1 has been selected for all further studies.

Further to get optimum composition of the ingredients in the membrane, different composition (w/w) was tried by varying the amount of I (Table II). The membrane with the composition of TMOPP-Co (I): NaTPB: PVC in the ratio 2:1:100 (membrane E) exhibited the best working concentration range of 1.9×10^{-5} – 1.0×10^{-1} M with a slope of 30.5 mV/decade of activity and a response time of 20 s. No improvement was observed in any of these characteristics by increasing the amount of I from 3.0 mg to 3.5 mg (Membrane F, Table II). Therefore the composition E (Membrane No. 1) was considered to be best for further studies.

Response and Lifetime

The response time is the time taken by the electrode to achieve a stable potential with no further change observable above the background noise. The membrane without plasticizer (No. 1) but with NaTPB showed a response time of 20s. It was reduced by 2-5s when the solvent mediators were added except in case of TBP where it was increased by 5s. The best response time was observed for the membrane having DBBP as solvent mediator, however the slope outgoes the Nernstian value (Table I). Therefore, Membrane No.1 was chosen for all further studies. The potentials

Table I
Composition and Response Characteristics of PVC Based TMOPP-Co (I) Membranes Selective to Co^{2+}

Sensor/ Membrane No.	Composition of the membrane (w/w)								Working concentration range (M)	Slope (± 1.0 mV/ decade of activity)	Response time (s)
	(I)	DOP	DBBP	TBP	DBP	CN	NaTPB	PVC			
1	2						1	100	1.9×10^{-5} - 1.0×10^{-1}	30.5	20
2	2	66					1	100	7.9×10^{-5} - 1.0×10^{-1}	32.6	15
3	2		64				1	100	5.6×10^{-4} - 1.0×10^{-1}	35.8	15
4	2			66			1	100	7.1×10^{-4} - 1.0×10^{-1}	40.0	25
5	2				66		1	100	8.9×10^{-5} - 1.0×10^{-1}	31.6	18
6	2					64	1	100	1.4×10^{-4} - 1.0×10^{-1}	31.2	17

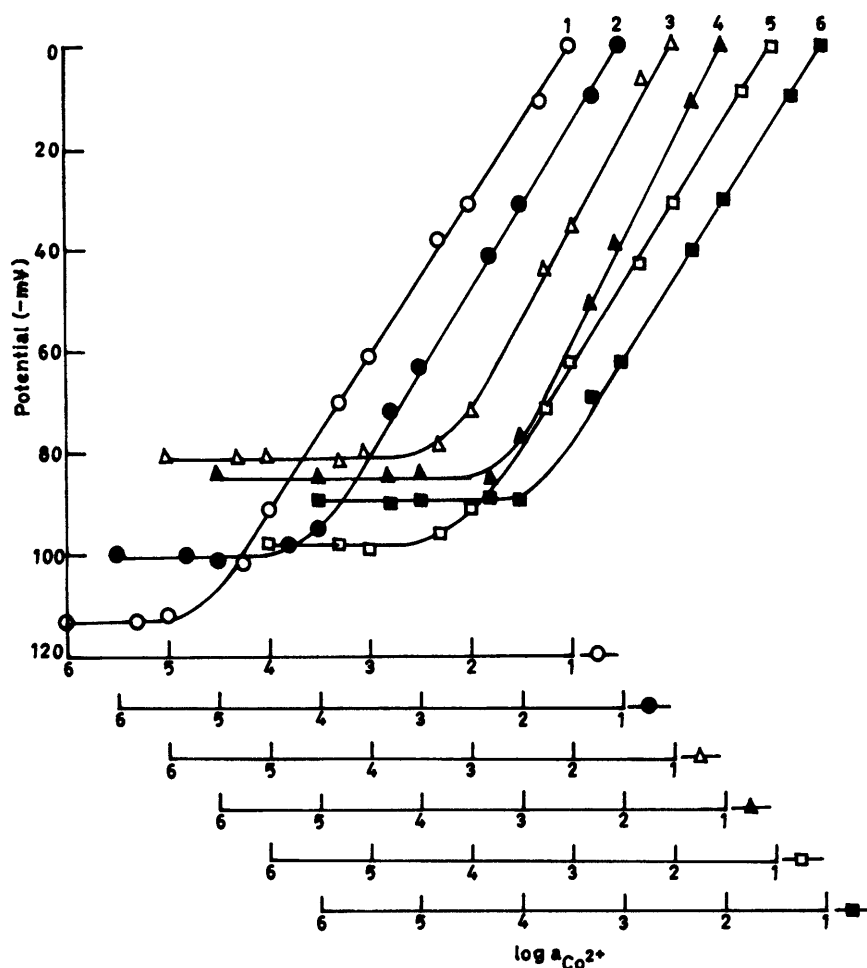


Fig. 1 Variation of membrane potential of PVC based membranes of (I) with varying concentration of Co^{2+} ions (1) without plasticizer, (2) with DOP, (3) with DBBP, (4) with TBP, (5) with DBP, and (6) with CN

Table II

Optimization of Membrane Ingredients and Response Characteristics of Cobalt Sensor (No. 1) Based on Them

Sensor/ Membrane No.	Composition of Membrane (w/w)			Working Concentration Range (M)	Slope (± 1.0 mV/ decade of activity)	Response time (s)
	(I)	NaTPB	PVC			
A	1.0	1.5	150	3.2×10^{-4} - 1.0×10^{-1}	30.6	~ 90
B	1.5	1.5	150	1.6×10^{-4} - 1.0×10^{-1}	30.5	50
C	2.0	1.5	150	7.8×10^{-4} - 1.0×10^{-1}	30.6	35
D	2.5	1.5	150	3.5×10^{-5} - 1.0×10^{-1}	30.5	20
E	3.0	1.5	150	1.9×10^{-5} - 1.0×10^{-1}	30.5	20
F	3.5	1.5	150	1.9×10^{-5} - 1.0×10^{-1}	30.5	20

generated by this membrane remained stable for more than 3 min after which it started deviating.

The lifetime of the electrodes was worked out by performing calibrations periodically with standard solutions and calculating the response, slope over the range of 1.0×10^{-6} - 1.0×10^{-1} M $\text{Co}(\text{NO}_3)_2$ solution. It was found that the electrode worked well over a period of

four months without observing any significant change in working concentration range. Whenever a drift in potential was observed, the membranes were reequilibrated with 0.5 M solution of Co^{2+} for 1 day. During usage it was dipped in 0.1 M Co^{2+} solution to avoid, drying, cracking and poisoning. Repeated monitoring of potentials (20 measurements) on the same

portion of the sample gave a standard deviation of ± 0.5 mV. The standard deviation of the slope was 0.8-1.0 mV, which shows good reproducibility.

pH and Solvent Effect

The pH response profile for the electrode was tested over the pH ranges 1.0-8.0 using 1.0×10^{-2} and 1.0×10^{-3} M Co^{2+} ions. The pH was adjusted by introducing small drops of hydrochloric acid (0.1M) and sodium hydroxide (0.1M). The influence of the pH response on the PVC membrane electrode is shown in Fig. 2. As seen, potentials remain constant from pH 1.9-5.8, beyond which a drift in potential was observed. The observed drift at higher pH values could be due to the formation of some hydroxy complexes of Co^{2+} in

solution. At low pH, the potentials decreased indicating that the membrane electrode responds to hydrogen ions.

The performance of the sensor system was also investigated in partially non-aqueous media using methanol-water, ethanol-water and acetone-water mixtures. The membrane does not show any appreciable change in working concentration range or slope in mixtures up to 15% (v/v) non-aqueous contents (Table III). Above this, developed potential showed an erratic behaviour.

Potentiometric Selectivity

The influence of interfering ions on the response behaviour of ion-selective membrane electrode is usually described in terms of selectivity coefficients,

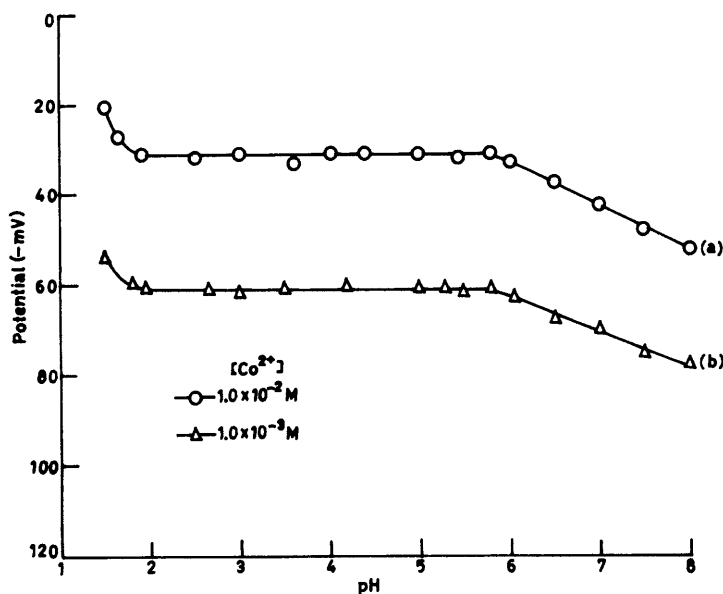


Fig. 2 Effect of pH on cell potential; $[Co^{2+}] = 1.0 \times 10^{-2} M$ (a) and $1.0 \times 10^{-3} M$ (b) for membrane No. 1

Table III
Performance of Co(II) Sensor (No. 1) in Non-Aqueous Media

Non-aqueous content (% v/v)	Slope (± 1.0 mV/decade of activity)	Working Concentration Range (M)
0	30.5	$1.9 \times 10^{-5} - 1.0 \times 10^{-1}$
Methanol		
10	30.5	$1.9 \times 10^{-5} - 1.0 \times 10^{-1}$
15	30.2	$2.0 \times 10^{-5} - 1.0 \times 10^{-1}$
20	25.2	$5.6 \times 10^{-5} - 1.0 \times 10^{-1}$
Ethanol		
10	30.6	$1.9 \times 10^{-5} - 1.0 \times 10^{-1}$
15	30.4	$2.1 \times 10^{-5} - 1.0 \times 10^{-1}$
20	24.6	$6.0 \times 10^{-5} - 1.0 \times 10^{-1}$
Acetone		
10	30.4	$1.9 \times 10^{-5} - 1.0 \times 10^{-1}$
15	30.2	$2.0 \times 10^{-5} - 1.0 \times 10^{-1}$
20	24.8	$5.9 \times 10^{-5} - 1.0 \times 10^{-1}$

$K_{A,B}^{Pot}$. The method based on Nicolsky-Eisenmann equation for the determination of potentiometric selectivity coefficient i.e., Fixed Interference Method, is the most commonly used method so far^{3, 21-23}. But the method shows some limitations in terms of values for ions of unequal charges, non-Nernstian behaviour of interfering ions, and activity dependence of values²⁴⁻²⁶. Thus in this work, the recommended Matched Potential Method^{24, 25, 27} was also used at 1.0×10^{-2} M concentration of interfering ions, which is independent of the Nicolsky-Eisenmann equation. According to this method²⁶, a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before by adding primary ions. The Matched Potential Method selectivity coefficients value is then given by the resulting primary ions to interfering ions activity (concentration) ratio, K_{AB}^{MPM} . As seen from the selectivity coefficient values in Table IV, the $K_{Co^{2+},B}^{Pot}$ values are in the order of 10^{-1} or smaller indicating that the electrode is moderately selective to Co^{2+} ions over a number of cations. However, Na^+ and Zn^{2+} may cause some interference as the values for these cations are

slightly higher but at low concentrations these would also not cause any interference, as selectivity is concentration dependent. To know the extent to which these ions may be tolerated, mixed run studied were carried out (Figs. 3 and 4). It can be seen from Fig. 3 that Na^+ at concentration $\leq 1.0 \times 10^{-5}$ M do not cause any deviation in the original plot obtained in pure Co^{2+} solution which depicts that the electrode can tolerate Na^+ at concentration $\leq 1.0 \times 10^{-5}$ M over the entire working concentration range. When present at higher concentrations, the electrode can be used over reduced concentration ranges. Fig. 3 shows that in the presence of 1.0×10^{-4} , 1.0×10^{-3} and 1.0×10^{-2} M Na^+ , the sensor

Table IV

Selectivity Coefficient ($K_{Ca^{2+},B}^{Pot}$) Values for Co(II)-Selective Sensor as Obtained by Modified Form of Fixed Interference and Matched Potential Method (Interfering Ion Concentration 1.0×10^{-2} M)

Interfering ion(B)	Selectivity Coefficient	
	Fixed Interference Method	Matched Potential Method
Li^+	2.8×10^{-2}	0.12
Na^+	3.9×10^{-1}	0.64
K^+	2.0×10^{-2}	0.15
Ti^+	3.5×10^{-2}	0.11
NH_4^+	3.2×10^{-2}	0.17
Ca^{2+}	3.5×10^{-2}	0.13
Mg^{2+}	2.5×10^{-2}	0.20
Cu^{2+}	2.0×10^{-2}	0.16
Zn^{2+}	2.8×10^{-1}	0.60
Pb^{2+}	2.2×10^{-2}	0.13
Ni^{2+}	3.5×10^{-2}	0.11
Sr^{2+}	3.5×10^{-2}	0.12
Be^{2+}	2.5×10^{-2}	0.18
Cd^{2+}	3.2×10^{-2}	0.17
Al^{3+}	3.5×10^{-2}	0.12
Cr^{3+}	3.5×10^{-2}	0.11
Fe^{3+}	2.5×10^{-2}	0.17

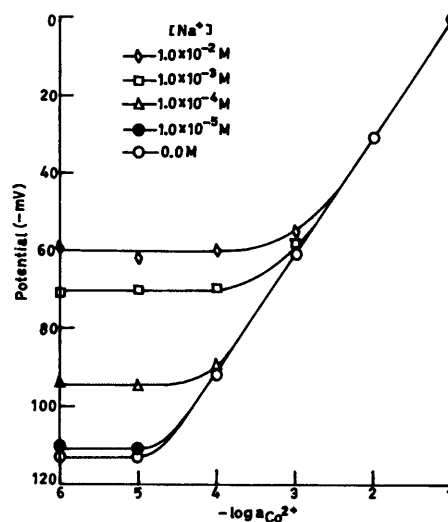


Fig. 3 Variation of cell potential with varying concentration of Co^{2+} at different concentration levels of Na^+ for Membrane No. 1

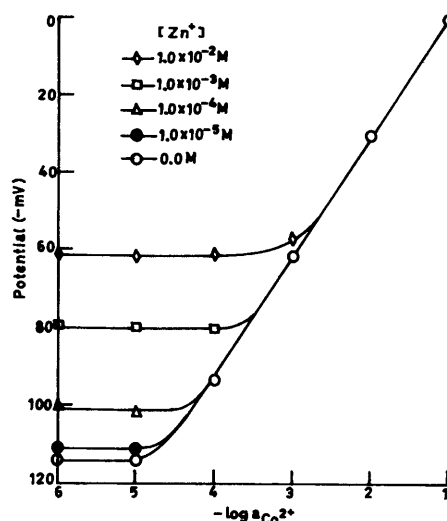


Fig. 4 Variation of cell potential with varying concentration of Co^{2+} at different concentration levels of Zn^{2+} for Membrane No. 1

assembly can be used to determine Co^{2+} in the reduced concentration ranges of $7.8 \times 10^{-5} - 1.0 \times 10^{-1}$, $5.1 \times 10^{-4} - 1.0 \times 10^{-1}$ and $1.1 \times 10^{-3} - 1.0 \times 10^{-1}$ M, respectively. Similarly Fig. 4 shows that Zn^{2+} can be tolerated over the entire concentration range when present at concentration $\pm 1.0 \times 10^{-5}$ M. Working concentration range reduces to $5.1 \times 10^{-5} - 1.0 \times 10^{-1}$, $2.5 \times 10^{-4} - 1.0 \times 10^{-1}$ and $9.6 \times 10^{-4} - 1.0 \times 10^{-1}$ M when Zn^{2+} is present at concentrations 1.0×10^{-4} , 1.0×10^{-3} and 1.0×10^{-2} M, respectively. It is pertinent to mention that the slope remained unaffected in both the cases.

Analytical Applications

a) Potentiometric Titration

The analytical applicability of the electrode was tested by using it as an indicator electrode to determine the end point in the potentiometric titration of Co^{2+} with EDTA. 10 ml of 1.0×10^{-3} M Co^{2+} solution was titrated against 1.0 ml of 1.0×10^{-2} M EDTA solution. The potential data are plotted against the volume of EDTA (Fig. 5). The curve is not a standard sigmoid shape,

which may be due to Na^+ interference as disodium salt of EDTA was used and has been observed earlier as well^{12,28-30}. However, the sharp break point corresponds to Co-EDTA stoichiometry, which shows that this sensor can be used for the determination of Co^{2+} potentiometrically.

b) Waste Analysis

Further, the practical utility of the sensor was tested by applying it for the estimation of Co^{2+} in a Eveready battery waste, collected from Eveready Industries Ltd., Lucknow (India). The waste was dissolved in distilled water by adding a few drops of 16 N nitric acid. It was then filtered and analyzed by AAS and ICP-AES. It was found that the waste contained various metals at different concentration besides Co^{2+} . The sensor for the sake of comparison (Table V) also determined the concentration of cobalt. It is clear from the values in Table V that these are in very good agreement with those obtained by ICP-AES and AAS. Hence the sensor can be successfully employed for the estimation of Co^{2+} in real samples.

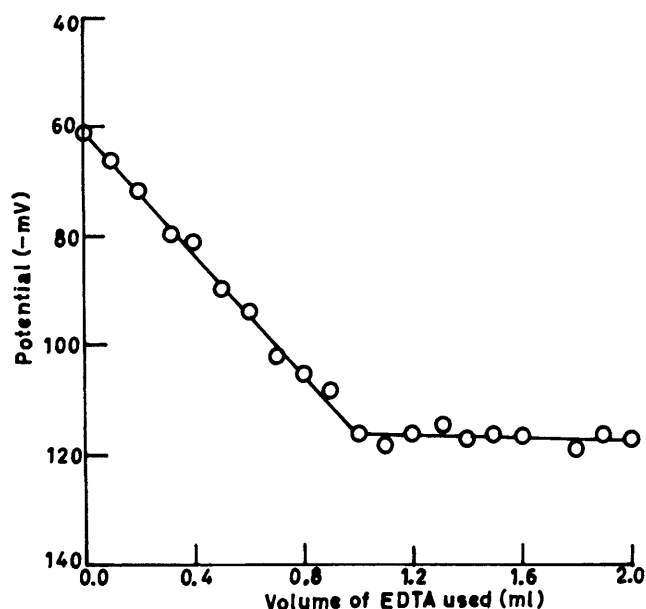


Fig. 5 Potentiometric titration of 10 mL of 1.0×10^{-3} M Co^{2+} with 1.0×10^{-2} M EDTA solution

Table V

Analytical Data for Eveready Battery Waste as Determined by ICP-AES, AAS and Cobalt Sensor (No. 1)

S. No.	Concentration of Co(II) as determined by ICP-AES (mg/L)	Concentration of Co(II) as determined by AAS (mg/L)	Concentration of Co(II) as determined by the proposed Sensor (mg/L)
1.	8.2	8.0	7.9
2.	10.5	10.2	10.3
3.	15.0	14.8	14.9

Conclusion

The membrane sensor with 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (TMOPP-Co) (I) as electroactive material and NaTPB as anion excluder in a PVC matrix in the ratio 2:1:100 is suitable for Co²⁺ estimation. It gives a Nernstian slope (30.5 ± 1.0 mV/decade of activity) over the pH range 1.9–5.8 and performs well in the concentration range 1.9×10⁻⁵–1.0×10⁻¹ M of Co²⁺. The response time of this sensor is 20s with a lifetime of about 4 months in aqueous as well as in non-aqueous medium. It can be

used to determine Co²⁺ in actual wastes as well as an indicator electrode in the potentiometric titration of Co²⁺. Further, after adjusting the pH, the sensor can be used for marine waters monitoring provided the Na⁺ concentration is within the permissible limit (≤ 1.0×10⁻⁵ M of Na⁺).

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