FABRICATION OF ION-SELECTIVE MEMBRANE FOR POTENTIOMETRIC ASSESSMENT OF COBALT ION

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Abstract: A newly synthesized PVC based cobalt ion selective electrode was fabricated using Schiff base ligand (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol as ionophore. The selectivity of the fabricated electrode for various ions was determined by fixed interference method. Various plasticizers were used as membrane components and membrane composition was optimized. The membrane electrode with the composition of BEHS: PVC: Ionophore: Anionic additive of 65%:32%:2%:1% (w/w) has a lower detection limit of 3.4×10^{-9} M in a linear concentration range of 2.0×10^{-8} M to 1.0×10^{-1} M with a Nernstian slope of 30.5 ± 1.0 mV/ decade of activity. The fabricated membrane electrode no.4 works satisfactorily in a pH range of 3.0–8.0 with a quick response time of < 8s.

Key words: **Cobalt, Selectivity, Ion-selective electrode.**

I. Introduction

Every aspect of living world is somehow dependent on various elements as nutrients in large to minute concentrations. The presence of these elements in excess quantities make them contaminants and causes adverse effects which may not be limited to one generation but may be passed to our successive generations. Consequently, various methods or techniques are being developed for the selective determinations of these elements as contaminants.

Cobalt is one of the essential micronutrient that is naturally found in various rocks, soil, water, animals and plant builds. In living organisms, it can occur both in organic and inorganic forms and is required at low concentrations, but significantly toxic at elevated concentrations [1].

It is an important precursor for vitamin B12 and can helps to treat disease like pernicious anemia and other certain infectious diseases. However, it may also pose severe threat to heart, thyroid, liver and kidneys if consumed in excess quantities. Considering the significant toxicity, extensive attention is required for the determination of Cobalt ion in a precise and rapid manner in various foodstuff, biological, environmental, and industrial samples.

Numerous techniques like induced coupled plasma mass spectroscopy (ICP-MS), gravimetric determination, atomic absorption spectroscopy (AAS), electro-chemiluminescence, cyclic voltammetry, spectrophotometry, and spectrofluorimetry isotopic dilution mass spectroscopy etc. have been successfully designed for the quantification assessment of various metal ions including cobalt. However, these techniques are either relatively costlier or time consuming comprising sample manipulations [2-4].

In last two decades, significant progress carried out on research based on potentiometric quantification assessment using ion selective chemical electrodes. These ion selective potentiometric electrodes offer several advantages over conventional sensing systems i.e. high sensitivity, ion selectivity and quick response time. These work safely in explosive environments and have excellent potential to thoroughly provide continuous quantitative and qualitative real-time analysis [5-7].

Literature survey revealed that limited research articles were reported by different group of workers on the fabrication and development of highly sensitive ion selective electrodes for determination of Cobalt in solutions. These earlier reported ion selective electrodes have been used for the detection of the Cobalt in narrow range of concentrations as detection of Cobalt at trace level is prime subject of scientific importance. The present study incorporates the synthesis, characterization and fabrication of cobalt ion-selective electrode based on (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol as an ionophore in PVC based membrane electrode. The fabricated ion selective electrode was successfully applied for quantification assessment of cobalt ions in real samples.

II. Experimental

2.1 Chemicals and Instruments

Chemicals that were used are for the synthesis of ionophore i.e. 3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde, *o*-amino phenol and high molecular weight PVC were obtained from Sigma-Aldrich, while chemicals Di-isobutyl phthalate (DBP), dioctylpthlate (DOP), Tris(ethylhexyl) phosphate (TEP), bis-(2-ethylhexylsebacate BEHS, sodium tetraphenyl borate (NaTPB) were purchased from SD-Fine Chem. Limited (Mumbai, India).

All other metal salts, acetone, absolute ethanol, and other chemicals were obtained from Fluka. No additional purification was made and all these chemicals or reagents were used as received. The stock solution of metal salts was prepared by dissolution of

estimated quantities of corresponding salts in double distilled water. Double distilled water was used throughout the investigation for making all sorts of aqueous solutions.

The 1H-NMR and 13C-NMR spectra were logged using deuterated chloroform (CDCl3) on a Bruker Avance 300 MHz spectrometer. The pH value determinations were recorded by using digital pH meter (Beckman Coulter PHI 450).

The FTIR spectrum of the ionophore was recorded by using Labtronics FTIR spectrometer in the range of 4000–350 cm^{-1}. The structure of ionophore was verified by 1H-NMR and 13C-NMR studies.

2.2 Synthesis of Ionophore: The ionophore (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol was prepared by the condensation reaction between 3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde with *o*-amino phenol. Equimolar quantities of 3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (0.01 mol) with *o*-amino phenol (0.01 mol) were dissolved in 30 ml of ethanol and the mixture was refluxed for 8 hrs under inert atmosphere of N_2 at 70-80ºC. The resultant product was poured over crushed ice and was filtered and washed with cold saturated solution of sodium bisulphate. The product was further recrystallized with ethanol and orange colour ionophore (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol was obtained [8].

The physical properties and analytical data of the ionophore is given below:

Empirical formula: $C_{22}H_{16}N_4O_3$, Molecular weight: 384.388 gmol^{-1}, yield: 86%, melting point: 141ºC.

¹H-NMR (ppm): 9.24 (s, 1H, Phenolic), 8.73 (s, 1H, azomethinic).

¹³C-NMR (ppm): (22 C); 195(C=N), 156.98(Phenolic C), 152.27, 150.92, 150.49, 139.08, 137.12, 130.11, 129.73, 129.36, 126.91, 126.64, 122.71, 121.82, 120.02, 119.91, 119.05, 118.53, 118.26, 115.53, 115.34, 114.31.

IR data- The IR spectrum of the free Schiff base ligand shows bands of intensity as: Schiff base free ligand: 3415-3425 v (OH), 1652–1659 v(C = N), 1044-1055 v (N - N) cm^{-1}.
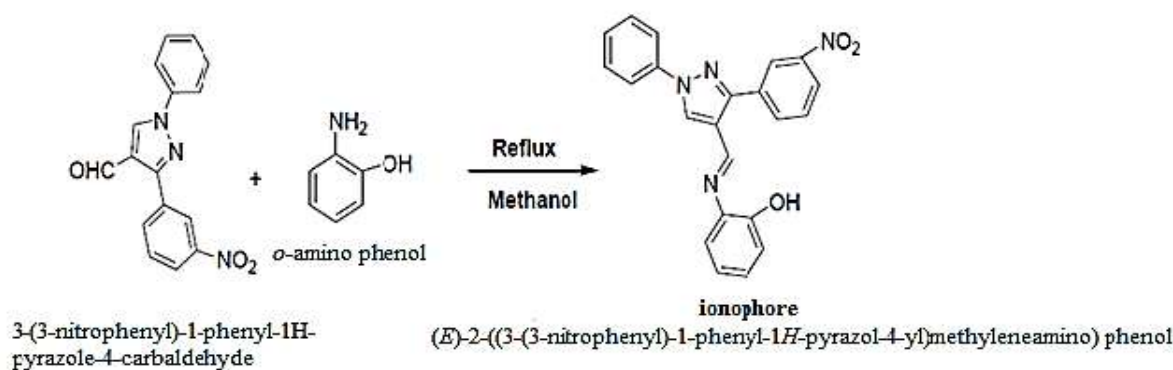

Fig. 1: Synthesis of Ionophore

2.3 Fabrication of the membrane

A PVC based ion selective membrane was fabricated using ionophore (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol and other membrane components were prepared as prescribed in the literature [9-10]. Various Plasticizers i.e. Di-isobutyl phthalate (DBP), dioctylpthlate (DOP), Tris(ethylhexyl) phosphate (TEP), bis-(2-ethylhexylsebacate (BEHS) in variable compositions (weight percentage) were used for the fabrication of different membranes. The fabricated membrane includes components such as high molecular weight PVC (31–34%), Plasticizers i.e. DBP, DOP, TEP and BEHS (61–65%), Anionic additive NaTPB (1–3%) and Ionophore (1–5%). All the components (w/w) were dissolved in 20 ml THF and the solution was shaken vigorously to remove the air bubbles. The viscous solution thus prepared was transferred into polyacrylate rings (25mm diameter). The solvent tetrahydrofuran (THF) was then allowed to evaporate at room temperature for about 20 hrs. The fabricated ion selective membrane of ~0.3 mm of width and 6 mm of diameter was detached from glass plate and joined to one end of a "Pyrex" glass tube with araldite. A silver electrode was then inserted in the tube to be used as a reference electrode.

2.4 Determination of formation constant

The Schiff base ligand (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol used as ionophore present in the fabricated PVC membrane selectively bonded the target metal ion in the solution. The formation constant (Kf) indicates the stability of ion-ionophore complexation kinetics. Since, the stability of ion-ionophore complex increases with increasing the K_f, formation constants for different metal ions with ionophore were determined to examine the stability of ion-ionophore complex using molar conductance ratio (equation 1 and 2) in acetonitrile solution at $25 \pm 1.0\ ^0C$. All measurements were carried out at constant ionic strength of solution.

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

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

Λ_M and Λ_{ML} represents the molar conductance of the metal ion and the molar conductance of the ion-ionophore complex respectively while and the molar conductance of the solution during titration and the analytical concentration of the ionophore are shown by Λ_{obs} and C_L respectively.

The formation constants (K_f) for ion-ionophore complex and the molar conductance of complex (Λ_{obs}) were determined by using a nonlinear least squares program KINFIT [11], and the results are tabularized in table 1.

Table 1: Formation constant of metal ions-ionophore (L)

Metal ions	Formation constants (log K_f) (L)	Metal ions	Formation constants (log K_f) (L)
Co^{2+}	3.9 ± 0.10	Pb^{2+}	2.7 ± 0.10
Ni^{2+}	3.4 ± 0.10	Zn^{2+}	2.5 ± 0.10
Cu^{2+}	3.5 ± 0.10	Ag^{+}	2.3 ± 0.10
Cd^{2+}	3.2 ± 0.10	Al^{3+}	1.9 ± 0.10
Hg^{2+}	2.8 ± 0.10	Sr^{2+}	1.6 ± 0.10
Mn^{2+}	3.1 ± 0.10	Ca^{2+}	1.3 ± 0.10
Fe^{3+}	2.7 ± 0.10	Na^{+}	0.3 ± 0.10

The greater value of formation constant (K_f) of Schiff base ionophore with Co^{2+} indicates that the ionophore (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol forms a most stable complex with Co^{2+} ion as compared to other metal cations. Thus the ionophore (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol can be used as potential carrier for the selective determination of Co^{2+} ion.

2.5 Conditioning of fabricated membrane and potential measurements

The conditioning of membrane is a significant and indispensable requirement of the fabricated membrane to be used as ion-selective electrode. This was carried out to avoid the long response time and to generate the reproducible potential. Thus all the fabricated membranes were conditioned by soaking them in corresponding metal salt solutions of different concentrations for different time periods.

2.6 Working principle:

Ion exchange equilibrium is developed at solution-membrane interface when membrane electrodes along with reference electrode are placed in the sample solution containing various metal ions. As a consequence of this charge transduction, a phase-boundary potential is established. The potential difference across the fabricated membrane is calculated by using following cell assembly:

Reference electrode	Internal reference solution	Polymeric ion-selective Membrane	Test solution of M⁺ ion	Second reference solution

Let the potential difference as E_{outer} and E_{inner} i.e. developed between the analyte side of the fabricated membrane and the reference side of the membrane respectively. Thus the potential difference i.e. developed between the electrodes (E_{meas}) is given as:

$$E_{meas} = E_{outer} - E_{inner} \quad \text{.... (1}$$

The potential developed across both side of the fabricated membrane is associated with the activity of metal ions (M⁺) as described by the Nernst equation as follows:

$$E_{outer} = E^0 - \frac{0.05916}{n} \log \frac{1}{a_{M^+(test)}} \quad ....(2$$

$$E_{inner} = E^0 - \frac{0.05916}{n} \log \frac{1}{a_{M^+(ref)}} \quad ....(3$$

Where, *n* is the charge on respective analyte (metal ion).

Since $a_{M^+(ref)}$ and E^0 both have constant value, so E_{inner} also become constant. Comprising equations 1, 2 and 3 we have,

$$E_{meas} = \text{constant} - \frac{0.05916}{n} \log \frac{1}{a_{M^+(test)}} \quad ....(4$$

The equation (4) thus obtained indicates that ion-selective electrodes should exhibit a Nernstian response in wide range of concentration [12-13].

III. Results and Discussion

3.1 Optimization of membrane composition

The response mechanism of the fabricated PVC based polymeric membrane is largely depends on the selective binding ability of the ionophore used along with the percentage composition of all membrane constituents. In order to develop the best possible

composition for the fabricated membrane, various compositions i.e. plasticizer (31-34%), PVC (61–65%), NaTPB (1.0–3.0%) and ionophore (1.0–5.0%) were prepared and their response characters were examined. It was observed that the fabricated membrane with composition i.e. Plasticizer: PVC: ionophore: NaTPB of 65%:32%:2%:1% (w/w) found to be most appropriate in various response characters like linear concentration range, response time, ion-selectivity and sensitivity. Hence, the fabricated ion selective membrane with the above optimized composition was selected as the most appropriate one and used for subsequent investigations. The data revealed in table 2 indicates that the fabricated membrane electrode no. 4 with composition BEHS: PVC: Ionophore: NaTPB of 65%:32%:2%:1% respectively has wide concentration range of $2.0 \times 10^{-8} – 1.0 \times 10^{-1}$ M with a slope 30.5 ± 1 mV/decay of activity. Thus the fabricated ionophore based membrane electrode no. 4 was used for the further investigations.

Table 2: Optimization of membrane composition of Co^{2+}-selective electrode

Electrode No.	Membrane Composition (%)				Linear working range (M)[a]	Slope (mV/dec. of activity)[a]	Response Time (sec)	Life time (months)
	PVC	Additive	Plasticizer	Ionophore				
1	32	3, NaTPB	0.00	5	$2.5 \times 10^{-5} - 1 \times 10^{-1}$	19.5 ± 1	28	-
2	31	2, NaTPB	65, BEHS	2	$3.1 \times 10^{-6} - 1 \times 10^{-1}$	28.3 ± 1	14	3
3	32	2, NaTPB	65, BEHS	1	$1.8 \times 10^{-7} - 1 \times 10^{-1}$	27.4 ± 1	~8	3
4	32	1, NaTPB	65, BEHS	2	$2.0 \times 10^{-8} - 1 \times 10^{-1}$	30.5 ± 1	~8	4
5	34	1, NaTPB	63, DOP	2	$4.1 \times 10^{-6} - 1 \times 10^{-1}$	26.6 ± 1	12	2
6	32	2, NaTPB	65, DOP	1	$2.5 \times 10^{-6} - 1 \times 10^{-1}$	30.8 ± 1	~9	1
7	33	3, NaTPB	62, DBP	2	$2.9 \times 10^{-6} - 1 \times 10^{-1}$	31.5 ± 1	15	3
8	32	2, NaTPB	65, DBP	1	$2.5 \times 10^{-7} - 1 \times 10^{-1}$	27.2 ± 1	15	2
9	34	2, NaTPB	61, TEP	3	$3.1 \times 10^{-6} - 1 \times 10^{-1}$	28.8 ± 1	20	2
10	32	2, NaTPB	65, TEP	1	$1.0 \times 10^{-6} - 1 \times 10^{-1}$	17.6 ± 1	12	-

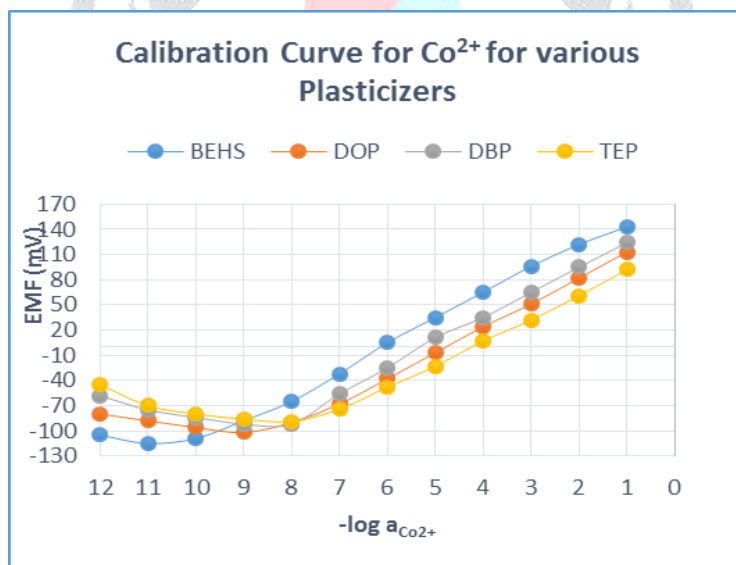[a] Mean value ± standard deviation (three measurements)

Fig. 2: Calibration curve for Co^{2+} with various Plasticizers

3.2. Effect of internal solution

Various response characters of the fabricated PVC based polymeric membrane electrode is based on the complexation and de-complexation kinetics at the ion selective membrane- solution interface. The target ion may possibly leach into the test solution as the concentration difference among test solution and internal solution increases resulting in an increase in the lower detection limit. Hence, the effect of concentration of internal solution on the working concentration range & lower detection limit was studied to evade this problem. The potential response of the ion-selective fabricated membrane electrode with an internal solution of 0.1 M $CoCl_2$ has a detection limit of 1.0×10^{-6} M in the concentration range of 2.0×10^{-6} M $– 1.0 \times 10^{-1}$ M of Co^{2+} ion, while 0.01 M solution of Cd^{2+} ion as internal solution has detection limit of 2.2×10^{-7} M. However, further decline in the concentration of Co^{2+} in internal solution does not have any substantial effect on the detection limit and linear concentration range of ion selective membrane electrode no.4. The concentration gradient is established by choosing an internal solution electrolyte to enhance the lower detection limit and linear concentration range of membrane electrode (*ISE*) no. 4. An ionic buffer was used to make the low activity of the target ion remains constant. Subsequently the effect of a new internal solution (5 mL 0.01 M $CoCl_2$

and 100 mL 0.01 M Na$_2$EDTA) solution over the linear concentration range and detection limit was observed and used for further studies. It was observed that the electrode no. 4 based on (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol as ionophore works effectively in the concentration range of 2.0 x 10^{-8} M to 1.0 x 10^{-1} M of Co^{2+} ion and has a lower detection limit of 3.4 x 10^{-9} M for Co^{2+} ion.

3.3. Effect of plasticizers and anionic additive

Plasticizers used as components for the fabrication of membrane plays a decisive role for developing response characteristics of ion-selective membrane electrodes by providing appropriate medium for the mobility of membrane components within the membrane phase. They behaves as solvent and considerably enhances the linear concentration range and detection limit of the fabricated membrane electrode. Consequently, variations in the potential response due to their presence, various membranes were fabricated with different plasticizers and their response characters were studied (fig. 2). The membrane fabricated without any plasticizer (electrode no. 1) displayed a narrow concentration range (2.5 x 10^{-5} M–1.0 x 10^{-1} M) with a slope of 19.5 ± 1.0 mV/ decay of activity and a response time of 28 seconds (table 2). The plasticizers DOP, DBP and TEP marginally improved the response characteristics of the membrane electrodes, while the addition of BEHS as plasticizer (Electrode no. 4) exhibited the best result. The ion-selective electrode no 4 have a Nernstian response (slope 30.5 ± 1.0 mV/ decade of activity) with linear concentration range of 2.0 x 10^{-8} M – 1.0 x 10^{-1} M with lower detection limit of 3.4 x 10^{-9} M of Co^{2+} ion and has fast response time of ~8 s.

The introduction of anionic additives provides the electro-neutrality to the ion-selective membrane as they acts as ion exchangers to extract significant number of counter ions into the membrane with the tested ion. NaTPB used as anionic additive reduces the ohmic resistance and also enhances the response behavior and selectivity of ion-selective electrode. Consequently, fabricated membrane is permeable towards ion with same charge and displays the Nernstian response. Potential responses of various PVC based membrane electrodes with ionophore (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol were analyzed. It was observed that the membrane with the ratio of ionophore / anionic additive ≈ 2 is quite appropriate for the suitable operation of membrane electrode and hence 1% NaTPB was used as an anionic additive in the fabrication of the membrane.

3.4. Selectivity coefficients

The ionophore used as electro-active material in the polymeric PVC membrane electrode may be reactive towards interfering ion (other cations) in the solution with Co^{2+} as primary ion.

Therefore the selectivity of the ionophore based electrode is a significant character of the ion-selective electrode which describes the selectivity of the membrane electrode towards Co^{2+} ion in occurrence of various interfering ions. In this current study the selectivity coefficient was determined by Fixed Interference Method (FIM) at 0.001 M concentration of interfering ions as recommended by IUPAC with modified Nicolsky equation (eq. 3).

$$K_{Co^{2+},M^{m+}}^{POT} = \frac{a_{Co^{2+}}}{a_{M^{m+}}^{z_{Co^{2+}}/z_{M^{n+}}}}$$

a$_{Co2+}$ represents the activity of the primary ion and $a_{M^{n+}}$ is the activity of interfering ion and Z$_{Co2+}$ and $z_{M^{n+}}$ are their respective charges. The result of selectivity coefficients are tabularized in table 3 [14-15].

Table 3: Selectivity constant of electrode no. 4

Metal ions	$\log K_{Co-M^{m+}}^{POT}$	Metal ions	$\log K_{Co-M^{m+}}^{POT}$
Ni^{2+}	3.9	Zn^{2+}	2.9
Cu^{2+}	3.8	Ag^{+}	2.7
Cd^{2+}	3.6	Al^{3+}	2.3
Hg^{2+}	3.1	Sr^{2+}	2.2
Mn^{2+}	3.5	Ca^{2+}	2.1
Fe^{3+}	3.1	K^{+}	1.6
Pb^{2+}	3.0	Na^{+}	1.2

3.5 Effect of pH

The potential response of the ion-selective membrane electrode may be affected by the pH of the test solution as of competition kinetics with ionophore. Consequently, the effect of pH on the potential response of the ion-selective membrane electrode no. 4 was evaluated for 1.0 x 10^{-2}, 1.0 x 10^{-3} and 1.0 x 10^{-4} M Co^{2+} ion. It was observed that the potential response of the electrode 4 in the pH range from 3.0-8.0 remains constant. This indicates that the recommended fabricated electrode can be effectively used for the direct determination of Co^{2+} ion in the pH range of 3.0-8.0. The adjustment to the pH of the test solution was made by the drop-wise addition of HNO$_3$ (0.1M) and / or NaOH (0.1M) solution. Figure 3 represents the variation of potential response with the change in the pH of the solution. It was observed that a significant drift occurs in the potential response beyond pH range of 3.0-8.0. This may be due to the competition kinetics of proton and ionophore at low pH, while development of hydroxyl complex of Co^{2+} ion in strong basic medium.
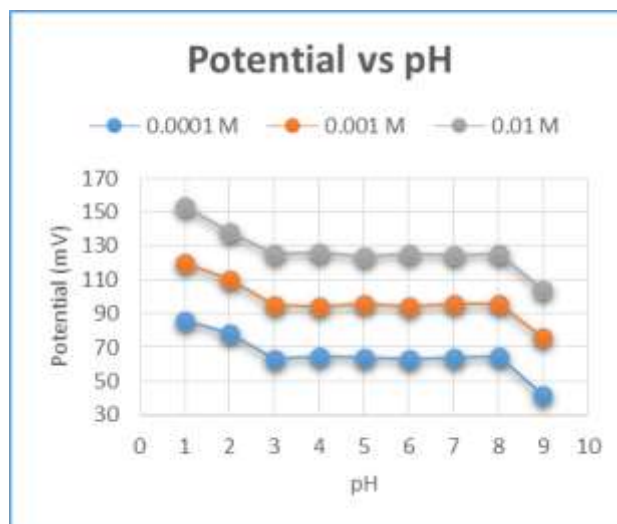
Fig. 3: Graphical representation of Potential response vs pH

3.6. Response time and Life time

Response time of membrane electrode no 4 can be described as the average time taken by the electrode to reach the equilibrium. The present work includes the study of response time that was determined using static potential after consecutive immersion of a series of Co^{2+} metal ions each with tenfold variation in concentration. Reversibility of the electrode was also assessed in terms of response time by performing experiments from lower concentration 1.0×10^{-10} M to higher concentration 1.0×10^{-1} M of Co^{2+} ion and vice versa. It was observed that the fabricated ion-selective membrane electrode no 4 produces the static potential in a quick time (~8 s). The average response time in above experiments observed to be similar which specifies that the membrane electrode no. 4 is highly reversible in the wide concentration range. The performance of the membranes degrades with time as the components present in the fabricated PVC based membrane electrodes leached into the solution. Hence, the stability of the ise-membrane electrode was determined as a function of time. The slope of calibration curve and detection limit of ise-membrane electrode observed to be similar with a result of 95% reproducibility for a time period of 4 months. However a significant change was observed in the slope of calibration curve and detection limit after 4 months. During this time period ise-membrane electrode was used at least 1hr /day and was stored in 0.001 M $Co(NO_3)_2$ solution while not in use (table 4).

Table 4: Lifetime of Co^{2+} selective membrane electrode no.4

S. No.	Months	Slope (mV/decade)	Working concentration range (M)	Detection Limit (M)
1	First	30.5 ± 1	$2.1 \times 10^{-8} - 1.0 \times 10^{-1}$	3.4×10^{-9}
2	Second	30.5 ± 1	$2.1 \times 10^{-8} - 1.0 \times 10^{-1}$	3.4×10^{-9}
3	third	29.0 ± 1	$2.7 \times 10^{-8} - 1.0 \times 10^{-1}$	4.6×10^{-9}
4	Forth	27.5 ± 1	$3.2 \times 10^{-7} - 1.0 \times 10^{-1}$	6.7×10^{-8}

IV. Analytical Applications

The fabricated electrode was successfully used for the analysis of Cobalt in various beer samples. Potentiometric determination of cobalt was carried out in different samples of beer using the direct potentiometric method and AAS. The obtained results from the recommended fabricated cobalt ion selective electrode with those obtained by AAS along with *t* test are tabularized in table 5 [16]. It shows that the results produced are within the 95% confidence level.

Table 5: Determination of Co^{2+} in different samples using electrode no. 4

Beer samples	Co^{2+}-ISE (mol /L)[a]	AAS (mol /L)[a]	t test[b]
1	2.57×10^{-6}	2.3×10^{-6}	2.45
2	2.86×10^{-6}	2.5×10^{-6}	2.59
3	3.36×10^{-6}	2.9×10^{-6}	2.96
4	2.61×10^{-6}	2.2×10^{-6}	2.42

[a] Mean value $\pm$ standard deviation (three measurements)

V. Conclusion

A Schiff base (*E*)-2-((3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methyleneamino) phenol have been used as an electroactive material for the selective determination of Co^{2+} by PVC based ion selective membrane electrode. Various plasticizers were used as membrane components and membrane composition was optimized. The membrane electrode with the composition of BEHS: PVC: Ionophore: Anionic additive of 65%:32%:2%:1% (w/w) has a lower detection limit of 3.4×10^{-9} M in a linear concentration

range of 2.0×10^{-8} M to 1.0×10^{-1} M with a Nernstian slope of 30.5 ± 1.0 mV/ decade of activity. The fabricated membrane electrode no.4 works satisfactorily in a pH range of 3.0–8.0 with a fast response time of < 8s. The fabricated electrode no 4 is successfully applied for the potentiometric assessment of cobalt content in various beer samples.

VI. References

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