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PVC membrane sensors for Cobalt based on cobalt (II) - 4- Formyl azohydrazoaniline antipyrine

Salem M Hamza[1], Nashwa MH Rizk[2] and Moushira M Salem[1]*
[1]Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-koum, Egypt
[2]Genetic Engineering and Biotechnology Research Institute, Menoufia University, Sadat city, Egypt, Box-79

A cobalt (II) ion-selective membrane sensor has been fabricated in a poly vinyl chloride matrix based on a recently synthesized cobalt (II) complex of 4-formylazohydrazoaniline antipyrine (Co-HL). The electrode worked well over wide concentration range (1.0×10^{-6} –1.0×10^{-2} M) between pH 4.5 and 8.5. The response time of the sensor is about 10 s and the limit of detection (LOD) of 6.3×10^{-7} M. the can be used over a period of two months without any divergence in potential. The proposed membrane sensor revealed good selectivity for Co^{2+} over a wide variety of other metal ions. The electrode has been used as an indicator electrode in potentiometric titration of Co^{2+} with EDTA and direct determination of Co^{2+} in tap water.

Keywords: Cobalt (II) ions, Ion-selective electrode, cobalt (II) complex of 4-formylazohydrazoaniline antipyrine, PVC membrane, Potentiometry.

INTRODUCTION

Cobalt is a hard, lustrous, silver-gray metal which is found in various ores, and is used in the preparation of magnetic, wear-resistant, and high-strength alloys. Its compounds are used in the production of inks, paints, and varnishes. It is frequently associated with nickel, copper, or iron, an important example is alnico; it is an essential alloying element in high temperature super alloys used for casting airfoils and structural parts in jet turbine engines. Cobalt-60 an artificially produced radioactive isotope of cobalt is which used in medicine as it produces gamma rays. These are used in radiotherapy (radioactive tracer and cancer-treatment agent), sterilizing medical supplies and waste, sterilizing food and measuring the density of an object. Some of its applications are: Making of super alloys, for parts in gas turbine aircraft engines, Corrosion- and wear-resistant alloys, high speed steels, Cemented carbides (also called hard metals) and diamond tools, Magnets and magnetic recording media, Alnico magnets, Catalysts for the petroleum and chemical industries, electroplating because of its appearance, hardness, and resistance to oxidation, Drying agents for paints, varnishes, and inks, ground coats for porcelain enamels, pigments, Battery electrodes. Having 0.13 to 0.30 mg/kg of cobalt in soils markedly improves the hearth of grazing animals. Mammals require small amounts of cobalt salts, it is a central component of the vitamin B-12, and Cobalt is an important nutritional element and a metallic component of thiamine. It can be either essential or toxic for many living beings, including humans. Toxic intake is 500 mg, and the total mass of the element in an average (70 kg) person is 1.5 mg [1]. Cobalt deficiency may lead to retarded growth, anemia and loss of appetite [2]. Therefore, it is clear that determination of trace amounts of Cobalt in biological and environmental samples plays an important role. Several methods for the determination of cobalt have been reported, which mainly focused on spectrophotometry [3–6], flow-injection [7, 8], liquid chromatography [9,10], capillary electrophoresis(CE) [11], atomic absorption spectrometry (AAS) [12–14], inductively coupled plasma- atomic emission spectrometry (ICP-AES) [15,16], inductively coupled plasma-optical emission spectrometry (ICP-OES) [17–19] and inductively coupled plasma-mass spectrometry (ICP-MS) [20, 21], solid phase extraction and determination [22], In addition, Korolczuk [23], Filichkina [24], Uchiyama [25], and Jiang [26] reported voltammetry, laser thermal lens spectrometry, photo acoustics and X-ray fluorescence spectrometry, respectively. These methods are characterized by good accuracy but they require time-consuming sample preparation and are relatively expensive. Therefore, new methods are being developed, including potentiometric methods with ion selective electrodes (ISEs). Potentiometry with ISE offers advantages such as selectivity, sensitivity, good precision, simplicity, low cost and short time of analysis. Recently, several greatly selective and sensitive PVC-membrane ion-selective electrodes for cobalt ion have been reported [27-36]. In this work we are going to introduce a simplest and sensitive sensor for potentiometric determination of cobalt (II).

MATERIALS AND METHODS

Reagents and chemicals: All chemicals were of analytical reagent grade and bi-distilled water was used throughout. Poly (vinyl chloride) powder (PVC) powder of molecular weight ca. 10000 was obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). Tetrahydrofuran (THF) with a purity of 99%, inhibited by 0.025% butylatedhydroxytoluene was obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). Dioctylsebacate (DOS) plasticizer with a purity of ca. 99 % was obtained from Aldrich Chem. Co (Milwaukee, WI, USA). Dioctylphthalate (DOP) plasticizer with purity of ca. 99 % was obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). The salts of all the cations used were of analytical grade and used without any further purification. Double distilled water was used for the preparation of metal salts solutions of different concentrations. $CoCl_2$ (1.0×10^{-7}–1.0×10^{-2} M) standard solutions were prepared by appropriate dilution of the stock $CoCl_2$ solution with 0.05 M phosphate buffer solution of pH 7. The following cations and compound solutions were prepared and standardized using the standard methods. Dilute solutions (1.0×10^{-2} –1.0×10^{-7}M) of these cations and compounds were prepared by10-fold dilution of the stock solutions. Sodium tetraphenylborate (NaTPB) as an additive

Corresponding Author:
Moushira M. Salem, Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-koum, Egypt
Email: moushira_salem@yahoo.com
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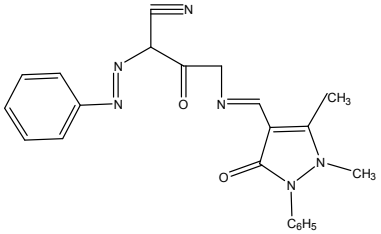
and it is effect of response of ion selective electrode membrane.

Apparatus: All potentiometric measurements were made at 25 ± 1°C with an Orion (model 720) pH/mV meter. Double junction Ag/AgCl reference electrode was used. An Orion electrode (model 90-02) filled with 10% (w/v) potassium chloride was used in the outer compartment. Combination glass (Ross pH) electrode (Orion model 81-02) was used for all pH measurements.

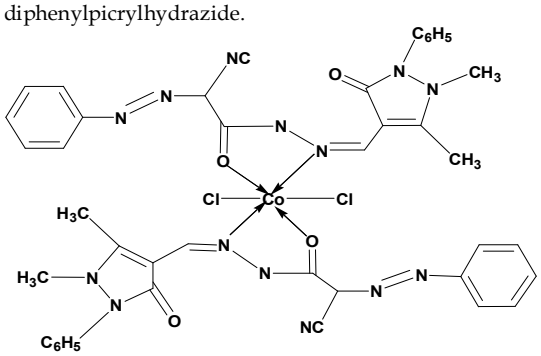
Synthesis of the ionosphere: The ionophere (Co-HL) was synthesized as previously described **[37].**

Synthesis of the legand (HL): 4-formylazohydrazoaniline antipyrine was prepared by coupling the diazonium salt of aniline with 4-formylcyanoacetohydrazid antipyrine in sodium hydroxide solution. The product was recylstallized several times from several times from ethanol Scheme 1.



(Scheme 1): Chemical structure of ligand (HL)

Synthesis of Co-HL: The cobalt complex Scheme 2 was prepared by stirring magnetically at *ca.*60°C the solution of 0.002 moles of $CoCl_2$ with 0.002, 0.004 or 0.001moles of 4-formylazohydrazoaniline antipyrine (HL) in ca. 50 ml ETOH for period of 6 h or more. The resulting solids were filtered off, washed several times with ETOH and dried under vacuum over P_4O_{10}. Elemental analysis (C, H, Cl) were preformed by the micro analytical unite of the university of Cairo. Metal analysis was carried out by standard methods. IR spectra were preformed as KBR discs; using aperkin-Elmer1430 recording spectrometer. H^1NMR spectrum was recorded in d^6-DMSO using a 300MHZ Varian NMR spectrometer. The electronic spectra were carried out in N, N-dimethylformamide (DMF) solution using a Perkin-Elmer lambda 4B spectrophotometer. The molar conductivity measurements were made in DMF solutions (10^{-3} M) using a Tacussel conductometer type CD6N. Magnetic susceptibilities were measured at 27°C by the modified Gouy method, the magnetic moments were calculated, and ESR spectra were recorded with a Varian E104 spectrometer and calibrated with diphenylpicrylhydrazide.



(Scheme 2): Chemical structure of Cobalt (II) complex (Co-HL)

Electrode preparation: The PVC master membranes were sectioned with a cork pore (10 mm diameter and glued to a poly ethylene tube 2 cm length, 8 mm diameter) by using THF. A homemade electrode body was used, which consisted of a poly ethylene, glass tube 8 cm length, 6 mm diameter, to which the polyethylene. Tubing was attached to one end and filled with the internal reference solution (1:1), (10^{-2} M aqueous $CoCl_2$ to 10^{-2} M KCl). An Ag/AgCl internal reference wire electrode (about1.0 mm diameter) was immersed in the internal solution. The electrode were conditioned by soaking in 10^{-2} M $CoCl_2$ solution for 9 h and stored in the same solution when not use.

Equilibration of membranes and potential: The membranes were equilibrated for three days in 1.0 M $CoCl_2$ solution. The potentials were measured by varying the concentration of $CoCl_2$ in the test solution in the range (1.0×10^{-7}–1.0×10^{-2} M). Standard $CoCl_2$. The solution prepared by 10-fold dilution of the stock solutions with 0.05 M phosphate buffer solution pH 7.

Table.1: Optimization of membrane ingredients and membrane performance.

No electrode	Membrane composition, mg					Measuring range, mol L^{-} (M)	Slope, mV/decade.
	DOP	DOS	PVC	NaTPB	Ionphore		
1	0.66	—	0.33	0.005	0.005	1.0×10^{-6}–1.0×10^{-2}	29±0.5
2	—	0.66	0.33	0.005	0.005	1.0×10^{-6}–1.0×10^{-2}	32±0.5
3	—	0.68	0.31	—	0.01	1.0×10^{-6}–1.0×10^{-4}	22±0.5
4	0.68	—	0.31	—	0.01	1.0×10^{-6}–1.0×10^{-4}	24±0.5

RESULTS AND DISCUSSION

The Co-PVC membrane sensor was calibrated by immersion in conjunction with the reference electrode in a solution of 10mL of phosphate in conjunction with the reference electrode in a solution of 10^{-2} ml of phosphate buffer of pH 7 in a 50ml beaker. After the addition of 1.0 mL aliquot of (1.0×10^{-7} – 1.0×10^{-2}) M $CoCl_2$ solution with continuous stirring, the potential was recorded after stabilization to ±0.2 and the EMF was plotted as a function of $CoCl_2$ Concentration. The resulting calibration graph Figure 1 was used for subsequent determination of unknown concentrations. Alternatively, the potentials displayed by $CoCl_2$ test solution before and after the addition of a 1.0 ml aliquot of known concentration of $CoCl_2$ were measured. The change in the potential readings was recorded and used to calculate the unknown $CoCl_2$ concentration in the test solution using the standard addition technique. The potential response of all membrane sensors was determined in cobalt chloride solutions of the concentration (1.0×10^{-7}–1.0×10^{-2} M) $molL^{-1}$. The working concentration range and the slope of characteristics are listed in Table 1 from the analysis of Figure 1 and Table 1 the response of the sensors is strongly dependent on the plasticizer used for membrane preparation. There are differences in E^0 values obtained for particular electrodes. The term E^0 incorporates all potential contributions of the measuring cell that are constant for this measurement and is unique for each membrane composition. The response of polymeric membrane electrode is connected from thermodynamic

constants such as the free enthalpies of transfer of the uncomplexed ions from the sample into the membrane and, in the case of ionophore based system, the complex formation constant of ion-ionophore complex in the membrane. These thermodynamic parameters are dependent on the membrane composition, especially on the membrane solvent. The optimal composition of memberane phase is composed of electrode no.1 containing (DOP) as plasticizer. The characteristic slope of this electrode is 29±0.5 mV/decade the limit of detection is 6.3×10^{-7} M, and the linearity range is $1.0 \times 10^{-6} – 1.0 \times 10^{-2}$ M.

Selectivity: Selectivity of a membrane ion-selective electrode is its response to the primary ion in the presence of other ions. This is an important characteristic of a sensor and determines the extent to which a sensor can be employed in the analysis of real samples. In this work, the selectivity coefficient of the sensors toward different cationic species (M^{n+}) was evaluated by using the matched potential method (MPM). This is a recently recommended method by IUPAC [38, 39] which gets ride of the limitation of the corresponding methods based on Nicolsky-Eisenman equation for the determination of potentiometric selectivity coefficients. As per Nicolsky-Eisenman formalism, the electrode response is given by the following simplified Nernst equation

$$E = E^0 + \frac{RT}{Z_I F}\ln(a_i)$$

Where a_i is the primary ion activity in pure solution, however, in presence of interfering ion Nernst equation is modified as follows

$$E = E^0 + \frac{RT}{Z_I F}\ln\left(a_i + K_{i,j}^{pot}\left(a_j\right)^{Z_i/Z_j}\right)$$

Where (a_j) is the activity of interfering and (Z_i) and (Z_j) are the charges on the primary and interfering ion. As per IUPAC recommended match potential method (MPM) selectivity is given by

$$K_{i,j}^{pot} = \frac{a_A^{'} - a_A}{a_B}$$

In this method, at first a known activity (a'_A) of the primary ion solution is added to a reference solution that contains fixed activity (a_A) of primary ion and the potential change is recorded. Secondly, a solution of interfering ions is added to the primary ion solution until the same potential change is observed. In the present studies a_A (1.0×10^{-3} M Co^{2+}), (a'_A) (1.0×10^{-2}M Co^{2+}) and a_B (1.0×10^{-2}M interfering ion) were taken to measure the selectivity coefficients. A number of mono-, di- and trivalent cations have been tested. It is evident the selectivity coefficient data that the sensor exhibit high preference for cobalt (II) ion compared with alkali, alkaline earth, transition and heavy metal ions. The selectivity studies were carried out only for sensors, which exhibited the best performance characteristics in terms of working concentration range, slope, response time and life time. The results indicated that, both the electrodes are substantially selective to Co^{2+} ions over all the interfering ions. The results can be observed from Table 2 no significant interference is caused by the examined ions.

Table 2. Selectivity coefficient values $(K_{Co(II),B}^{pot})$ of various interfering ions at 1.0×10^{-2} M with membrane no .1(with DOP).

Interferent (B)	Selectivity coefficient $(K_{Co(II),B}^{pot})$
Cu^{2+}	5.53×10^{-3}
Ni^{2+}	3.64×10^{-3}
Ca^{2+}	8.40×10^{-3}
Pb^{2+}	1.29×10^{-3}
Hg^{2+}	8.1×10^{-2}
Cd^{2+}	3.15×10^{-3}
Pb^{2+}	5.08×10^{-3}
Ag^{2+}	5.16×10^{-3}
K^{+}	2.74×10^{-4}
$NH4^{+}$	1.66×10^{-4}
Na^{+}	6.33×10^{-4}
Fe^{2+}	7.14×10^{-3}
Mg^{2+}	5.81×10^{-3}
Ba^{2+}	6.84×10^{-3}
Sr^{2+}	7.32×10^{-3}
Mn^{2+}	5.36×10^{-3}
Zn^{2+}	9.30×10^{-2}

Effect of pH: The pH response profile for the electrode using (HL) was also examined at two Co^{2+} concentrations Figure 3(a, b) pH adjustments in solutions were made with dilute hydrochloric acid or sodium hydroxide solutions. The pH dependence of the electrode potential was listed over the range of 2–11 for a 1.0×10^{-3} and 1.0×10^{-4} M Co^{2+} ions that the useful range is 4.5–8.5 because the potential remain constant in this range.

Effect of internal solution concentration: The influence of concentration of the internal solution on the potential response of the membrane electrode was also studied, it was found that the variation of concentration of the internal solution corresponding to significant change in the intercept of the resulting Nernstian plots in range (1.0×10^{-4}–1.0×10^{-6} M). A1.0 $\times10^{-2}$ M concentration of the reference solution is quite proper functioning of the electrode system Figure 4 (a, b).

Life time and long term stability: The sensor prepared could be used for at least 2 months without any measurable divergence. During this period, the sensor was in use over an extended period of time (at least 2h per day). After two months, the observed drift in the slope of the resulting Nernstian potentiometric response was at the most 0.5 mV/ decades. The static response time of the membrane sensor thus obtained was 5–10 s for concentrations ≥1.0×10^{-3} M and <15 s for concentration of ≥1.0×10^{-6} M the dynamic response of sensor no.1 in Table 3.

Table.3: Effect of life-time on the properties of proposed electrode no.1 (with DOP)

Life times, days	Slope mV\decade	Measuring range Mol L^{-1}
Fresh	29.0±0.5	1.0×10^{-6}– 1.0×10^{-2}
10	29.0±0.5	1.0×10^{-6}– 1.0×10^{-2}
20	29.0±0.5	1.0×10^{-6}– 1.0×10^{-2}
30	28.5±0.5	1.5×10^{-6}– 1.0×10^{-2}
40	28.1±0.5	2.0×10^{-6}– 1.0×10^{-2}
50	27.5±0.5	4.0×10^{-6}– 1.0×10^{-2}
60	27.0±0.5	5.5×10^{-5}– 1.0×10^{-2}

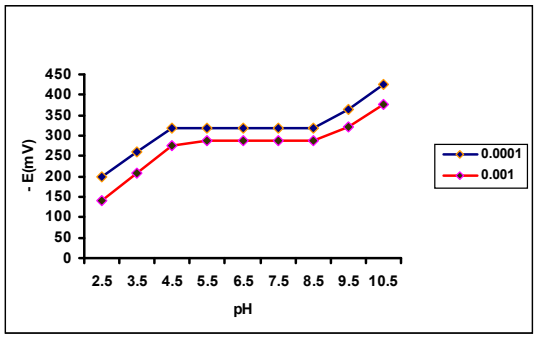


Figure 3(a). Effect of pH on the potential for electrode (no. 1) which has DOP as plasticizer at 1.0×10^{-3}, 1.0×10^{-4}M.

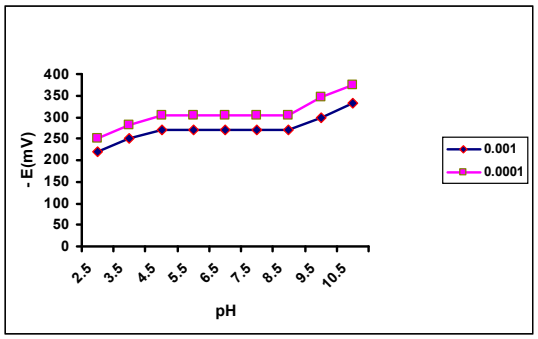


Figure 3(b). Effect of PH on the potential of electrode (no. 2) which has DOS as plasticizer at 1.0×10^{-3}, 1.0×10^{-4}M.

Analytical application of electrode: The analytical application of the sensor no.1with (DOP) as plasticizer was tested, and so it was used as an indicator electrode to determine the endpoint in the potentiometric titration of Co^{2+} with EDTA. 10 mL of a 1.0×10^{-3} M Co^{2+} solution was titrated against a 1.0×10^{-2} EDTA solution at pH 6.0.The plot obtained Figure 5 is of sigmoid shape, the sharp inflexion point observed corresponds to the stoichiometry of the Co (II)-EDTA complex. Thus, Co^{2+} can be successfully determined potentiometrically by using this sensor. The electrode was also successfully applied to the direct determination of cobalt in tap water samples. Four samples were prepared and determined with the proposed electrode (no1) and atomic absorption spectrometry (AAS) are summarized in Table 4 as it is seen, the electrode resulted in acceptable recoveries of copper ion, which are also in satisfactory agreement with those obtained by AAS.

Table 4: Determination of cobalt spiked in tap water using electrode no.1 (with DOP).

No	Cobalt added (M)	Cobalt found(M)	
		ISE*	AAS*
1	1.7×10−3	1.6×10−3	1.65×10−3
2	2.8×10−3	2.7×10−3	2.75×10−3
3	3.7×10−3	3.63×10−3	3.65×10−3
4	4.4×10−3	4.3×10−3	4.4×10−3

*Results are based on three measurements.

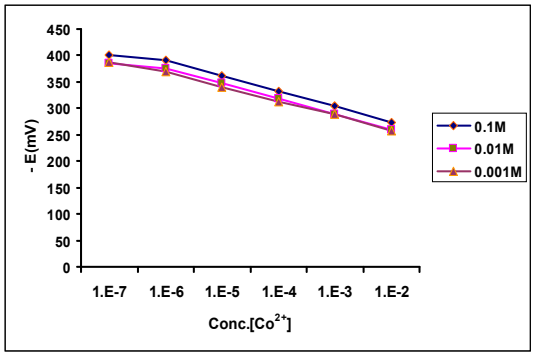


Figure 4(a). The effects of internal reference solution concentration on the electrode (no.1) response.

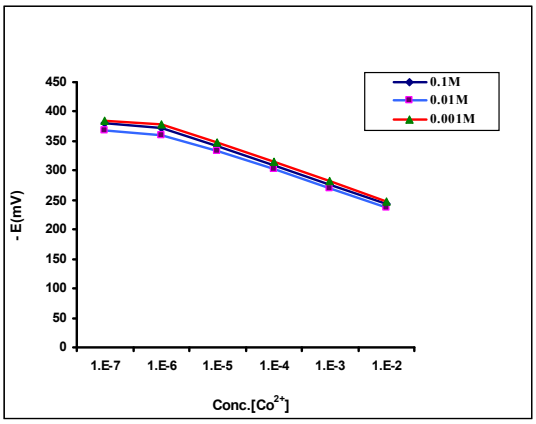


Figure 4(b). The effects of internal reference solution concentration on electrode (no.2) response.

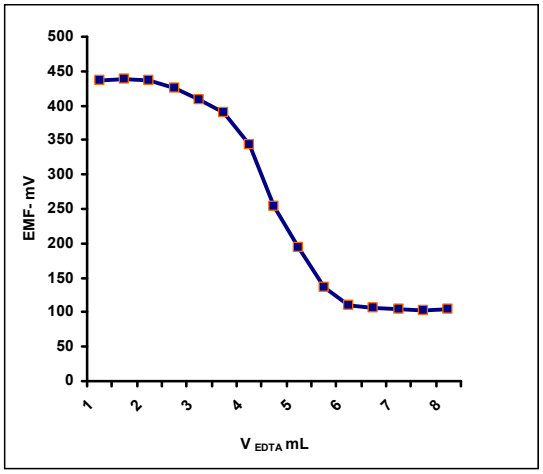


Figure 5. Potentiometric titration plots of 1.0×10^{-3} M Co^{2+} solution with 1.0×10^{-2} EDTA using sensor no.1 (with DOP).

CONCLUSIONS

A cobalt-selective PVC membrane electrode was prepared with (cobalt (II) - 4 -formalhyrazoaniline Antipyrine) a carrier, and different plasticizers (DOP, DOS). The membrane with the DOP plasticizer bearing the composition (w/w) of 33:0.005: 66.0: 0.055 (PVC: ionophore: DOP: NaTPB) gives the best performance, showing the best response characteristics

with Nernstian behavior over the concentration range of 1.0×10^{-6}–1.0×10^{-2} M Co^{2+}, with very low interference from common alkali, alkaline earth, transition and heavy metal ions and a fast response time of 5–10 s, and the limit of detection 6.3×10^{-7} M. The proposed sensor potential responses are independent of pH in the range 4.5-8.5. The constructed Co (II) - PVC membrane sensor was successfully applied as indicator electrode in titration of cobalt ion with EDTA. The electrode was also successfully applied to the direct determination of cobalt in tap water samples.

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