Cobalt(ii)-selective potentiometric electrode based on salen-base chelate

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Abstract

A poly (vinyl chloride) based membrane using N-(2-Hydroxybenzylidene)-N'-(2-picolyl) ethylenediamine Cobalt (II)as an ionophore(**I**) has been developed and explored as selective potentiometric electrode for Co (II). Various membranes have been prepared with and without plasticizer viz., tris(2-ethylhexyl) phosphate (TEHP), tri-n-butylphosphate (TBP), di-octylphthalate (DOP), chloronapthalene (CN) and anion excluder, sodiumtetraphenylborate (NaTPB) were studied in detail. The best performance was observed for the membrane electrode having a composition of I:PVC:NaTPB:CN as 3:140:2:80 (w/w, mg). The electrode exhibits Nernstian response over a wide concentration range of 7.9×10^{-6} to 1.0×10^{-1} M with a slope of 30.0 mV per decade of concentration between pH range 3.0-9.0. The slope and working concentration range of membrane electrode remain constant in a partially non-aqueous medium having up to 25% (v/v) of methanol and ethanol water mixtures. The response time of the electrode is about 12 sec and can be used for a period of up to ~3 month without any drift in potential. The electrode revealed good selectivity over a range of cations including alkali, alkaline earth, heavy and transition metal ions. This electrode was successfully applied for the determination of cobalt ion in various samples and could also be used as indicator electrode in potentiometric titration.

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Introduction

Cobalt is a natural and essential element for plants, animals and human body having relatively high concentration in liver, bone and kidney [Singh, *et al*. (2009)]. It plays an important role in the metabolism of iron and synthesis of hemoglobin. In the field of industrial chemistry, cobalt is widely used in the paint and varnish industries, in ink as drying agent, in the preparation of pigments like cobalt blue and cobalt green in ground coats for porcelain enamels, in lithium ion battery electrodes and in electroplating industry. Cobalt has both a beneficial and

harmful effects on human health. It is beneficial in the form of vitamin B12 which is required for the biosynthesis of porphyrins ring and treatment of anaemia [Bianci, *et al.* (1989)] while long term exposure of cobalt may cause lung cancer [Mur, *et al.* (1987)]. The maximum dietary tolerable level of cobalt is 10 mg L^{-1} [Venugopal, and Luckey, (1979)] and higher consumption level could causes heart effects, thyroid damage, vomiting, diarrhea, high blood pressure, and slow respiration. In view of toxicity and widespread use of cobalt, it is important to determine its concentration in environmental samples.

A number of sophisticated methods have been reported for cobalt ion detection including atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasmamass spectrometry (ICP-MS), neutron activation analysis, flow injection chemiluminscence and fluorescence spectroscopy [Souza, and Tarley, (2009); Steffan, and Vujicic, (1993); Lagerström, *et al.* (2013); Garg, *et al.* (1993); Li, *et al.* (2006); Yu, *et al.* (2014)]. These methods provide accurate determination of cobalt ion in sample but required large infrastructure backup, are time consuming and also required complicated sample preparation. Ion selective electrodes (ISEs) provides analytical procedures that overcome the above drawbacks since they are fast, convenient and require no sample pretreatment and also suitable for online analysis [Cosofret, and Buck, (1993)]. A number of ISEs for estimation of cobalt concentration have also been reported [Gupta, *et al.* (2008); Kumar, and Shim,

(2009); Singh, *et al.* (2009); Singh, *et al.* (2006); Ghiaci, *et al.* (2010); Isa, *et al.* (2011); Mashhadizadeh, *et al.* (2002)] however most of them electrode exhibit limitation with regard to narrow working concentration range, non-Nernstian potential response, narrow pH range, and high response time. Keeping this in view, in this article Co (II) salen-based complex was immobilized in PVC matrix to prepare the electrode for sensing the cobalt ion. The results showed that the electrode is optimal selective and sensitive for cobalt ion.

Experimental: Reagent

N-(2-Hydroxybenzylidene)-N'-(2-picolyl) ethylenediamine Cobalt (II) (I) fig. 1 was synthesized using a reported method [Adam and Moeller, (2004)]. High molecular weight poly vinyl chloride (PVC), Aldrich (USA); sodiumtetraphenylborate (NaTPB) and tri-n-butylphosphate (TPB), BDH (England); dioctylphthalate (DOP); Riedel (New Delhi, India); tris-(2-ethylhexyl)phosphate (TEHP) and chloronaphthalene (CN) from E-Merck (Germeny) were used as obtained. Analytical reagent grade tetrahydrofuran (THF), nitric acid and sodium hydroxide were obtained from Ranbaxy, India. The nitrate 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 working solutions of different concentration by diluting stock solution of 0.1M concentration.
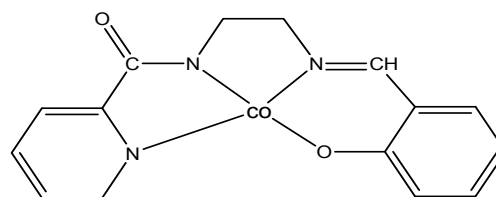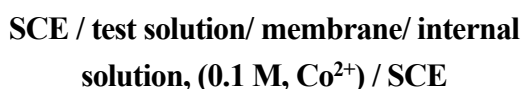

Fig. 1: Structure of N-(2-Hydroxybenzylidene)-N'-(2-picolyl) ethylenediamine Cobalt (II)

Preparation of membranes

The membrane was prepared using a reported method [Craggs, *et al*. (1993)]. Homogenous membranes of the metal salen-base complex were prepared by mixing ionophore (I), anion excluder (NaTPB), solvent mediators (TEHP, TBP, DOP and CN) and PVC in THF (5-10 mL) in their appropriate amount. The resulting mixture was vigorously stirred with a glass rod and after removing all air bubbles it was poured in acrylic ring placed on a smooth glass plate. THF was allowed to evaporate for 48h at room temperature. A transparent membrane of 5mm thickness was obtained which was then cut in to circular disc and glued to one end of a pyrex glass tube with araldite. The membrane thus prepared was equilibrated for 2 days in $0.1 M Co^{2+}$ solutions.

Apparatus and potential measurement

 The potential measurement were carried out at $25 \pm 0.1^{0}C$ with a digital potentiometer (Model 5652A, ECIL, India) and Century Micro Voltmeter (Model CVM 301, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrode

SCE / test solution/ membrane/ internal solution, (0.1 M, Co^{2+}) / SCE

The potentials were measured by varying the concentration of Co $(NO_3)_2$ in test solution in the range 1.0×10^{-6} to $1.0 \times 10^{-1}M$. Standard Co $(NO_3)_2$ solutions were obtained by gradual dilution of 0.1 M Co $(NO_3)_2$ solution.

Result and discussion

Working concentration range and slope

Before starting any potentiometric study the membrane was equilibrated with 0.1 M Co^{2+} solutions. It was found that equilibrium time of two days was optimum as equilibrated membranes gave reproducible results and no drift in potential was observed. The potential of the electrode set up having membrane with or without plasticizers was determined in the concentration range 1.0×10^{-6} to $1.0 \times 10^{-1}M$ of Co^{2+} solution and plotted in fig.2. The working concentration ranges and slopes from the plots of different electrodes have been determined and given in table.1. The electrode no.1 having membrane without plasticizer exhibits working concentration range of 3.0×10^{-5} - $1.0 \times 10^{-1}M$ with a slope of 40 mV per decade of concentration. The response time of the electrode was found to be 35 s. The slope for the membrane is non-Nernstain and the working concentration range is narrow. An improvement in the performance was attempted by the addition of plasticizers to the membranes. The addition of the plasticizers not only improves the workability of the membranes but also contribute significantly towards the improvement in the working concentration range, stability and shelf life of the electrode. Thus, different plasticizers viz; TEHP, TBP, DOP and CN were added to the membrane and the results obtained are also given in Table.1. It was observed that the addition of different plasticizers to the membrane has affected the performance to different extent. Of all the used plasticized membranes, the one with CN plasticizer (electrode no.5) and having a composition of (mg) of I: PVC: NaTPB: CN as 3:140:2:80 which gave the best performance with respect to wide concentration range, response time and near Nernstain slope, was used for further studies.

Response and life time

The response time has been measured as the

time taken by the electrode to attain a steady potential, and their values are included in table 1. It can be seen from the table that the response time of the electrode no.1 without a plasticizer is very high (40s). However, with the addition of plasticizers to the membranes (numbers 2-5), the response time is sufficiently reduced. Among all the electrode prepared with different plasticizers, electrode number 5 with the CN plasticizer improved the response time to a maximum extent. This electrode generates a stable and reproducible potential within 12 s. To enhance stabilized the membrane electrode was stored in 0.1 M Co^{2+} solution. Since the electrode no.5 exhibited the best performance characteristic, the same was chosen for further studies.

pH and solvent effect

In order to investigated the pH effect on the potential response of the electrode, the potential was measured at Co^{2+} concentration of 1.0×10^{-3} and 1.0×10^{-4} M in working pH range of 1.0-12.0 and the potential variation as a function of pH is plotted in figure 4. It can be seen that the potential is independent in the pH range of 3.0-9.0. The performance of the electrode was also investigated in a partially non-aqueous media using 10%, 20%, 25% and 30% (v/v) in methanol/water and ethanol/water (v/v) mixtures, and the results are given in table 2. It can be seen from the table that the electrode worked satisfactorily up to 25% (v/v) non-aqueous content as the working concentration range and slope remain almost constant. However, above a 25% non-aqueous content, the slope and working concentration range are appreciably decreased due to the leaching of ion at higher non-aqueous content.
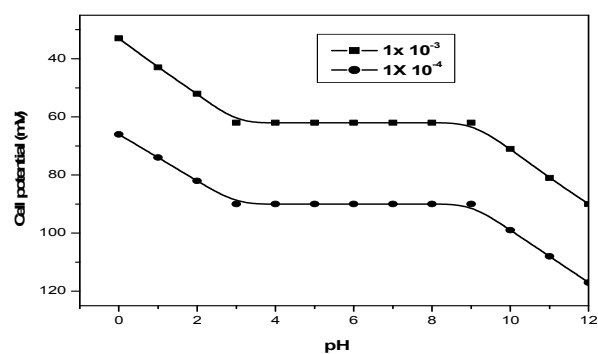

Fig.3: Effect of pH on cell potential; $[Co^{2+}]$ =1.0 × 10^{-3} and 1.0×10^{-4} M

Non-aqueous content(% v/v)	Working activity range (M)	Slope (mV/decade of activity)
0	7.9×10^{-6} - 1.0×10^{-1}	30.0
Methanol		
10	7.9×10^{-6} - 1.0×10^{-1}	30.0
20	7.9×10^{-6} - 1.0×10^{-1}	29.8
25	8.1×10^{-6} - 1.0×10^{-1}	29.0
30	1.0×10^{-5} - 1.0×10^{-1}	25.7
Ethanol		
10	7.9×10^{-6} - 1.0×10^{-1}	30.0
20	7.8×10^{-6} - 1.0×10^{-1}	30.0
25	8.3×10^{-6} - 1.0×10^{-1}	29.5
30	1.6×10^{-5} - 1.0×10^{-1}	25.0

Table 2: Performance of Co^{2+} -selective electrode no. 5 in non-aqueous media

Selectivity

The most important characteristic of any electrode is its response to the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficients. In this work, the selectivity coefficients of the electrode towards different cationic species (M^{n+}) were evaluated by using fixed interference method (FIM) [Sa'ez de Viteri, and Diamond, (1994)]. The selectivity coefficients so calculated by this method are summarized in Table 3. It showed that the electrode exhibits selective response toward Co^{2+}. A value of selectivity coefficient equal to 1.0 indicates that the membrane responds equally to primary as well as interfering ion. A value smaller than 1.0 indicates that it responds more to primary ion than interfering ion and in such a case the electrode is said to be selective to primary ion over interfering

ion. Further, smaller selectivity coefficient value reflects higher selectivity order. From table 3. revealed that the selectivity coefficients are in order of 10^{-4} or lower for almost all diverse ions tested. Thus, these ions would not cause significant interference in the estimation of Co^{2+} ions by this electrode unless present in large amounts. Thus the electrode can be used for the determination of Co^{2+} by direct potentiometric method even in presence of foreign ions.

Interfering ion (B)	Selectivity coefficient $(K_{Co^{2+},B}^{Pot})$
Li^+	7.4×10^{-4}
Na^+	7.6×10^{-4}
K^+	8.3×10^{-4}
Ca^{2+}	8.1×10^{-4}
Ba^{2+}	8.5×10^{-4}
Mg^{2+}	8.4×10^{-4}
Sr^{2+}	8.2×10^{-4}
Hg^{2+}	2.7×10^{-3}
Cu^{2+}	9.2×10^{-4}
Zn^{2+}	1.4×10^{-3}
Cd^{2+}	1.2×10^{-3}
Ni^{2+}	4.4×10^{-3}
Pb^{2+}	2.4×10^{-3}
Mn^{2+}	8.6×10^{-4}

Table 3. Selectivity coefficients of electrode no. 5 as determined by fixed interference method (FIM)

Potentiometric titration

The utility of electrode has also been used successfully to determine the end-point in the potentiometric titration of Co^{2+} with EDTA. A 25-mL sample of 1.0×10^{-3} M Co^{2+} was titrated against EDTA (1.0×10^{-3} M) at pH 4.0 and the change in cell potential was noted and plotted in fig.7. The titration plot is of sigmoid shape, thus indicates that the electrode is sufficiently selective for Co^{2+} and the end point corresponds to 1:1 stoichiometry of Co-EDTA complex. Thus,

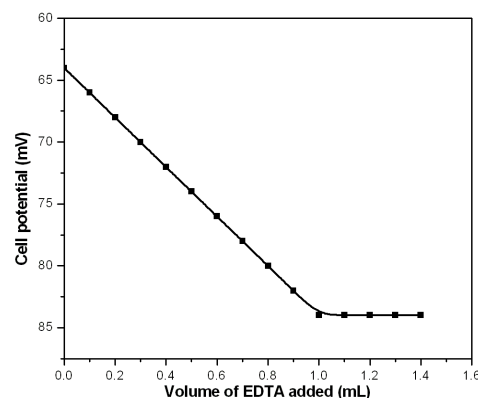the electrode can be used to determine cobalt by potentiometric titration.

Fig. 4: Potentiometric titration curve of 25 mL of Co^{2+}(1.0×10^{-3}M)with EDTASolution

Potentiometric titration

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Conclusion

The result indicates that the membrane of salen-base complex is sufficiently selective for the Co^{2+} ion over a number of other ions. Among membranes examined, the electrode no.5 having membrane with composition of I:PVC:NaTPB:CN as 3:140:2:80 exhibited wide working concentration range of 7.9×10^{-6} to 1.0×10^{-1}M with near-Nernstian slope of 30.0 mV per decade of concentration. The electrode showed a lowest response time of 12 s and operates in a pH

range 3.0-9.0 and also satisfactorily works in partially non-aqueous media. The selectivity studies of the electrode, evaluated with the fixed interference method showed that the electrode under consideration possesses excellent selectively for Co^{2+}over a large number of alkali, alkaline earth and heavy metals. Thus, the electrode can be used for the determination of Co^{2+} in the presence of various interferences ions by direct potentiometry.

References

Singh, A. K. and Singh Bhattacharjee, P. G. (2009): Determination of cobalt ions at nano-level based on newly synthesised pendant armed macrocycle by polymeric membrane and coated graphite electrode, Talanta. 80: 685–693.

Bianci, C.; Bertanza, L.; Pietre, R. and Sabbioni, E. (1989): Cobalt-induced hypothyroidism, cardiomyopathy, polycythemia and hypertricosis in an infant, J. Trace Elem. Exp. Med. 2: 311-319.

Mur, J. M.; Moulin, J. J.; Charruyer-Seinerra, M. P. and Lafitte, J. (1987): A cohort mortality study among cobalt and sodium workers in an electrochemical plant, Am. J. Ind. Med. 11: 75-81.

Venugopal, B. T. and Luckey, D. (1979): A Metal Toxicity in Mammals, Plenum Press, New York.

Souza, J. M. O. and Tarley, C. R. T. (2009): Sorbent separation and enrichment method for cobalt ions determination by graphite furnace atomic absorption spectrometry in water and urine samples using multiwall carbon nanotubes, Int. J. Environ. Anal. Chem. 89: 489–502.

Steffan, I. and Vujicic, G. (1993): Determination of cobalt, molybdenum and vanadium in Austrian mineral waters by ICP-AES after ion-exchange separation and preconcentration, Mikrochim. Acta. 110: 89–94.

Lagerström, M. E.; Field, M. P.; Séguret, M.; Fischer, L.; Hann, S. and Sherrell, R. M. (2013): Automated on-line flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open ocean seawater: application to the GEOTRACES program, Mar. Chem. 155: 71–80.

Garg, A. N.; Weginwar, R. G. and Chutke, N. L. (1993): Radiochemical neutron activation analysis of Fe, Co, Zn, Sb and Se in biomedical and environmental samples, Sci. Total Environ. 139: 421–430.

Li, B.; Wang, D.; Lv, J. and Zhang, Z. (2006): Chemometrics-assisted simultaneous determination of cobalt(II) and chromium(III) with flow-injection chemiluminescence method, Spectrochim. Acta A 65: 67–72.

Zhang, X. P.; Liu, Q.; Li, Y.; Zhen, X.; Zhang, Y. and Ma, Z. (2014): An "off–on" fluorescent and colorimetric probe bearing fluorescein moiety for Mg2+andCa2+ via a controlled

supramolecular approach, Mater. Sci. Eng. C 39: 73–77.

Cosofret, V. V. and Buck, R. P. (1993): Recent advances in pharmaceutical analysis with potentiometric membrane sensors, Crit. Rev. Anal. Chem. 24: 1.

Gupta, V. K.; Jain, A. K.; AlKhayat, M. S.; Bhargava, K. and Raisoni, J. R. (2008): Electroanalytical studies on cobalt(II) selective potentiometric sensor based on bridge modified calixarene in poly(vinyl chloride), Electrochim. Acta 53: 5409–5414.

Kumar, P. and Shim, Y. B. (2009): A novel cobalt(II)-selective potentiometric sensor based on p- (4-n-butylphenylazo)calix[4]arene, Talanta 77: 1057–1062.

Singh, A. K.; Singh, P. and Bhattacharjee, G. (2009): Determination of cobalt ions at nano-level based on newly synthesised pendant armed macrocycle by polymeric membrane and coated graphite electrode, Talanta. 80: 685–693.

Singh, A. K.; Singh, R. P. and Saxena, P. (2006): Cobalt(II)-selective electrode based on a newly synthesized macrocyclic compound, Sensors Actuators B 114: 578–583.

Ghiaci, M.; Rezaei, B.; Sadeghi, Z. and Safaei-Ghomi, J. (2010): A Co2+-selective poly(vinyl chloride) membrane electrode based on a newly synthesized 3,3′-(dodecylazanediyl)bis(N-(2-(2-aminoethylamino)ethyl)propanamide) compound, J. Chem. Eng. Data 55: 2792–2798.

Isa, I. M.; Mustafar, S.; Ahmad, M.; Hashim, N. and Ghani, S. A. (2011): Cobalt (II) selective membrane electrode based on palladium(II) dichloroacetylthiophenefenchoneazine,Talanta 87: 230–234.

Mashhadizadeh, M. H.; Momeni, A. and Razavi, R. (2002): Cobalt (II)-selective membrane electrode using a recently synthesized mercapto compound, Anal. Chim. Acta. 462:45–252.

Adam, W. and Moeller, C. R. (2004): A convenient synthesis of nickel(II) and cobalt(II) complexes of unsymmetrical salen-type ligands and their application as catalysts for the oxidation of 2,6-dimethylphenol and 1,5-dihydroxynaphthalene by molecular oxygen, Ind. J. Chem. 43: 56-62.

Craggs, A.; Moody, G. J. and Thomas, J. D. R. (1993): PVC matrix membrane ion-selective electrodes. Construction and laboratory experiments, Pure Appl. Chem. 65: 1849-1858.

Sa'ez de Viteri, F. J. and Diamond, D. (1994): Determination and application of ion-selective electrode model parameters using flow injection and simplex optimization, Analyst 119: 749-758.