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A Liquid membrane based electrode containing an electroactive chelating substance selective for cobalt (II) ions

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ABSTRACT

Spectrophotometric and conductometric studies on the binding properties of 1,4,8,11-tetraazacyclotetradecane-5,7-dione (I) toward Co^{2+} and different metal ions have been done. Data revealed the occurrence of 1:1 (ligand/metal ion) complexation with a stability order of $Co^{2+}>Cu^{2+}>Pb^{2+}>Ni^{2+}>Ag^{+}$. Consequently, (I) was also used as a neutral carrier for the preparation of a novel liquid membrane based electrode selective for Co^{2+} ions. The electrode revealed a Nernstian slope 31mV/decade over wide concentration range 1.0×10^{-6} - 1.0×10^{-1} M and detection limit 5.0×10^{-7} M. It has response time of <10 sec and can be used over a constant pH range of 5.0-8.0. The electrode possesses a fast response time and can be used for at least 4 months without observing any considerable deviation in the response behavior and selectivity. Electrode shows a very good selectivity for Co^{2+} over a number of alkali, alkaline earth, transition, and heavy metal ions. The proposed electrode was successfully applied as an indicator electrode, in potentiometric titration of Co^{2+} ions with ethylene diamine tetra acetic acid (EDTA).

KEYWORDS

Poly vinyl chloride (PVC);
Ionophore;
Liquid membrane;
Selectivity coefficients;
Indicator electrode;
Cobalt ions.

INTRODUCTION

Cobalt is essential in trace amounts for human life. Cobalt is essential for the growth of red blood cells in the body hence used as the treatment for anemia. The toxicity of cobalt is quite low compared to many other metals in soil. Exposure to very high levels of cobalt can cause health effects like effects on lungs, including asthma, pneumonia and wheezing. Cobalt is widely distributed in the environment and the average abundance of cobalt in earth crust is 29ppm, 1.0 to 14ppm in soil, 0.2ppm streams, 1 to10ppm in ground water[1]. It is widely used in various alloys like, steels, in electroplating, in fertilizers, and in porcelain glass[2]. Most of cobalt consumed is used in the manufacture of alloys, and although not released extensively in the environment, it may represent a hazard to human health. Higher exposures can occur for workers who are exposed to cobalt in industries that process it or make products containing cobalt.

Cobalt is considered essential for algae, some bacteria and for animals. Occupational toxicology of cobalt, hygienic and epidemiologic aspects, and monitoring of cobalt poisoning are also topics of special inter-

TABLE 1: Optimization of membrane ingredient

S.no	Components of the membrane(% w/w)				Slope (mV/decade)	Working concentration range, (M)	Detection limit (M)
	(I)	PVC	Plasticizer(%)(NPOE)	Anion-excluder			
1	-	33	-	-	-	-	-
2	-	33	67	-	15	1×10^{-3}-1×10^{-1}	1×10^{-3}
3	1	33	66	-	31	1×10^{-5}-1×10^{-1}	1×10^{-5}
4	2	33	65	-	32	1×10^{-6} -1×10^{-1}	5×10^{-6}
5	3	33	64	-	34	1×10^{-6} - 1×10^{-1}	4×10^{-6}
6	4	33	63	-	36	5×10^{-6} -1×10^{-1}	6.3×10^{-6}
7	5	33	62	-	35	1×10^{-5}-1×10^{-1}	4×10^{-6}
8	6	33	61	-	20	1×10^{-5}-1×10^{-1}	5×10^{-5}
9	7	33	60	-	21	1×10^{-5}-1×10^{-1}	5×10^{-5}
10	1	33	(DOP)	-	14	1×10^{-5}-1×10^{-1}	1×10^{-5}
11	1	33	(BES)	-	23	5×10^{-5}-1×10^{-1}	1×10^{-4}
12	1	33	(DBP)	-	26	5×10^{-5}-1×10^{-1}	5×10^{-5}
13	1	33	65.5	0.5	31	5×10^{-6}-1×10^{-1}	5×10^{-6}
14	1	33	65	1.0	30	1×10^{-6}-1×10^{-1}	5×10^{-7}
15	1	33	64.5	1.5	22	1×10^{-5} - 1×10^{-1}	5×10^{-5}
16	1	33	64	2.0	18	5×10^{-5}-1×10^{-1}	5×10^{-5}

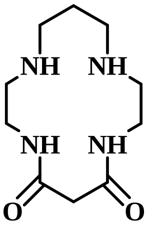

Figure 1: 1,4,8,11-tetraazacyclotetradecane-5,7-dione

est. Cobalt is a metal with marked allergenic potential. Asthma, interstitial lung disease and combined asthma and alveolitis have been described as occupational health hazards. Ethylene diamine tetra acetic acid(EDTA), diethylene triamine pentaacetic acid(DTPA), and N-acetyl-L-cysteine have been suggested as possible antidotes in cobalt intoxication[3]. Because of increased use of Co^{2+} and its hazardous effects on plants and humans its determination in the environment is important.

The available methods of the low level determination of Co^{2+} ions in solution include inductively coupled plasma mass spectroscopy(ICP-MS), inductively coupled plasma atomic emission spectroscopy(ICP-AES), isotope dilution mass spectrometer, and neutron activation analysis, etc are also used[4-8]. These methods are either time consuming involving multiple sample analysis or too much expensive for most analytical laboratories.

Potentiometric ion selective electrode are known to many metal ions and low cost tool for the selective, sensitive and rapid determination of a vast variety of analytes in different fields of application[9-17]. This has led to an increasing interest in the development of the sensors for several ionic species, increasing the number of available electrodes and microelectrodes over the last few years[18-21]. The following neutral carrier type ISEs have been used for Co^{2+} determination such as Singh et al.,[18] reported 2,3,4-pyridine-1,3,5,8,11,14-hexaazacyclohexadeca-2-ene and 5-amino-3-methylisothiazole, Gupta et al.[19,20] N,N'-bis (salicylidene)-3,4-diaminotoluene and Mashhadizadeh et al.,[21] 2-mercapto-4-methylphenyl-2-benzamido-3-phenyl-thiopropenoate and Shamsipur et al.[22] reported 9-t-Butyl-3,9,15,21-tetraaza-4,5,13,14-dibenzo-6,12-dioxabicycl0[15.3.1] herucosa-1(2),17,19-triene-2,16-dione as a neutral carries for cobalt ion. The aim of this study is the design of a highly sensitive and selective membrane electrode for Co^{2+} determination. To achieve this aim we have used the commercial available ionophore shown in figure 1. Although this ionophore is not new but its application as an electroactive material in the ion selective electrode for Co^{2+} ions is the current study. To the best of our knowledge no one has reported such study based on this compound.

EXPERIMENTAL

Reagents and apparatus

The ionophore(I), 1,4,8,11-tetraazacyclotetradecane -5,7-dione was purchased from Fluka(Buchs, Switzerland, puriss grade). Reagent grade dioctyl phthalate (DOP), bis-2-ethyl sebacate(BES), dibutyl phthalate (DBP), 2-nitrophenyl octyl ether (2-NPOE), potassium tetraphenylborate(KTClPB), high relative molecular weight PVC and all the metal salts were purchased from Aldrich Chemical Company, USA. All solvents used in investigations were of analytical reagent grade. Aqueous salt solutions were prepared by dissolving the appropriate salt in double distilled water. Potentials were measured with digital potentiometer EQ-602 Equiptronics(accuracy, 0.001V, INDIA).

pH measurements were carried out on an ISFET pH meter (Shindengen, Japan).

Electrode preparation

The general procedure[23] was used to prepare the liquid membrane. A 200mg of a mixture containing(I), plasticizer and PVC (as given in TABLE 1) in 2-3mL of THF mix thoroughly and poured in a glass ring of 30mm diameter placed on a pyrex glass plate. The solvent was then evaporated slowly at room temperature. The membrane was then removed from the glass ring and circular pieces of 1.25cm diameter were cut and mounted on a Pyrex glass tubes with suitable adhesive and conditioned from both side with Co^{2+} solution of nitrate salt(0.1 M) for 24 hours. A silver/silver chloride electrode was used as the internal reference electrode.

EMF measurements

All potential measurements with the polymeric membrane were carried out at room temperature (25 ± 0.1^0C) in stirred solutions with the following cell assembly;

Ag/AgCl, $Cl^-_{(satd.)}$ // internal sol. /membrane/ test solution// $Cl^-_{(satd.)}$, AgCl/Ag

The performance of each electrode was investigated by measuring its potential in cobalt nitrate solutions prepared in the range of 1×10^{-1} M to 1×10^{-9} M by serial dilution of the 0.1M stock solution. The solutions were stirred throughout the experiment and potential readings were recorded when they reached steady state values. The data were plotted as observed EMF versus the logarithm of the Co^{2+} activity. The activities were calculated from the Debye-Huckel equation[24]. The response time of the electrodes were obtained by measuring the time required to achieve a steady state potential (within ±1mV) when the electrodes were immersed in Co^{2+} solutions of different concentrations under stirring.

RESULTS AND DISCUSSION

Investigation of complexation

Three different experiments have done to monitor interaction between metal ion and neutral molecule as well as their complexation. Due to rigid structure of 14-membered dioxo-cyclam derivative (I) and presence of four nitrogen atoms in the cavity, macrocyclic diamide seemed to be selective for soft transition and heavy metal ions. Thus before preceding any potentiometric studies, spectro-photometric and conductometric studies have been done to determine the complexation behavior of the metal/ligand system. In this context the picrate extraction studies show maximum ligand complexation with Co^{2+} ions ($Co^{2+}>Cu^{2+}>Pb^{2+}>Ni^{2+}>Ag^+$). Log K_f values obtained by conductometric method also confirm this trend of complexation.

In order to estimate the complex stoichiometry the mole ratio method was applied[25]. A series of solution were prepared with a constant concentration/ volume of $Co^{2+}(1\times10^{-3}M)$ and variable concentration of ligand. The curve of UV absorbance change vs ligand/metal ion ratio at ligand concentration 1×10^{-3}M has plotted which confirms the 1:1 complexation ratio. The trend of this curve(after 1:1, a continuous increase of the absorbance of the complex with increasing ligand concentration) also indicates that a complex of lower stability formed. The stability of complex between the complex and metal ion should be intermediate not necessarily the highest one. Further, picrate extraction were done by taking a DCM solution 5mL of ligand (1×10^{-3}M) and 5mL aqueous solution containing (1×10^{-3}M) metal picrate were placed in a stoppered flask and shaken for around 1 hour[26] at 25°C±1°C the resulting mixture were allowed to stand for over night to complete the phase separation. The concentration of picrate ion remaining in the aqueous phase was then determined by spectrophotometer at 355nm. Blank experiments have shown that no picrate extraction occurred in the absence of ligand. The percentage of extraction Co^{2+} and Cu^{2+} ions are 93% and 69% respectively by picrate extraction.

Calibration curve

In order to get much suitable Co^{2+}ion selective electrode after proper conditioning in a 1.0×10^{-1} M solution of Co^{2+} each electrode was examined potentiometrically. It is well understood that the sensitivity, linearity, and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature and amount of additive used. Figure 2 shows the calibration curve, which was plotted using the data obtained by the potential measurements using solutions having different concentration of Co^{2+} varying from 1.0×10^{-9} to 1.0×10^{-1}M. From the TABLE 1, it is clear that the electrode containing PVC, (I), plastisizer and liphophilic additive in the ratio of 33: 1: 65: 1, exhibits good response characteristics in terms of slope, detection limit, working concentration range and response time. Electrode no.14, TABLE 1 shows reproducible response in terms of Nernstian response slope 30mV/decade (±0.5mV standard deviation for 5 sets of measurements) in the concentration range 1.0×10^{-5} to 1.0×10^{-1}M of Co^{2+} with a detection limit of 5.0×10^{-7} M and a response time of ~15 seconds.

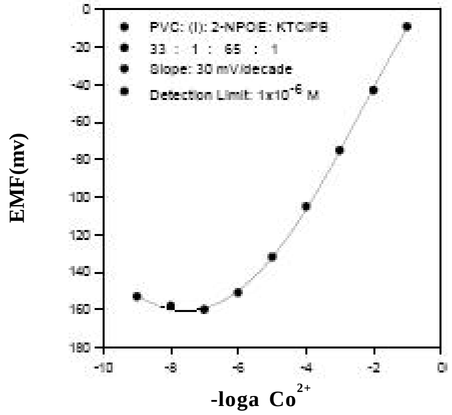

Figure 2: Calibration curve of Co^{2+} ISE

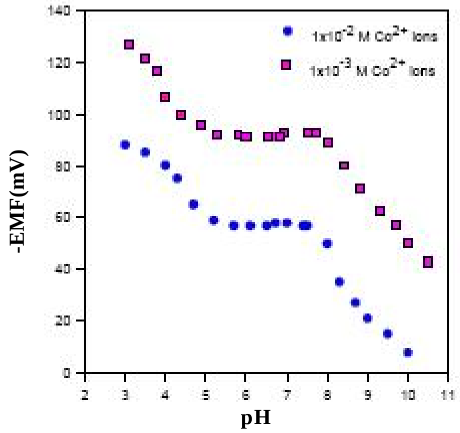

Figure 3: Effect of pH on Co^{2+} ISE

3. Effect of membrane solvent and lipophilic additive

Any membrane electrode, based on principle of concentration cell imparts some potential. But to enhance their electrode characteristics membrane solvent plays a very important role. Thus taking different aspects of plasticizer into the consideration the amount of plastisizer were optimized. The potentiometric response of the membrane ion-selective electrodes based on neutral ionophores is greatly influenced by the polarity of the membrane medium, which is defined by the dielectric constants of the major membrane components [28-31]. The influence of the nature of plasticizer on the Co^{2+} response was studied on electrodes containing three types of plasticizers having different dielectric constants, namely, DBP, DOP and O-NPOE. As shown in TABLE 1, O-NPOE with the highest dielectric constant in the series resulted in the best sensitivity of the potential responses. It should be noted that the nature of the plasticizer affects not only the dielectric constant of membrane phase but also the mobility of ionophore molecules and the state of the ligands[27-31].

The use of lipophilic additives as membrane constituents also significantly influences the performance characteristics of a membrane electrode[32-36]. It is clear from the TABLE 1, the membrane electrode incorporating KTClPB as liphophillic additive improve the sensitivity of the Co^{2+} electrode considerably (interms of detection limit). As is obvious from TABLE 1, electrode no. 14 with a PVC: (I): NPOE: KTClPB percent ratio of 33:1:65:1 resulted in Nernstian behavior of the membrane electrode over a wide concentration range.

Effect of pH

The influence of pH on the electrode response was studied at two different concentrations 1×10^{-2}M and 1×10^{-3}M Co^{2+} ion solution. pH was adjusted with 0.1N HNO_3 and 0.1N NaOH solutions as per requirement. As it is seen from figure 3, the potential response remains constant between the pH range 5.0-8.0 beyond which the potential changed considerably. At pH below this range, the emf gets altered probably due to

TABLE 2: Potentiometric selectivity coefficients for interfering ions by FIM and MPM

Interfering ions (B)	FIM	MPM
Na^+	-2.1	-2.0
K^+	-1.9	-2.0
Mg^{2+}	-2.0	-2.1
Ca^{2+}	-2.1	-2.2
Sr^{2+}	-2.2	-2.2
Pb^{2+}	-2.3	-2.4
Cu^{2+}	-2.1	-2.2
Ni^{2+}	-2.1	-2.2
Zn^{2+}	-2.0	-2.3
Cd^{2+}	-2.0	-2.2
Hg^{2+}	-2.1	-2.2
Fe^{3+}	-2.2	-2.2

TABLE 3: Electrode response in mixed solvent media

Non-aqueous medium	Percentage (V/V)	Slope (mV/decade)	Detection limit(M)
Water	--	31.0	5.0×10^{-7}
Methanol:water	10:90	30.0	3.0×10^{-6}
	20:80	31.0	1.9×10^{-5}
	30:70	33.0	3.4×10^{-5}
	40:80	37.0	7.9×10^{-5}
Acetone:water	10:90	31.5	6.3×10^{-6}
	20:80	32	3.1×10^{-5}
	30:70	31	5.0×10^{-5}
	40:60	35	7.9×10^{-5}
Acetonitril:water	10:90	30	1.0×10^{-5}
	20:80	31.5	3.1×10^{-5}
	30:70	33	5.0×10^{-5}
	40:60	36	8.0×10^{-5}

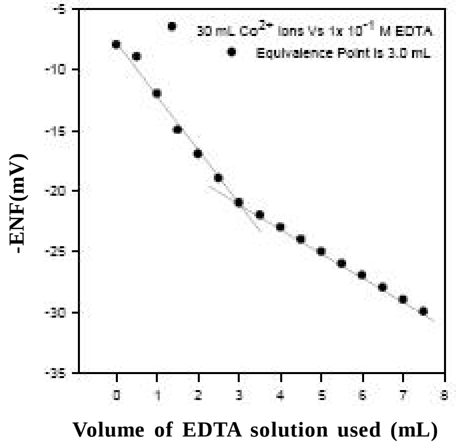

Figure 4: Potentiometric titration of Co^{2+} ions with EDTA

interference of H^+ ions and above this pH range due to formation of some hydroxyl complexes of Co^{2+} in solution.

Potentiometric selectivity coefficients

The effect of metal ions other than targeted one on the response behavior of the electrode is measured in terms of potentiometric selectivity coefficients. In this work the selectivity coefficients were determined by fixed interference(FIM) and matched potential (MPM) methods[37,38]. The results are summarized in TABLE 2. It is clear from the TABLE 2, the selectivity coefficients obtained by both methods are in close agreements. As seen from the TABLE the negative sign of each value implies the more selectiveness of electrode for primary metal ion in the presence of other interfering ions in the solution. TABLE 2 shows that, for all divalent ions used, the selectivity coefficients are in the order of 10^{-2} or smaller, indicating that they would not significantly disturb the functioning of the Co^{2+} ion selective electrode.

Effect of mixed solvent medium

The working nature of the electrode was also studied in partially non-aqueous medium using methanol-water, acetone-water and acetonitrile-water mixtures. The membrane showed satisfactory response to Co^{2+} ions in partially non-aqueous medium containing upto 30% (V/V) non-aqueous content. The results are summerised in TABLE 3. The best results are observed at 30% non-aqueous medium.

Analytical applications

1. Potentiometric titration with EDTA

The electrode was used as an indicator electrode in the potentiometric titration of Co^{2+} solution. 30mL of 1.0×10^{-2} M Co^{2+} solution was titrated against 1.0×10^{-1} M EDTA solution (Figure 4) at a pH 5-8. A very good inflection point, corresponds to Co^{2+}-EDTA stoichiometry was observed which shows that this electrode can be used as an indicator electrode for the determination of Co^{2+} potentiometrically.

2. Concluding remarks

The electrode based on 1,4,8,11-tetraazacyclotetra decane-5,7-dione (I) shows excellent response towards Co^{2+} in terms of measuring range, detection limit and selectivity coefficient of interfering ions in comparison to reported electrodes.

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