

Dibenzocyclamnickel(II) as Ionophore in PVC-Matrix for Ni²⁺-Selective Sensor

Vinod K. Gupta*, Rajendra Prasad and Azad Kumar

Department of Chemistry, Indian Institute of Technology, Roorkee, Roorkee -247667, India.

Tel: 91-1332-85801(O), 85043 (R). Fax: 91-1332-3560

* Author to whom correspondence should be addressed. E-mail: vinodfcy@iitr.ernet.in

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Abstract: The tetramethyldibenzocyclam derivative, was synthesized and characterized and was used for fabrication of potentiometric sensor for Ni²⁺ metal ion. 5,7,8,14-tetramethyldibenzo[b,i]-1,4,8,11-tetrazacyclotetradecanenickel(II)chloride, ([Ni(Me₄Bzo₂[14]ane N₄)]Cl₂) (II) was obtained in good yield as orange red salt by Fe/HCl reduction of the corresponding tetraazaannulene complex [Ni(Me₄Bzo₂taa)], (I). Membrane having [Ni(Me₄Bzo₂[14]aneN₄)]Cl₂ (II) as electroactive material, sodium tetraphenylborate (NaTPB) as an anion discriminator, dibutyl butylphosphonate (DBBP) as plasticizer in PVC matrix in the percentage ratio 5.0:2.5:200:200 (II:NaTPB:DBBP:PVC)(w/w) exhibits a linear response to Ni²⁺ in the concentration range 7.0×10⁻⁶- 1.0×10⁻¹M with a slope of 29.8±0.2 mV/decade of activity and a fast response time of 12s. The sensor works well in the pH range 2.0-7.6 and can be satisfactorily used in presence of 40% (v/v) methanol, ethanol or acetone. The sensor is highly selective for Ni²⁺ over a large number of mono-, bi- and trivalent cations. The sensor has been successfully used as indicator electrode in the potentiometric titration of Ni²⁺ against EDTA. These electrodes can be used to determine the concentration of Ni²⁺ in real samples.

Keywords: Dibenzocyclam, Ni²⁺; Potentiometric Sensor; PVC, Selectivity

Introduction

Nickel is frequently used in catalytic processes and occurs in industrial effluents. It is also present in low concentration in chocolates, soyabeans, nuts, oatmeal, cottonseed, cornmeal, hydrogenated vegetable oils, milk and milk products. Dissolved nickel levels in unpolluted fresh waters typically

range from 0.001 to 0.005 mgL⁻¹ [1]. If nickel concentration exceeds the normal level it may become potential health hazard. Nickel toxicity can cause acute pneumonitis, dermatitis, asthma, eczema, cancer of lungs and sinus, stomachaches, adverse effects on blood (increase red blood cells) and kidneys (increase protein in urine), other disorders of respiratory system and central nervous system. Availability of highly selective and economic ionophores has opened up the prospect of fabricating newer/better ion-selective electrode for the determination of nickel.

The cyclam derivatives exhibit very rich coordination chemistry with a variety of transition metal ions [2,3]. Among these, the planar nickel(II) complexes in particular, due to their remarkable thermodynamic and kinetic stability, have been used in several catalytic reactions *viz.* electroreduction of CO₂ [4] and NO₂⁻ [5], epoxidation of olefins [6], chemical and electrochemical reduction of alkyl halides [7], medical diagnosis as contrast media for NMR imaging [8] and in the fabrication of ion-selective membrane electrodes [9]. The ion-selective electrodes reported for the determination of Ni²⁺ in literature till date has poor selectivity, narrow concentration range, non-Nernstian response, long response time and poor reproducibility [10-20]. Contrary to this, the dibenzocyclam macrocycles could prove to be a better candidate for development of Ni²⁺ selective electrodes. The γ -carbon atoms in MR₄taa complexes possess remarkable nucleophilicity [21], which can be exploited for binding a variety of groups in order to build molecular super-structures and supramolecular assemblies [22]. The R₄Bzo₂[14]aneN₄ type dibenzocyclam derivatives due to their flat geometry are also expected to form stacks in solid lattices and are also expected to possess good miscibility with the PVC matrix for the rapid exchange of metal ions [23]. Consequently, they can be used as active material in the membrane phase to prepare selective electrode for a particular metal ion [24-26]. In this paper, results on the PVC matrix membrane sensor incorporating ([Ni(Me₄Bzo₂[14]ane N₄)]Cl₂) ionophore for the determination of nickel in aqueous solutions have been presented and discussed.

Experimental

Reagents and Materials

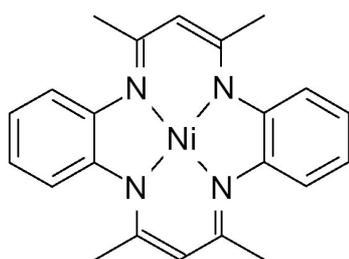
All the reagents were of Analytical Grade and were used as received, unless otherwise stated. Nickel acetate from Veb lab (Germany); acetylacetone from Sigma (U.S.A.) and o-phenylenediamine, and Butanol from Loba Chemie (India) were employed. Different solvent mediators/plasticizers such as chloronaphthalene (CN), and tri-n-butyl phosphate (TBP) were obtained from Merck (Germany), dibutyl butylphosphonate (DBBP), tri-n-butyl phosphate (DOP) and dibutyl phthalate (DBP) from Reidel (India). High molecular weight poly(vinyl chloride) (PVC) was obtained from Fluka (Switzerland) and sodium tetraphenyl borate (NaTPB) from BDH (U.K.) and used as such. AR grade tetrahydrofuran (THF), nitric acid and sulfuric acid were obtained from E.Merck (India) and sodium hydroxide from Ranbaxy (India). All the metal salts used were of analytical reagent grade. Solutions of metal nitrates were prepared in doubly distilled water and were standardized by appropriate chemical methods. Solutions of different concentration were prepared by diluting the stock solution of 0.1 M concentration.

Synthesis of [Ni(Me₄Bzo₂taa)] Complex(I)

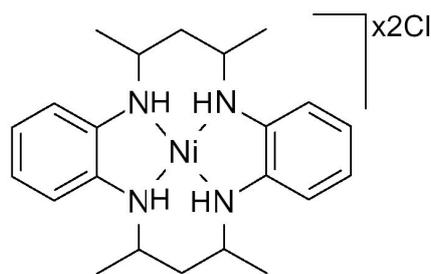
This was prepared using template synthesis as given by Chipperfield and Woodward [27]. 10 mmol (2.547 g) of nickel acetate tetrahydrate and 20 mmol (2.1628 g) of o-phenylene diamine were placed in a 100 mL round bottom flask equipped with a reflux condenser, 30 cm³ of dry butane-1-ol was added to it. The solution was refluxed using oil bath and was continuously stirred throughout using magnetic stirrer. 20 mmol (2.017 cm³) of acetyl acetone was added drop wise during the initial stages of refluxing. The mixture was subsequently refluxed with continuous stirring for 3 hours. The solution was cooled to room temperature (*ca* 25°C), and 30 cm³ of dry methanol was added to it. It was subsequently cooled in refrigerator overnight. Dark purple microcrystals separated out. They were collected by filtration. Compound was washed with water followed by methanol twice and dried in air. Yield: 0.32 g (70%).

Synthesis of [Ni(Me₄Bzo₂[14]aneN₄)]Cl₂ Macrocycle (II)

[Ni(Me₄Bzo₂taa)], (I) (1.0 g, 2.5 mmol) and concentrated HCl (30 cm³) were placed in a two-necked 100 cm³ round bottom flask. Iron fillings (*ca* 2.0g) were added and the mixture was gently warmed at 50-60 °C for 30 min. The solution was stirred and a slow stream of HCl was passed through it. The initial yellow solution gradually changed to orange-red and, finally, a copious amount of red solid separated. It was filtered off, washed with concentrated HCl (5 cm³) and the unreacted iron fillings were removed by extracting the compound with Me₂CO. The HCl washing was combined with the aqueous filtrate, which was evaporated to dryness on a rotatory evaporator. The dry solid was extracted with Me₂CO (3x10cm³) portions. All Me₂CO extracts were combined and evaporated to dryness on a rotatory evaporator, then re-extracted with Me₂CO, so as to remove traces of the FeCl₂. The product was purified by passage through a 20x2.5 cm Al₂O₃ column eluting with 1:1 CHCl₃/Me₂CO. The initial rapidly moving yellow band was discarded. The main orange-red band, which moved fairly slowly, was collected and the solvent was removed at reduced pressure. The residue was recrystallized from MeOH/CHCl₃ and was dried over CaCl₂. Yield: 0.9 g (75%). [¹H NMR (CDCl₃): δ 14.72(br, 4H, NH), 7.47-7.71(d, 8H, C₆H₆), 2.73(d, 12H, CH₃), 2.47(m, 4H, C-H), 1.17(t, 4H, CH₂). IR (KBr pellet) 3488m, 3456m (N-H), 2911w (CH₃), 1627vs(N-H gr. Bending), 1500w, 1461w, 1400m (C=C,Ph), 750m (δ C-H, Ph), Electronic spectra at λ_{max} 435, 276, 242 nm. Λ_M 290 Ω⁻¹ (at 1x10⁻⁴ M in Me₂CO). ESI MS observed m/z 410, 412 (M + e)⁺, calcd. For C₂₂H₃₂N₄Ni, 410,412].



[Ni(Me₄Bzo₂taa)] (I)



[Ni(Me₄Bzo₂[14]aneN₄)]Cl₂ (II)

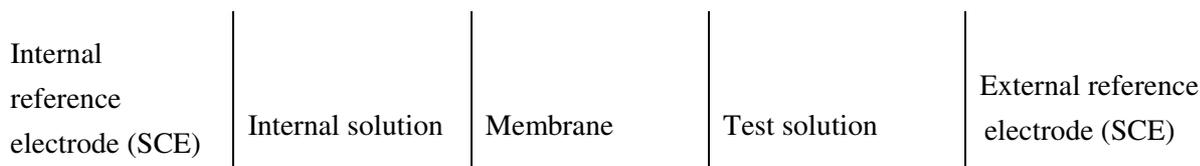
Preparation of Membranes

Varying amount of ion-active material (ca. 3.0-20 mg), an appropriate amount of high molecular weight PVC (ca. 50-200 mg), varying amount of solvent mediators/plasticizers (ca.50-250 mg) and an anion discriminator (ca. 1.0-10 mg) were dissolved in ~20 mL tetrahydrofuran (THF). The solution mixture was vigorously shaken and the air bubbles were removed. It was poured into polyacrylate rings, which were placed on a smooth glass plate and THF was allowed to evaporate slowly at room temperature. The membranes, thus obtained, were detached from the glass plate, cut to suitable size and glued to one end of a “Pyrex” glass tube with araldite.

Equilibration of Membranes and Potential Measurements

Proper equilibration of a membrane, to be used as a sensor, is essential for generating stable and reproducible potentials and to avoid long response time. It is necessary to optimize the concentration of the contacting solution and the time required for complete equilibration. Thus, all the membranes were immersed in respective metal salt solutions of different concentrations for different time periods.

The potential measurements were carried out at 25 ± 0.1 °C by using saturated calomel electrodes (SCE) as the reference electrodes. The following cell assembly was set up to measure the potentials.



The potentials were measured by varying the concentration of the test solution in the range 1.0×10^{-6} – 1.0×10^{-1} M. To optimize the concentration of the internal solution, the potentials were measured as a function of metal ion concentration for the three concentrations of internal solution, viz. 1.0×10^{-2} , 5.0×10^{-2} and 1.0×10^{-1} M.

Dissolution of Waste Samples

Treatment of Electroplating Waste

40 mL of electroplating waste was first filtered and added 5 mL of concentrated sulphuric acid. The final volume of solution was made up to 50 mL maintaining the pH between 3.0-4.0 and solutions were suitably diluted.

Dissolution of Spent Fe-Cr catalyst

1.0 g of Spent Fe-Cr catalyst was dissolved by heating it with 2x10 mL of concentrated HCl to near dryness. The residue was dissolved in 10 mL of 0.1 M H_2SO_4 and made up to 100 mL and pH 4.0 of the solution was maintained.

Dissolution of Chocolates Samples

A 10 g chocolate sample was ashed in silica crucible for 4 h on a hot plate and the charred material was transferred to Muffle furnace for overnight heating at 350 °C. The residue was cooled, treated with 2.0 mL concentrated nitric acid and again kept in furnace for 2 h at the same temperature so that no carbon traces are left. The final residue was treated with 0.5 mL concentrated hydrochloric acid and 1-2 mL 70% perchloric acid and evaporated to fumes, so that all the nickel metal change to nickel ions. The solid residue was dissolved in water, filtered and by keeping the pH at ~4.0 made up to 25 mL.

The all dissolved solutions were suitably diluted and metals concentration were determined with Atomic Absorption Spectrophotometer.

Result and Discussion

The potential response of all the membranes (numbered 1-6) for Ni²⁺ ions was studied at 1.0×10⁻¹M concentration of internal solution and by varying the concentration of the test solution from 1.0×10⁻⁶-1.0×10⁻¹M. The potentials observed are plotted against the activity of Ni²⁺ions in Fig.1. The effect of concentration of the internal solution on the functioning of the membrane sensors was also studied by measuring the potentials at varying concentration of internal or reference solution *viz.* 1×10⁻², 5×10⁻² and 1.0×10⁻¹ M Ni²⁺. The results showed that the variation of the concentration of the internal solution do not cause any significant difference in the corresponding potential response, except for an expected change in the intercept of the resulting Nernstian plots. The potential generated showed opposite sign when the concentration of the test solution became more than that of the reference solution. Since the upper limit of the concentration of the test solution was 1.0×10⁻¹ M, the concentration of the internal solution was, therefore, chosen as 1.0×10⁻¹ M for the sake of convenience.

The working concentration ranges with slopes of the least square fit line and standard deviation in the observed values of potential from this line for all membranes are given in Table 1. It has been observed that the membrane no.1 without plasticizer exhibits a narrow working concentration range of 1.12×10⁻⁴ – 1.0×10⁻¹ M with a non-Nernstian slope of 34.9±0.5 mV/decade of activity with standard deviation of 2.78 mV in potential. The characteristics of the membrane improved, especially the working concentration range and slope, by the addition of anion discriminator (NaTPB) and solvent mediators (DBBP, DBP, TBP, DOP or CN) (Table 1). Further, the best performance is exhibited by membrane no. 2 incorporating DBBP as solvent mediator, which works well over a wide concentration range (7.08×10⁻⁶ – 1.0×10⁻¹ M) with a Nernstian slope (29.8±0.2 mV/decade of activity). The composition of this membrane is 5.0:2.5:200:200 (II:NaTPB:DBBP:PVC). This membrane gives standard deviation of 1.4 mV in potentials from the least square fit line and excellent consistency in slope with 90% confidence limit lying within ±0.2 mV/decade of activity. A comparative data for the sensors presented in this paper with those reported in literature is summarized in Table 2.

Response and Life Time

The response time i.e., the time required by the electrode assembly to generate stable, noiseless and reproducible potentials is 40s for the sensor (no. 1) fabricated without any solvent mediator (Table 1).

This is not desirable as it makes the electrode unfit in applications like on-line monitoring. However, the addition of solvent mediators improves the response time, as observed for membranes 2-6. It can be seen from Table 1 that best performance, with regard to response time, is given by sensor no.2 containing DBBP as the plasticizer as it shows a fast response time of 12s as compared to the rest of the sensors.

Table 1. Compositions and characteristics of PVC based membranes of Nickel-5,7,12,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraazacyclotetradecane(II) and performance characteristics of Ni²⁺-selective electrodes based on them.

Sensor No.	Composition of the membranes (% w/w)								Working concentration Range (M)	Slope with 90% confidence limit (mV/decade of activity)	Response time (±2s)	Standard deviation in potential (mV)
	(II)	NaTPB	DBBP	DBP	TBP	DOP	CN	PVC				
1.	5.0	-	-	-	-	-	-	200	$1.12 \times 10^{-4} - 1.0 \times 10^{-1}$	34.9±0.5	40	2.78
2.	5.0	2.5	200	-	-	-	-	200	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8±0.2	12	1.42
3.	5.0	2.0	-	100	-	-	-	200	$6.30 \times 10^{-5} - 1.0 \times 10^{-1}$	36.9±0.5	18	3.89
4.	5.0	2.5	-	-	90	-	-	200	$3.98 \times 10^{-4} - 1.0 \times 10^{-1}$	31.6±0.5	25	3.98
5.	5.0	2.0	-	-	-	150	-	200	$8.91 \times 10^{-5} - 1.0 \times 10^{-1}$	37.0±0.7	20	3.75
6.	5.0	2.5	-	-	-	-	150	200	$1.58 \times 10^{-5} - 1.0 \times 10^{-1}$	35.5±0.2	25	1.31

Table 2. Comparison of the proposed Ni²⁺-selective electrode (No. 2) with the reported electrodes.

Sensor No.	Working concentration range (M)	Slope (mV/decade of activity)	pH range	Response time (s)	Life time (months)	Selectivity	Reference no.
1	$1.0 \times 10^{-3} - 1.0 \times 10^{-1}$	Non Nernstian	NM	NM	NM	NM	12
2	$8.0 \times 10^{-6} - 5.0 \times 10^{-2}$	Near Nernstian	1.7-5.4	10	6	Highly selective	11
3	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	Non Nernstian	3.5-8.0	40	NM	Interference due to Mn ²⁺ , Co ²⁺ , Cu ²⁺ and Zn ²⁺	10
4	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	Non Nernstian	3.5-6.5	NM	5-6	Poorly selective	13
5	$6.3 \times 10^{-4} - 1.17 \times 10^{-2}$	Near Nernstian	NM	NM	NM	Poorly selective	17
6	$4.0 \times 10^{-5} - 1.0 \times 10^{-1}$	Nernstian	3.0-7.5	10	2	Sufficiently selective	14
7	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	NM	4.0-8.0	NM	NM	NM	19
8	$7.1 \times 10^{-7} - 1.2 \times 10^{-2}$	NM	3.0-6.0	NM	2	NM	20
9	$7.9 \times 10^{-6} - 1.0 \times 10^{-1}$	Nernstian	2.7-7.6	15	6	Highly selective	9
10	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	Nernstian	2.0-7.5	12	6	Highly selective	Proposed sensor

The reproducibility (with 1% maximum error) of the potential data was checked by making twenty measurements on a solution of concentration 1.0×10^{-3} M Ni^{2+} . The sensors could be used satisfactorily over a period of six months. However, they were stored in 0.1 M Ni^{2+} solution, when not in use, and reequilibrated with 1.0M Ni^{2+} solution whenever any drift in potentials was observed.

All further studies were carried out on sensor no.2 as it exhibits the best response characteristics.

pH and Solvent Effect

One of the ions present in aqueous solution is the hydrogen ion. It interferes in the functioning of the electrode in many instances. In view of this it is essential to get the optimum pH range where the electrode functions devoid of interference from the hydrogen ions. The pH dependence of the membrane sensor (no.2) has been investigated at 1.0×10^{-2} and 1.0×10^{-3} M Ni^{2+} ions and shown in Fig. 2. The pH of the solutions was adjusted by the addition of HNO_3 or hexamine. It can be seen from Fig. 2 that potentials remain steady between pH 2.0-7.5 and consequently, the same may be taken as valid pH range of the projected sensor. The sharp change in potentials below 2.0 and above pH 6.9 may be due to H^+ ion co-fluxing and hydrolysis of Ni^{2+} ions, respectively.

In order to assess the performance of the sensor in partially non-aqueous medium, its functioning was studied in methanol-water, ethanol-water and acetone-water mixtures and the results are tabulated in Table 3 with the standard deviation in slope and potential from least square fit line. It is observed that the performance of the electrode is satisfactory in non-aqueous solution containing up to 40% partially non-aqueous content, as the working concentration range and slope do not change considerably. However, these values reduce significantly when the non-aqueous content exceeds this concentration.

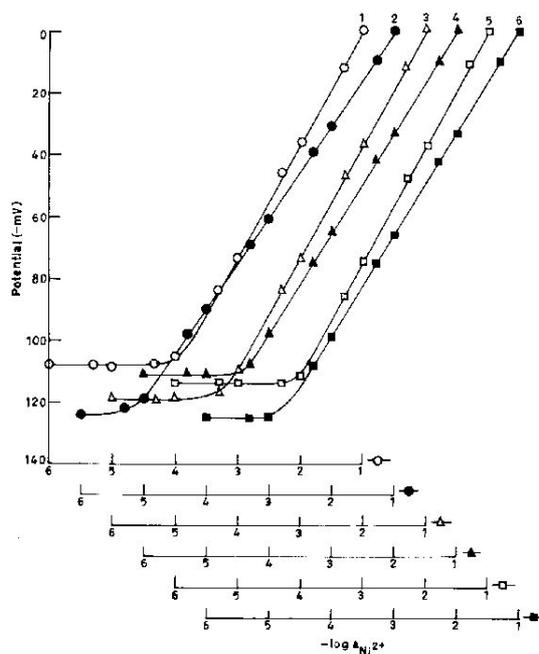


Figure 1. Variation of potential of PVC based membrane of (II) no. 1 without plasticizer and (nos. 2-6) with plasticizers, DBBP, DBP, TPB, DOP and CN, respectively with Ni^{2+} concentration.

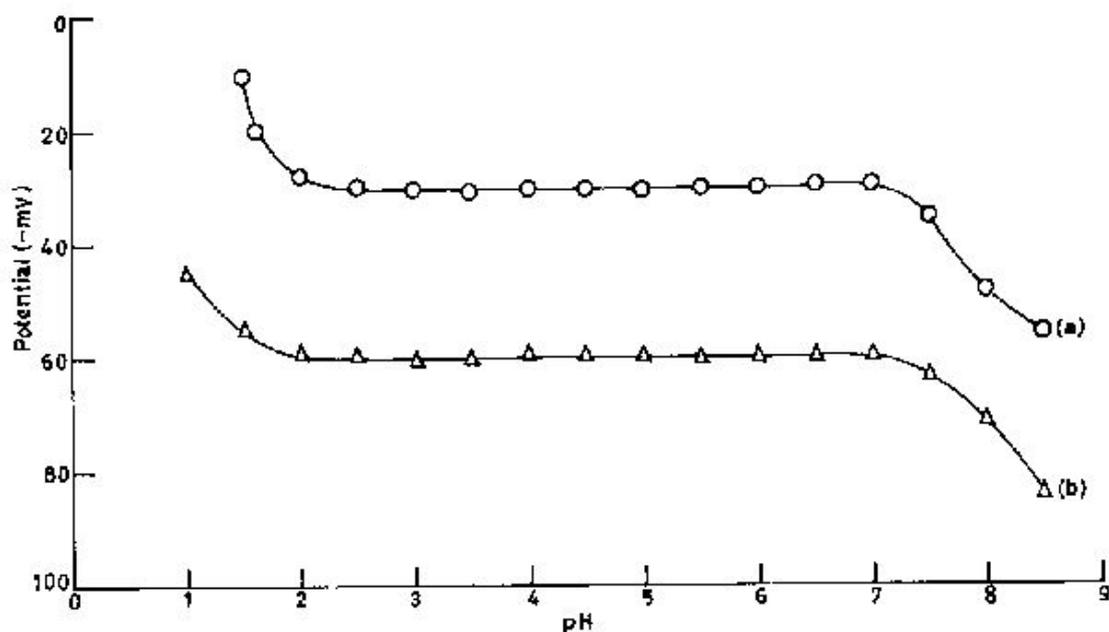


Figure 2. Effect of pH on potential, $[\text{Ni}^{2+}] = 1.0 \times 10^{-2} \text{ M}$ (a) and $1.0 \times 10^{-3} \text{ M}$ (b) for sensor no. 2.

Table 3. Performance of Nickel-5,7,12,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraaza cyclotetradecane (II) based membrane sensor (No. 2) in non-aqueous medium.

Non aqueous Content % (v/v)	Working concentration range (M)	Slope with 90% confidence limit (mV/decade of activity)	Standard deviation in potential (mV)
0	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.42
Methanol			
10	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.42
20	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.52
30	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.50
40	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.5 ± 0.2	1.76
45	$1.99 \times 10^{-5} - 1.0 \times 10^{-1}$	28.1 ± 0.3	1.95
Ethanol			
10	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.42
20	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.42
30	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.50
40	$8.91 \times 10^{-6} - 1.0 \times 10^{-1}$	29.5 ± 0.2	1.75
45	$2.23 \times 10^{-5} - 1.0 \times 10^{-1}$	26.5 ± 0.3	2.08
Acetone			
10	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.42
20	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.42
30	$7.08 \times 10^{-6} - 1.0 \times 10^{-1}$	29.8 ± 0.2	1.42
40	$7.94 \times 10^{-6} - 1.0 \times 10^{-1}$	28.8 ± 0.3	1.53
45	$3.16 \times 10^{-5} - 1.0 \times 10^{-1}$	26.0 ± 0.5	1.98

Selectivity

Selectivity is the most significant characteristic of any sensor, which defines the extent to which it may be used to estimate that meticulous ionic species in real samples. To be a good sensor, it is essential for it to be selective over all the ions likely to be present in real samples along with the analyte. The selectivity of a sensor is specified by the selectivity coefficient values defined in terms of Nicolsky equation. The selectivity coefficients were evaluated by modified form of the fixed interference method as recommended by Sa'ez de Viteri and Diamond [28] and also by matched potential method [29] at 1.0×10^{-2} M interfering ion concentration. The selectivity coefficient values $K_{Ni^{2+},B}^{Pot}$ (Table 4) clearly point out that the electrode is moderately selective to Ni^{2+} over a number of other cations except for Na^+ and Cu^{2+} . Even though Na^+ and Cu^{2+} are likely to cause some interference as the selectivity coefficient values for these ions are higher than other cations, but at low concentrations still these would not cause much interference. To determine the maximum tolerance limit of these ions in the determination of Ni^{2+} , some mixed run studies were performed [30-34]. It is clear from Fig.3 that Na^+ at $\leq 5.0 \times 10^{-5}$ M do not cause any deviation in the original plot obtained in pure Ni^{2+} . Thus the electrode can tolerate Na^+ at $\leq 5.0 \times 10^{-5}$ M over the entire working concentration range. When Na^+ is present at higher concentration, 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 assembly can be used to determine Ni^{2+} in the concentration ranges of $2.0 \times 10^{-5} - 1.0 \times 10^{-1}$, $1.0 \times 10^{-4} - 1.0 \times 10^{-1}$ and $7.1 \times 10^{-4} - 1.0 \times 10^{-1}$ M, respectively. Similarly it can be seen from Fig.4 that Cu^{2+} can also be tolerated over the entire concentration range when present at concentrations $\leq 5.0 \times 10^{-5}$ M. The working concentration reduces to $4.4 \times 10^{-5} - 1.0 \times 10^{-1}$, $2.0 \times 10^{-4} - 1.0 \times 10^{-1}$ and $7.9 \times 10^{-4} - 1.0 \times 10^{-1}$ M in the presence of 1.0×10^{-4} , 1.0×10^{-3} and 1.0×10^{-2} M Cu^{2+} respectively. It is significant to point out that the slope remains unaltered in both cases.

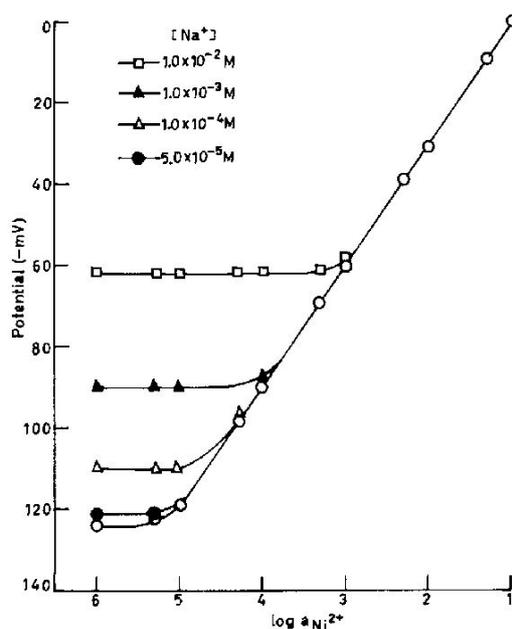


Figure 3. Variation of potential with Ni^{2+} concentration in presence of different concentration of Na^+ .

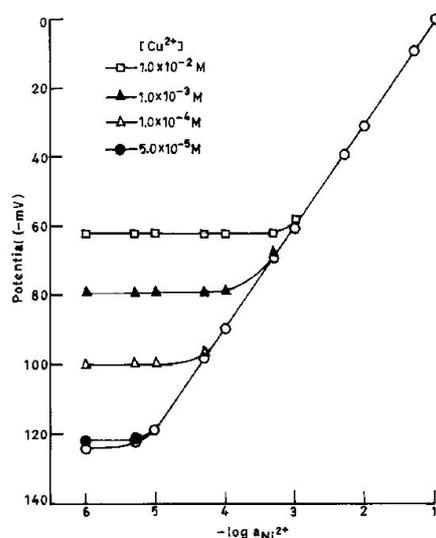


Figure 4. Variation of potential with Ni^{2+} concentration in presence of different concentration of Cu^{2+} .

Table-4: Selectivity coefficient values of membrane sensor (No.2) in the presence of 1.0×10^{-2} M concentration of interfering ions as calculated by fixed interference method using the expression without superscript and also by matched potential method.

Interfering ion (B)	Selectivity coefficient values $K_{\text{Ni}^{2+}, \text{B}}^{\text{Pot}}$	
	Fixed interference method (M)	Matched Potential method
Li^+	2.3×10^{-2}	0.11
Na^+	6.8×10^{-1}	0.67
K^+	5.4×10^{-2}	0.27
Ag^+	1.3×10^{-2}	0.14
NH_4^+	1.5×10^{-2}	0.13
Tl^+	2.4×10^{-2}	0.21
Ca^{2+}	1.1×10^{-3}	0.18
Mg^{2+}	2.4×10^{-3}	0.17
Sr^{2+}	3.4×10^{-3}	0.13
Ba^{2+}	5.6×10^{-3}	0.19
Cu^{2+}	8.9×10^{-2}	0.59
Cd^{2+}	2.9×10^{-3}	0.21
Co^{2+}	1.7×10^{-3}	0.13
Pb^{2+}	3.9×10^{-3}	0.14
Zn^{2+}	4.7×10^{-3}	0.14
Mn^{2+}	2.3×10^{-3}	0.17
Pb^{2+}	3.4×10^{-3}	0.10
Hg^{2+}	2.3×10^{-3}	0.11
Cr^{3+}	3.4×10^{-3}	0.13
Al^{3+}	1.8×10^{-3}	0.27
Ce^{3+}	1.0×10^{-3}	0.19
Fe^{3+}	3.9×10^{-3}	0.32
Bi^{3+}	1.5×10^{-3}	0.18

Analytical applications

Potentiometric titration

The analytical applicability of the proposed sensor has been tested by using it as an indicator electrode to find out the end point in potentiometric titration of Ni^{2+} with EDTA. 10 mL of 1.0×10^{-3} M Ni^{2+} solution was brought to pH 6.0 with hexamine and then titrated with 1.0×10^{-2} M EDTA solutions. The potential data are plotted against volume of EDTA in Fig.5. The conventional sigmoid type plot is not obtained which may be due to the electrode response to the other ions being added to the test solution during titration. However, the break point obtained is sharp and can be taken as the end point because it corresponds to Ni (II)-EDTA complex stoichiometry.

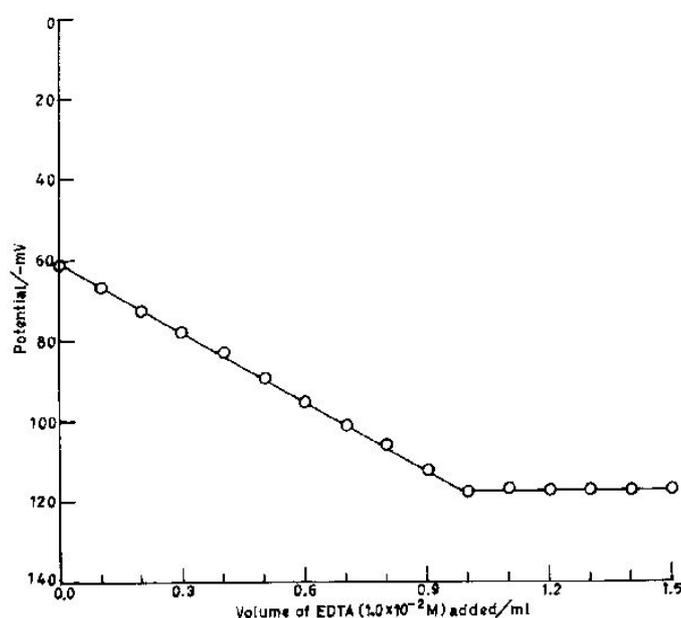


Figure 5. Potentiometric titration of Ni^{2+} ions (1.0×10^{-3} M, 10 ml) with EDTA (1.0×10^{-2} M).

Waste analysis

Further, the practical utility of the sensor was tested by applying it for the estimation of Ni^{2+} in a Electroplating waste and Spent iron-chromium catalyst. The waste was dissolved in distilled water by adding a few drops of 16N nitric acid. It was then filtered and analyzed by AAS. It was found that the waste contained various metals at different concentration besides.

Ni^{2+} . For the sake of comparison (Table 5) the concentration of copper was also determined by the sensor. It is clear from the values in Table 1 that these are in good agreement with those obtained by AAS. Hence the sensor can be successfully employed for the estimation of Ni^{2+} in real samples. This electrode can also be used for the quantitative determination of Ni^{2+} in some Indian brand chocolates. The results were found quite comparable to those obtained by AAS (Table 6). This also shows the practical utility of the proposed sensor.

Conclusion

The membrane sensor using [Ni(Me₄Bzo₂[14]aneN₄)]Cl₂ (II), NaTPB as anion discriminator and DBBP plasticizing solvent mediator in PVC matrix in the ratio 2.5:1:100:100 (II:NaTPB:DBBP:PVC)(w/w) works well in the concentration range 7.0x10⁻⁶-1.0x10⁻¹M with a slope 29.8±0.2 mV/decade of activity, response time as fast as 12s and good selectivity over a number of cations. The useful pH range of the electrode is 2.0-7.6. The sensor can work satisfactorily in 40%(v/v) water-methanol, ethanol and acetone mixtures, and can be used over a period of 5 months without any drift in potentials. The electrode has been used as an indicator electrode in the potentiometric titration of Ni²⁺ against EDTA and can be used in the determination of Ni²⁺ in real samples.

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Sample Availability: Available from the authors.

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