

PVC Based Selective Sensors for Ni²⁺ Ions Using Carboxylated and Methylated Porphine

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Abstract: Poly vinylchloride (PVC) based membranes of 4,4',4'',4'''-21*H*,23*H*-porphine–5,10,15,20 –tetrayl) tetrakis (benzoic acid) (TBAP) and 2,3,7,8,12,13,17,18-octamethyl -21*H*, 23*H*-porphine (OMP) were prepared using dibutyl phthalate (DBP), dioctylphthalate (DOP), dibutyl(butyl)phosphonate (DBBP) and 1-chloronaphthalene (CN) as plasticizing solvent mediators and sodium tetraphenylborate (NaTPB) as an anion excluder for Ni²⁺ selective sensors. TBAP based membrane exhibits linearity over a wide concentration range 2.0×10^{-6} – 1.0×10^{-1} M (0.12 – 5.8×10^3 ppm) with a slope of 29.6 mV/decade of activity while OMP based membrane showed linear potential response in the concentration range 1.0×10^{-5} – 1.0×10^{-1} M (0.60 – 5.8×10^3 ppm) with a Nernstian slope of 29.0 mV/decade of activity. The electrode assembly works between pH 2.0 – 7.0, exhibits a fast response time of 10-15s and performed satisfactorily over a period of six months with good reproducibility. Excellent selectivity of the order of 10^{-3} over a number of cations and quantitative determination of Ni²⁺ in effluents discharged from electroplating industry demonstrates the utility of the proposed sensor. The electrode assembly was also used as an indicator electrode in the potentiometric titration of Ni²⁺ with EDTA.

Keywords: porphine, Sensors, Ion-selective Electrodes, Nickel

Introduction

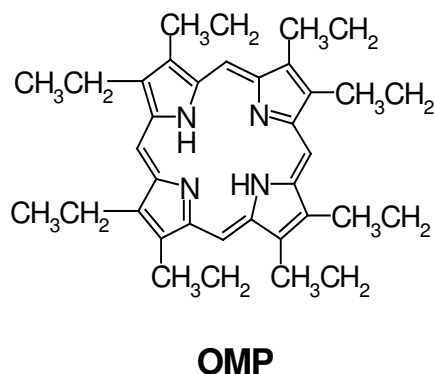
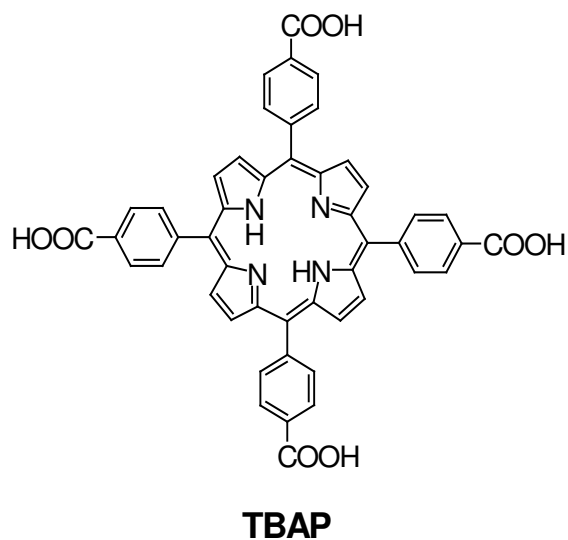
Utility of chemical sensors responding selectively to a specific ion in diverse samples viz. soils, industrial effluents, pharmaceutical compounds, clinical analyses etc. is well established. The technique is fast, accurate, low-cost and the sample used for analysis is small and non-destructive. Extensive efforts made during the last 4-5 decades resulted the availability of sensors for alkali, alkaline earth metals and few anions, however, success with regard to heavy metals is still limited and lacks in commercial availability. Efforts are therefore, continued to develop sensors for heavy metals exhibiting better performance with regard to selectivity, sensitivity and reproducibility. Determination of nickel assumes importance due to its toxic nature, widespread use in catalytic processes and its presence in various effluents. The toxicity of nickel can cause dermatitis, asthma and disorder of central nervous system. A survey of literature reveals that the first nickel-selective electrode was reported by Pungor and co-workers using a nickel-dimethylglyoxime complex[1]. Later heterogeneous membranes of nickel phosphate in paraffin and silicone rubber [2], nickel bis-(2-ethylhexyl) phosphate in PVC [3] and a nickel complex of 1,4,8,11-tetraazacyclotetradecane in Araldite [4] were used for preparing electrodes. In addition to these solid membrane ion selective electrodes (ISEs), liquid membrane electrodes for nickel using O,O'-diisobutyldithiophosphatonickel(II) in chlorobenzene [5], bis (tetraethyl ammonium) bis (dithiobenzophenazine) nickelate in nitrobenzene [6] and nickel diethyl dithiocarbamate in chloroform [7] have also been reported. Apart from these, few other sensors have also been reported using inorganic and organic ion-exchangers as sensor materials [8-10].

The use of Porphines as sensor material for membrane has been reported recently [11-13]. Porphines are aza, cyclic molecules capable of forming electron rich interior cavities in which metal cation is encapsulated through ion-dipole interactions as two pyrroline nitrogens are capable of accepting two protons and two -NH groups capable of losing equal number of protons. In continuation of our work on the development of selective nickel-sensor [14-16], the use of carboxylated and methylated porphines as active constituents for the membranes has been investigated and the results are presented herein.

Experimental

Reagents

All reagents were of analytical– reagent grade. Porphine, (4,4',4'',4'''-21*H*,23*H*-porphine–5,10,15,20-tetrayl)tetrakis(benzoic acid)(TBAP) and 2,3,7,8,12,13,17,18-octamethyl-21*H*, 23*H*-porphine (OMP) were procured from Aldrich (Milkwaukee, USA) and high molecular mass poly vinylchloride (PVC) was obtained from (GSC, India). Sodium tetraphenylborate (NaTPB) from BDH (Poole, Dorset, UK), dibutylphthalate (DBP) and dioctylphthalate (DOP) from Reidel (India), dibutyl(butyl)phosphonate (DBBP) from Mobil, (Richmond, USA) and 1-chloronaphthalene (CN) from Merck (Darmstadt, Germany) were used without further purification. Organic solvents were purified by distillation and solutions of metal salts (nitrates) were prepared in double distilled water.



Preparation of membranes

The PVC-based membranes were prepared by the method of Craggs et al. [17]. Varying amounts of the ion-active phase (porphine) and an appropriate amount of PVC were dissolved in 20 ml THF. The anion excluder, NaTPB and solvent mediators, DBP, DOP, DBBP and CN were also added in some cases to get membranes of different compositions. The solution thus obtained, after complete dissolution of the various components, was poured into acrylic rings placed on a smooth glass plate and allowed to evaporate at room temperature. After 48h, transparent membranes of 0.5mm thickness were obtained. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the membranes produce reproducible, noiseless and stable potentials. Membrane to membrane reproducibility was assured by carefully following the optimum conditions of fabrication. Composition of the membranes, which gave best performance, is listed in Tables 1 and 2 along with other characteristics.

Potential measurements

The membranes were equilibrated for 3-5 days in 0.5 M Ni²⁺ solution. The potential measurements were carried out at 25 ± 0.1°C with a Mettler Toledo pH/ion analyzer (model MA235) by setting up the following cell assembly.

Internal reference electrode (SCE)	Ni ²⁺ 0.1 M internal solution	Membrane	Test solution	External reference electrode (SCE)
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Saturated calomel electrodes (SCE) were used as reference electrodes. The response time of the membrane sensors is the time in which stable and constant potentials are obtained.

Table 1: Composition and response characteristics of PVC based TBAP membranes selective for Ni²⁺ ions

Electrode/ Membrane No.	% (w/w) of various components							Working concn. range, M	Slope, mV/decade of activity	Response time, sec
	TBAP	DBP	DOP	DBBP	CN	NaTPB	PVC			
1	10	-	-	-	-	5	85	$5.5 \times 10^{-5} - 1.0 \times 10^{-1}$	26.0	60
2	10	30	-	-	-	5	55	$2.0 \times 10^{-5} - 1.0 \times 10^{-1}$	28.5	15
3	10	-	30	-	-	5	55	$5.5 \times 10^{-5} - 1.0 \times 10^{-1}$	34.0	20
4	10	-	-	30	-	5	55	$2.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6	15
5	10	-	-	-	30	5	55	$5.6 \times 10^{-5} - 1.0 \times 10^{-1}$	35.3	10

Table 2: Composition and response characteristics of PVC based OMP membranes selective for Ni²⁺ ions

Electrode/ Membrane No.	% (w/w) of various components							Working concn. Range, M	Slope, mV/decade of activity	Response time, sec
	OMP	DBP	DOP	DBBP	CN	NaTPB	PVC			
6	10	-	-	-	-	5	85	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	32.4	60
7	10	30	-	-	-	5	55	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	37.7	20
8	10	-	30	-	-	5	55	$3.6 \times 10^{-5} - 1.0 \times 10^{-1}$	38.8	15
9	10	-	-	30	-	5	55	$5.6 \times 10^{-5} - 1.0 \times 10^{-1}$	30.1	15
10	10	-	-	-	30	5	55	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	29.0	10

Results and Discussion

Working concentration range

The potential response of all the membrane sensors was studied in the concentration range $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M Ni²⁺ (Figs.1 & 2). TBAP based membrane electrode No.1 (without solvent mediator) exhibited linearity in the concentration range $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M with a slope of 26.0 mV/decade of activity while the membrane consisting of OMP as electroactive ingredient showed a linearity in the concentration range $1.0 \times 10^{-4} - 1.0 \times 10^{-1}$ M with a slope of 32.4 mV/decade of activity. The potentials generated across these membranes are ascribed to the uptake of nickel ions on porphine. Plasticizers are frequently used to enhance the response characteristics, i.e. working concentration range, slope etc. The effect of addition of plasticizers to the membrane was, therefore, studied and significant improvement with regard to working concentration range and slope was observed. Addition of solvent mediators DBP and DBBP improved the performance of TBAP based membrane, exhibiting a working concentration range of $2.0 \times 10^{-5} - 1.0 \times 10^{-1}$ and $2.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M

with slopes of 28.5 and 29.6 mV/ decade of activity, respectively. The addition of solvent mediators DOP and CN had no significant improvement in the performance of the electrode.

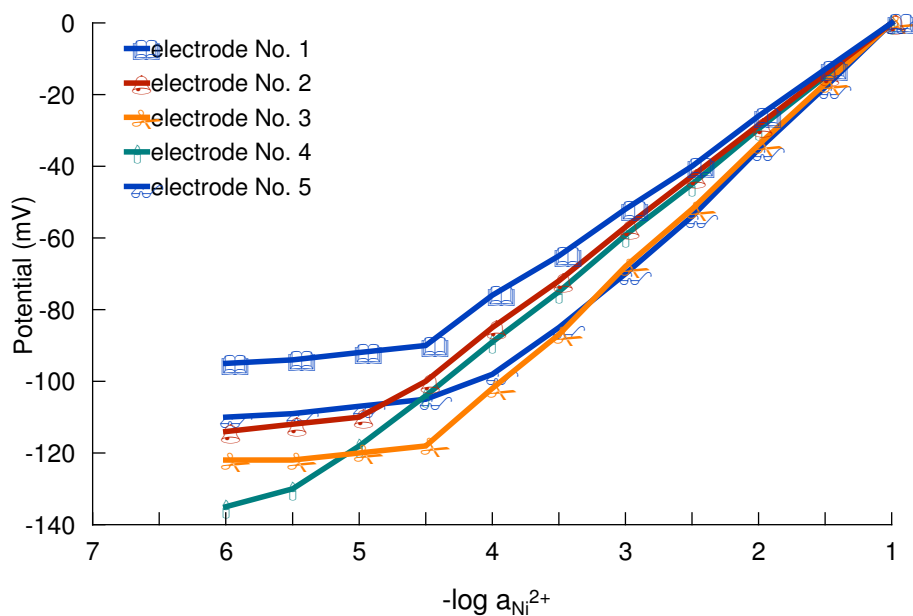


Figure 1: Variation of cell potential with Ni^{2+} concentration; PVC based membranes of TBAP without plasticizer (1), with plasticizers, DBP(2), DOP(3), DBBP(4) and CN(5).

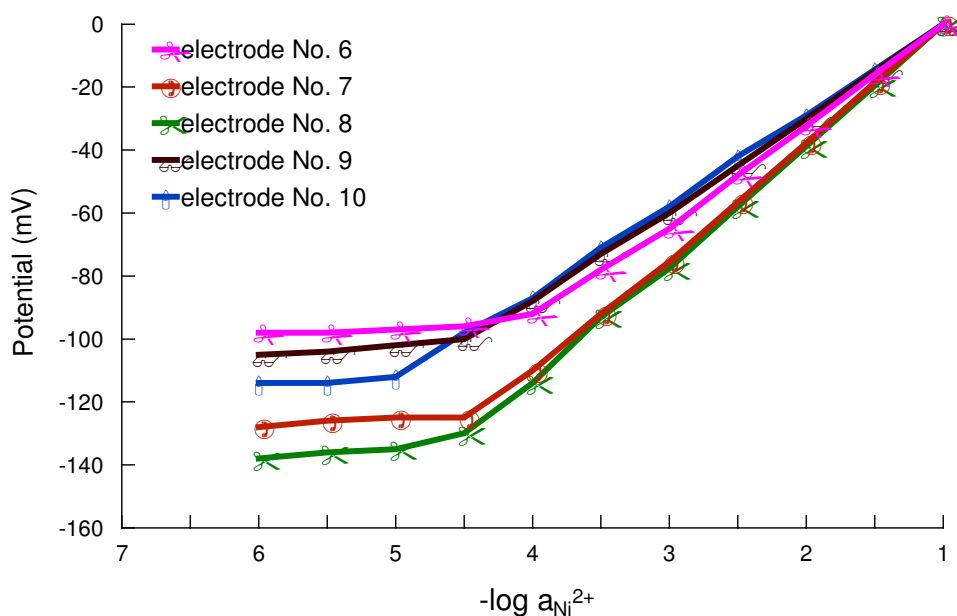


Figure 2: Variation of cell potential with Ni^{2+} concentration; PVC based membranes of OMP without plasticizer (6), with plasticizers, DBP(7), DOP(8), DBBP(9) and CN(10).

For OMP based membrane, addition of solvent mediators CN improved the electrode characteristic with a wide working concentration range of 1.0×10^{-5} – 1.0×10^{-1} M and a Nernstian slope value i.e., 29.0 mV/decade of activity while addition of other solvent mediators, DBP, DOP and DBBP slightly improved the performance of the electrode. Similar behaviour has been observed by us as well as other workers [18-20]. Repeated monitoring of potentials on the same portions of the sample gave a standard deviation of ± 0.3 mV. The standard deviation of the slope was ± 0.8 mV, which shows good reproducibility of the electrode assembly.

Response and lifetime

The response time of the membranes without solvent mediators was found to be approximately 1 min. The addition of solvent mediators improved the response time significantly with the best results shown by electrode nos. 4(15s) and 10(10s) (Fig.3) over the entire concentration range, the potentials remain constant for more than 5 min. Membrane electrode nos. 4 and 10 were henceforth selected for further studies. The membranes could be used over a period of six months without observing significant change in slope and response time and this could be corrected by re-equilibrating the membrane with 0.5 M Ni^{2+} solution for 2-3 days. During usage, they were stored in 0.1M Ni^{2+} solution.

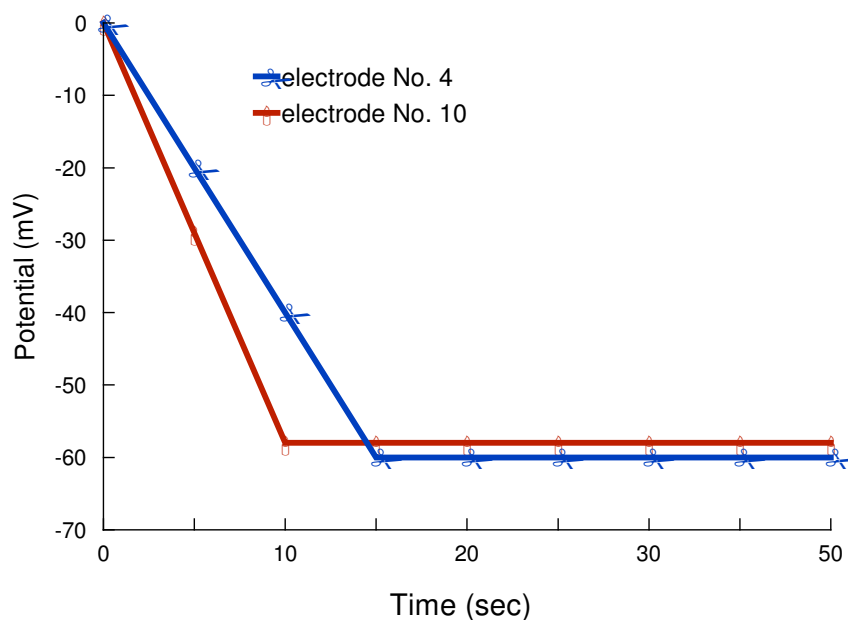


Figure 3: Response time of membrane electrode (Nos. 4 and 10) at 1.0×10^{-3} M Ni^{2+} concentration

pH and non-aqueous effect

The pH dependence of the electrodes potential for 1.0×10^{-3} and 1.0×10^{-4} M Ni^{2+} ions was tested over the pH range 1.0-8.0 (adjusted with HNO_3 or NaOH). It can be seen from Fig. 4 that the potentials

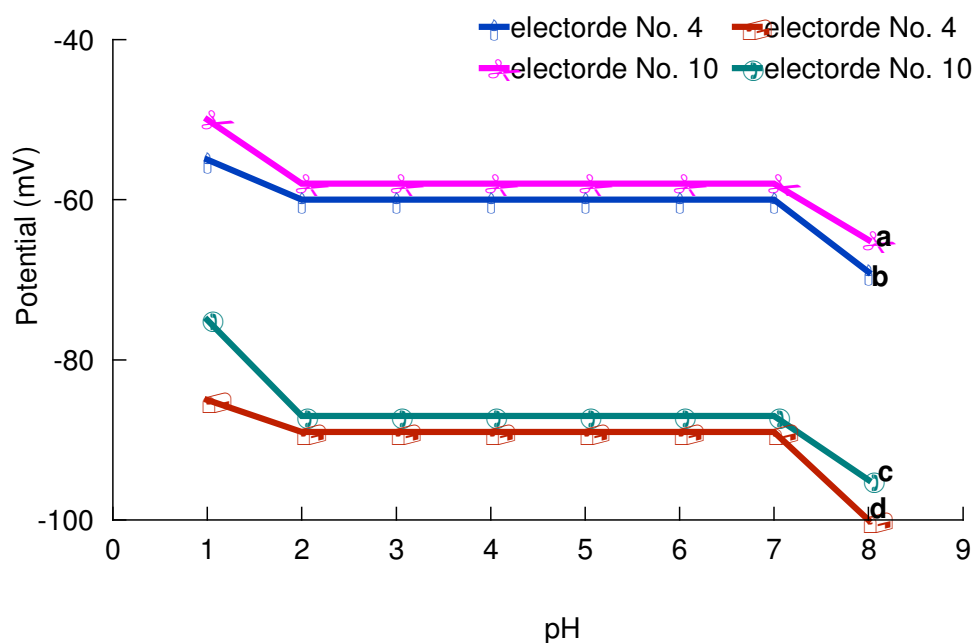


Figure 4: Effect of pH on cell potential of electrode Nos. 4 and 10 at $1.0 \times 10^{-3} \text{M}$ (a, b) and $1.0 \times 10^{-4} \text{M}$ (c, d) Ni^{2+} concentration.

are independent of pH in the range 2.0 to 7.0 and the same can be taken as the working pH range of the electrodes. Above and below these pH values, the sharp change in potentials may be due to the hydrolysis of Ni^{2+} and H^+ ions co-transport, respectively.

The utility of the membrane sensors was also investigated in partially non-aqueous media using methanol-water and ethanol-water mixtures. The membranes work satisfactorily in mixtures having up to 25% (v/v) non-aqueous content without showing any appreciable change in working concentration range or slope. However, above 25% non-aqueous content, potentials show drift with time.

Potentiometric selectivity

The usefulness of a sensor depends on its selectivity over other ions. It is the most important characteristic, which defines the extent to which the device may be successfully employed. Potentiometric selectivity was investigated by using IUPAC recommended Match Potential Method (MPM). The selectivity coefficient values of the order of 10^{-3} (Table 3) clearly indicate that the electrodes are selective to Ni^{2+} over a number of other cations (except for Co^{2+}). The electrode based on TBAP (electrode no. 4) is more selective to Ni^{2+} ions in comparison to that based on OMP (electrode no. 10).

Table 3: Selectivity coefficient values $K_{Ni^{2+},B}^{Pot}$ for Ni^{2+} -selective sensors (electrode nos. 4 and 10) as calculated by Match Potential Method

Interfering ion, B	Selectivity coefficients, $K_{Ni^{2+},B}^{Pot}$	
	Electrode No. 4	Electrode No. 10
NH_4^+	1.4×10^{-2}	2.0×10^{-2}
Na^+	9.0×10^{-2}	8.2×10^{-2}
K^+	5.3×10^{-2}	2.0×10^{-2}
Tl^+	3.2×10^{-2}	1.9×10^{-2}
Cs^+	4.7×10^{-2}	1.4×10^{-2}
Cu^{2+}	1.2×10^{-3}	1.8×10^{-3}
Ca^{2+}	1.4×10^{-3}	1.2×10^{-3}
Sr^{2+}	1.9×10^{-3}	2.5×10^{-3}
Ba^{2+}	2.0×10^{-3}	2.0×10^{-3}
Mg^{2+}	1.4×10^{-3}	2.8×10^{-3}
Co^{2+}	2.3×10^{-1}	4.8×10^{-1}
Cd^{2+}	2.6×10^{-3}	2.4×10^{-3}
Zn^{2+}	2.2×10^{-3}	2.6×10^{-3}
Hg^{2+}	1.4×10^{-3}	1.4×10^{-3}
Pb^{2+}	1.4×10^{-3}	1.6×10^{-3}
Fe^{3+}	1.8×10^{-3}	1.4×10^{-3}
Al^{3+}	2.0×10^{-3}	1.9×10^{-3}
Ce^{3+}	2.8×10^{-3}	1.8×10^{-3}

Co^{2+} ions are likely to cause some interference, as the selectivity coefficient values are high (0.23 and 0.48), however, if Co^{2+} is present in lower concentration these will not interfere, as selectivity is concentration dependent [21]. Thus, to determine the concentration of Co^{2+} ions, which can be tolerated in the determination of Ni^{2+} , some mixed runs studies were carried out [22-26]. It is seen from Fig. 5 that Co^{2+} ions at $\leq 5.0 \times 10^{-4}M$ cause no deviation in the original working concentration plot (as obtained in pure Ni^{2+} solution for electrode no. 4). Thus, the electrode can tolerate Co^{2+} ions up to the concentration $5.0 \times 10^{-4}M$ over the entire working concentrations range i.e., the presence of Co^{2+} ions does effect in the working of the electrode assembly. However, when Co^{2+} is present at higher concentrations, the electrode can be used to determine Ni^{2+} over reduced concentration range only. Fig. 5 shows that at 1.0×10^{-3} and $1.0 \times 10^{-2}M$ Co^{2+} ions, the electrode assembly can be used to determine Ni^{2+} in the concentration ranges 5.0×10^{-5} - $1.0 \times 10^{-1}M$ and 1.0×10^{-3} - $1.0 \times 10^{-1}M$, respectively.

Analytical applications

Estimation of Ni^{2+} in effluents

The sensor has been successfully used to determine the nickel in effluent discharged from local electroplating works. Four samples of plating waste were collected, filtered and stored. After adjusting the pH, the nickel in each sample was determined from potential measurement data using the calibration graph. The data presented in Table 4, indicates that the amount of nickel determined in

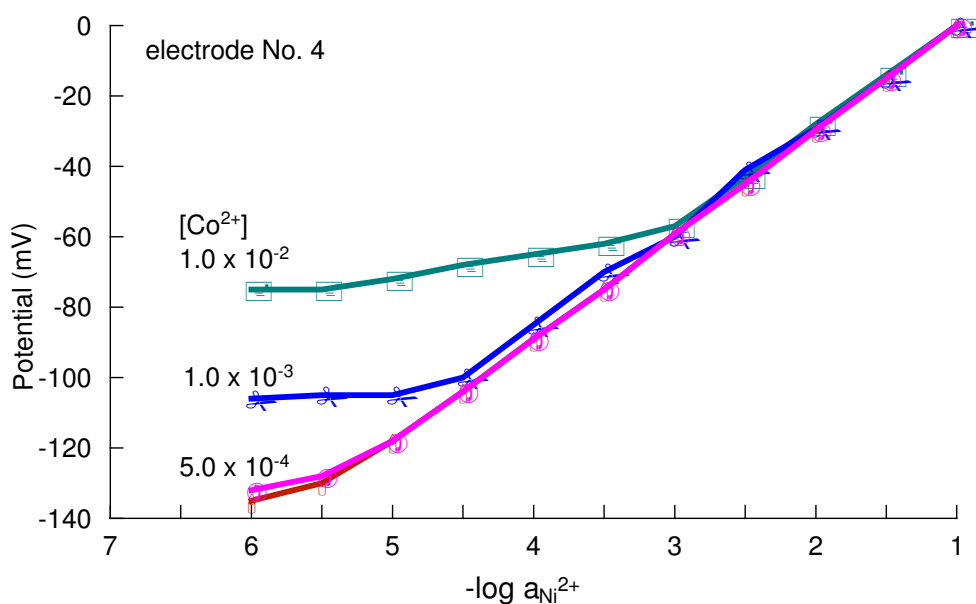


Figure 5: Variation of cell potential with Ni^{2+} concentration at different concentration levels of Co^{2+} ions (electrode no. 4).

Table 4 : Nickel concentration in effluents from electroplating industry as determined with AAS and membrane sensor

Samples	PH		Ni^{2+} as determined by AAS, mg l^{-1}	Ni^{2+} as determined by sensor 4, mg l^{-1}
	Found	after Adjustment		
1	6.80	3.70	44.0	47.0
2	6.65.	3.80	43.5	47.0
3	6.70	3.65	43.0	46.0
4	6.90	3.75	42.0	45.0

effluent by sensor is in close agreement with that determined by use of atomic absorption spectrophotometer (AAS).

Potentiometric titration

The analytical application of the electrode was tested by using it as an indicator electrode in the potentiometric titration of Ni^{2+} with EDTA. A 10 ml of $1.0 \times 10^{-3} \text{M}$ Ni^{2+} solution was titrated against $1.0 \times 10^{-2} \text{M}$ EDTA solution at pH 7.0 (Fig. 6). A sharp break point was observed which corresponds to the stoichiometry of Ni(II)-EDTA complex, therefore, Ni^{2+} can be determined potentiometrically using the proposed electrode assembly.

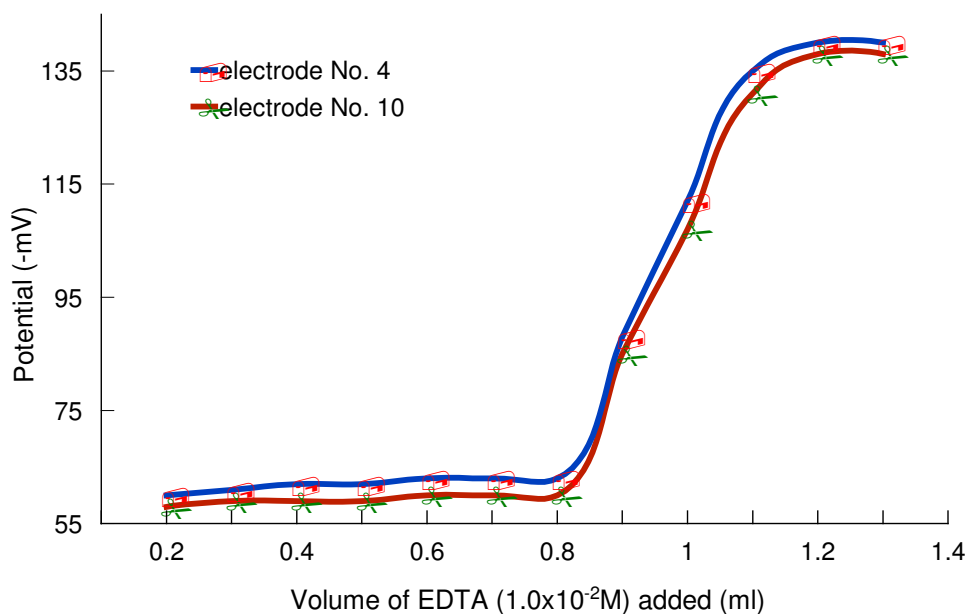


Figure 6: Potentiometric titration plot of Ni^{2+} ions (1.0×10^{-3} M) with EDTA (1.0×10^{-2} M), electrode no. 4 and electrode no. 10

Conclusion

The membrane assembly prepared using TBAP as membrane ingredient with plasticizers (DBBP) and anion excluder (NaTPB) exhibited linearity over a wide concentration range (2.0×10^{-6} – 1.0×10^{-1} M) with Nernstian slope (29.6 mV/ decade of activity), fast response time (15s), long lifetime (6 months) and selectivity (of the order of 10^{-3}) over a number of cations. The results presented in this paper show that the PVC matrix membrane of TBAP is superior sensor than those reported earlier [1-10, 14-16]. The results obtained during the investigation are indicative of the applicability of the sensor for evaluation of Ni^{2+} in effluents, wastewater and industrial wastes for subsequent use in building products.

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Sample Availability: Available from the authors.