Original Paper

A PVC plasticized membrane sensor for nickel ions

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Abstract. A new PVC membrane sensor, which is highly selective towards Ni (II) ions, has been developed using a thiophene-derivative Schiff base as the ionophore. The best performance was exhibited by the membrane having the composition percentage ratio of 5:3:61:31 (ionophore:NaTPB:DBP:PVC) (w/w), where NaTPB is the anion excluder, sodium tetraphenylborate and DBP is the plasticizing agent (dibutyl phthalate). The membrane exhibited a good Nernstian response for nickel ions over the concentration range of 1.0×10^{-1}–5.0×10^{-6} M (limit of detection is 1.8×10^{-6} M) with a slope of 29.5 ± 1.0 mV per decade of activity. It has a fast response time of <20 s and can be used for a period of 4 months with good reproducibility. The sensor is suitable for use in aqueous solutions of a wide pH range of 3.2–7.9. The sensor shows high selectivity to nickel ions over a large number of mono-, bi- and trivalent cations. It has been successfully used as an indicator electrode in the potentiometric titration of nickel ions against EDTA and also for direct determination of nickel content in real samples – wastewater samples from electroplating industries and Indian chocolates.

Key words: Nickel-selective sensor; PVC matrix; thiophene-derivative Schiff base; potentiometry.

Ion-selective electrodes are being used as an analytical tool in many chemical analyses. Plasticized PVC membranes have attracted much interest as the incorporated carrier can chemically recognize the ion of interest and thus be selective to that particular ion. The major challenge of research in this field has been the design and subsequent synthesis of the different types of ionophores.

The need for nickel monitoring is important due to its toxic nature. It is widely used in electroplating industries and many catalytic processes. It is found in low concentrations in hydrogenated vegetable oils, milk, chocolate, cornmeal, cottonseed, oatmeal, nuts, soy beans, raw meat etc. Acute pneumonitis, dermatitis, asthma, nasal and lung cancer are the common ailments seen due to nickel toxicity [1]. The carcinogenic action of nickel and its salts has been studied with the help of animal experiments [2]. Conventional methods, such as the gravimetric method using dimethylglyoxime [3] or the spectrophotometric method [4], are not only time-consuming but also have some practical inconveniences. Although a number of ion-selective electrodes have been reported in the literature [5–16], most of them suffer from one or more drawbacks.

In continuation to our work on metal analysis at trace level [17, 18], this paper presents the results of a PVC matrix membrane sensor incorporating a thiophene derivative Schiff base as ionophore and its use in the determination of nickel in real samples. The proposed sensor could be effectively applied in the direct determination of nickel content in real samples.

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Experimental

Reagents

All reagents used were of analytical reagent grade. Thiophene-2-carboxaldehyde, ethylene diamine, Dioctyl phthalate (DOP), Dioctyl sebacate (DOS), Dioctyl adipate (DOA), Dimethyl sebacate (DMS), Dibutyl phthalate (DBP) and sodium tetraphenylborate (NaTPB) were obtained from Lancaster (UK) and were used without any further purification. The metal salts, high relative molecular weight PVC, tetrakis-[-3,4-bis(trifluoromethyl)phenyl] borate and dibutyl sebacate (DBS) were purchased from Merck and used without further purification. Tetrahydrofuran (THF), oleic acid and methanol were purchased from s.d. fine-chem ltd, India, and were distilled before use. All metal salt solutions were prepared in doubly distilled water, and solutions of different concentrations were made by serial dilution of the 0.1 M stock solutions.

Electrode preparation

The Schiff base, (1E,4E)-N^1,N^2-bis(thiophen-2-yl)methylene)-ethane-1,2-diamine (TED), was synthesized by refluxing thiophene-2-carboxaldehyde (0.02 mol, 0.74 g) and ethylenediamine (0.01 mol, 0.60 g) in 20 mL methanol as reported [19]. The structure of the product was confirmed by analytical and spectrophotometric methods [20] (Fig. 1).

A mixture of PVC, plasticizer (DBP), and the anion excluder (NaTPB) at a ratio of 31:61:3 (w/w%) was dissolved in 5–7 mL of THF. To this mixture, the ionophore (5%) was added, and the solution was mixed well. It was then poured into a petri dish and allowed to evaporate for 24 h. Small disc-shaped membranes were cut out and glued to one end of a hollow Pyrex glass tube using Araldite. The membrane was conditioned by immersing it in a 1.0×10^{-1} M nickel nitrate solution for 2 days.

Potential measurement and calibration

Potentials were measured at $27 \pm 0.1\,^\circ$C on a Systronics digital ion meter. An Ag/AgCl reference electrode was used in conjunction
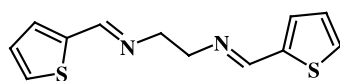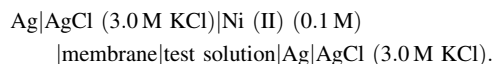

Fig. 1. Structure of TED

with the developed Ni (II) sensor. The cell assembly for potentiometric measurements can be represented as follows:

Ag|AgCl (3.0 M KCl)|Ni (II) (0.1 M)
|membrane|test solution|Ag|AgCl (3.0 M KCl).

The performance of the developed Ni (II) sensor was investigated by measuring the potential in Ni (II) solutions prepared in the concentration range of 1.0×10^{-1}–1.0×10^{-7} M. The solutions were stirred, and a stable potential reading was taken.

Preparation of chocolate samples

The solution of chocolate sample was prepared as reported earlier [21]. The pH was adjusted to 5.0.

The solution was suitably diluted, and the nickel content was determined using the ICP technique on Thermo Elemental, IRIS INTREPID II XSP DUO.

Results and discussion

The potential response of the developed sensor was tested for different cations, and it was found that the sensor was highly responsive to nickel ions compared to other ions, which may be attributed to the ion-exchange process at the membrane-sample interface.

The optimum membrane composition was determined, and this membrane was then used for testing the membrane characteristics.

Effect of plasticizers and ionophore compositions

A number of membrane compositions were investigated by varying the ratio of plasticizers and the ionophore. The results are given in Table 1. A membrane without plasticizer was first prepared and its effect was studied (sensor A). It was observed that sensor C with DBP as plasticizer was gave the best response in terms of slope and concentration range. Generally, the use of plasticizers improves certain characteristics

Table 1. Optimization of membrane ingredients[a]

Sensor	% (w/w) composition of each membrane				Working concentration range (M)	Slope (mV/decade of activity)	Response time (s)
	PVC	TED	Plasticizer	NaTPB			
A	92	5	0	3	1.0×10^{-1}–1.0×10^{-5}	20.3 (± 1.0)	40
B	31	2	DBP, 64	3	1.0×10^{-1}–2.6×10^{-6}	22.5 (± 1.0)	11
C	31	5	DBP, 61	3	1.0×10^{-1}–1.8×10^{-6}	29.5 (± 1.0)	18
D	31	7	DBP, 59	3	1.0×10^{-1}–5.7×10^{-6}	21.4 (± 1.0)	25
E	31	5	DOP, 61	3	1.0×10^{-1}–1.6×10^{-5}	19.8 (± 1.0)	30
F	31	5	DOA, 61	3	1.0×10^{-1}–7.2×10^{-5}	23.5 (± 1.0)	30
G	31	5	DMS, 61	3	1.0×10^{-1}–9.3×10^{-4}	12.8 (± 1.0)	22
H	31	5	DBS, 61	3	1.0×10^{-1}–1.0×10^{-5}	12.9 (± 1.0)	20
I	31	5	DOS, 61	3	1.0×10^{-1}–2.2×10^{-5}	13.0 (± 1.0)	30

[a] Values in parentheses are RSDs based on three replicates.

of the membranes, and in some cases, the slopes are affected adversely. Here, the slopes in the case of the sebacates are highly sub-Nernstian. Also, in neutral carrier membranes, plasticizers that are compatible with the ionophore provide a smooth surface to the membrane and hence enhance the response characteristics [22]. The potentiometric response of the sensor towards Ni (II) ions is found to be dependent on the concentration of the ionophore used. Different compositions (w/w%) of ionophore were also tried to obtain the composition that gives the best response characteristics. The maximum sensitivity was observed for 5 wt.% of ionophore.

Sodium tetraphenylborate (NaTPB), oleic acid and tetrakis-[-3,4-bis(trifluoromethyl)phenyl] borate were taken to investigate the effect of the anionic excluders. There is a great improvement in the potentiometric response upon addition of the anionic excluder NaTPB (3 wt.%), while the others gave a sub-Nernstian response. Such anionic excluders are beneficial to both neutral and charged carrier-based sensors [23, 24]. In the case of sensors based on neutral ionophores, these ionic sites with a charge sign opposite to that of the primary ion are necessary for the sensor to give the Nernstian response [25–28]. Also, these lipophilic excluders help to reduce the membrane resistance [29], improve the selectivity [30–32] and reduce interference from sample anions [33, 34]. However, in the case of charged carrier-based sensors, the charge sign of the ionic sites that gives the highest potentiometric selectivities depends on the charge of the ionophore and that of the primary and interfering ions [28]. Thus, the effect of the charge of the added ionic sites in charged carrier-based sensors is different from that of the neutral ionophore-based sensors [35, 36].

Response characteristics of the electrodes

The response characteristics of the Ni (II) sensor are shown in Table 2. The potential response of the Ni (II) sensor to varying concentrations of Ni (II) ions was examined. The calibration graph for the Ni (II) sensor is shown in Fig. 2. It indicates a linear range from 1.0×10^{-1}–5.0×10^{-6} M with a Nernstian slope of 29.5 ± 1.0 mV per decade of activity.

The detection limit was calculated from the graph by the intersection of the two extrapolated linear segments of the calibration plot and was found to be 1.8×10^{-6} M.

Table 2. Response characteristics of sensor C

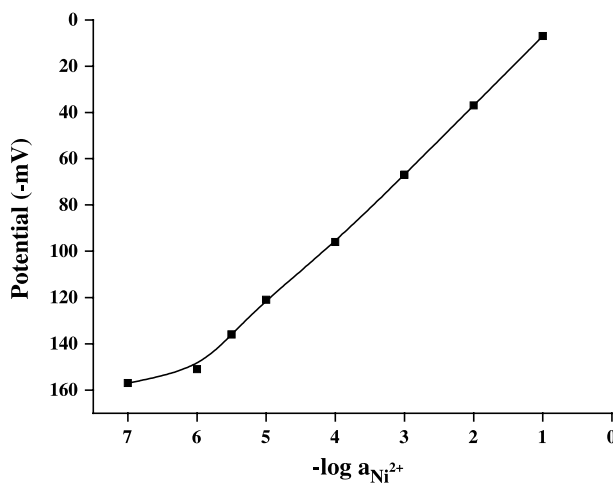| Parameter	Characteristics
Working concentration range	1.0×10^{-1}–5.0×10^{-6} M
Slope	29.5 ± 1.0 mV per decade of activity
Detection limit	1.8×10^{-6} M
Response time	<20 s
pH range	3.2–7.9
Shelf life	4 months

Fig. 2. Calibration plot of sensor C based on TED at pH 5.5

The response time of the Ni (II) sensor, which is the average time for the sensor to reach a potential within ± 1 mV of its final equilibrium value, was found to be less than 20 s.

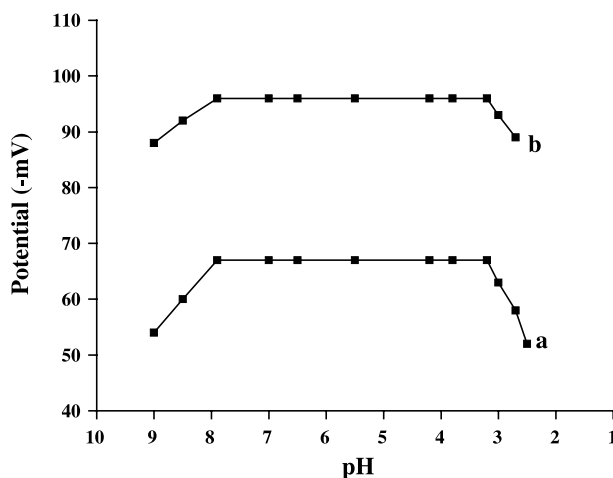The pH dependence of the developed Ni (II) sensor was examined for the 1.0×10^{-3} M and 1.0×10^{-4} M

Fig. 3. Effect of pH on the cell potential of sensor C based on a TED at 1.0×10^{-3} M (*a*) and 1.0×10^{-4} M (*b*)

solutions over the pH range of 2.0–9.0. The pH was adjusted by adding drops of 1.0 M HNO_3 or NH_3. The results presented in Fig. 3 reveal that the potentials are independent of pH in the range of 3.2–7.9, and it is taken as the working pH range of the Ni (II) sensor. Variation of potentials above and below these pH values can be related to hydrolysis of Ni (II) (at higher pH) and the competition of H^+ with Ni (II) (at lower pH values).

The sensor was used over a period of 4 months without observing any significant change in the potentials.

Potentiometric selectivity

A sensor's essential quality is that it is selective towards one particular ion over all the other ions. The selectivity of the developed Ni (II) sensor was determined using the fixed interference method [37, 38] and the following equation:

$$K_{A,B}^{pot} = a_A/(a_B)^{z_A/z_B}$$

where $K_{A,B}^{pot}$ is the selectivity coefficient; a_A is the value obtained from the intersection of the extrapolated linear portions of the plot of EMF values versus the logarithm of the activity of the primary ion; a_B is the activity of the interfering ion, which is fixed; $z_A \& z_B$ are charge numbers of the primary ion, A, and of the interfering ion, B.

The selectivity coefficients were determined at a 1.0×10^{-2} M concentration of foreign ions. The selectivity coefficient values are shown in Table 3. They

Table 3. Selectivity coefficients of sensor C using the fixed interference method at a 1.0×10^{-2} M concentration of interfering ions

Interfering ion (X)	$K_{Ni^{2+},X}^{pot}$
Na^+	1.4×10^{-2}
K^+	1.7×10^{-2}
Mg^{2+}	4.2×10^{-3}
Ca^{2+}	2.5×10^{-3}
Ba^{2+}	1.9×10^{-3}
Sr^{2+}	2.4×10^{-3}
Cr^{3+}	5.3×10^{-3}
Mn^{2+}	7.9×10^{-3}
Co^{2+}	6.4×10^{-3}
Fe^{2+}	9.7×10^{-3}
Cu^{2+}	8.8×10^{-3}
Zn^{2+}	4.7×10^{-3}
Sn^{2+}	6.6×10^{-3}
Hg^{2+}	3.8×10^{-3}
Pb^{2+}	1.1×10^{-2}
Ag^+	1.3×10^{-2}
Cd^{2+}	5.0×10^{-3}

Table 4. Determination of the Ni (II) content in real samples

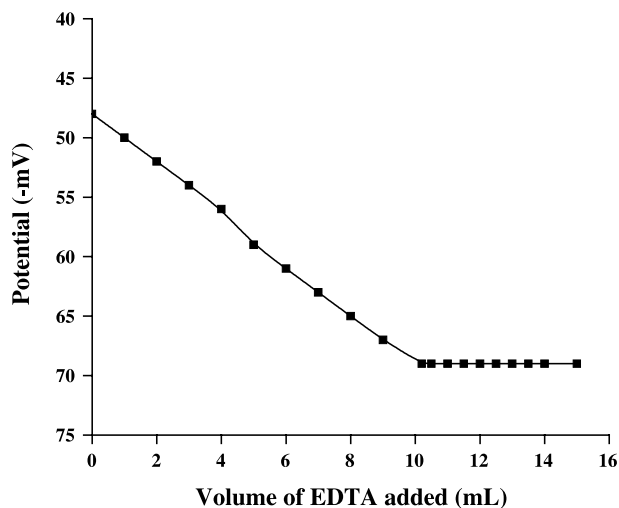| Sample	Sensor C (mg kg^{-1})*	ICP-AES (mg kg^{-1})
Nestle Milky Bar	1.19 ± 0.02	1.18
Cadbury Diary Milk	1.32 ± 0.01	1.30
Effluent sample	2.94 ± 0.02	2.93

* Average of three replicates.

Fig. 4. Potentiometric titration curve of 20.0 mL of 5.0×10^{-3} M Ni (II) solution with 1.0×10^{-2} M EDTA using sensor C as an indicator electrode

indicate that the developed Ni (II) sensor is selective towards the Ni (II) ion over a number of cations.

Analytical applications

The developed Ni (II) sensor was successfully applied to the determination of nickel in some branded Indian chocolates and wastewater sample from electroplating industries. The results are comparable to those obtained by ICP-AES and they are listed in Table 4.

The developed Ni (II) sensor was also successfully applied as an indicator electrode in conjunction with Ag/AgCl in the potentiometric titration of Ni (II) solution with EDTA. The titration curve is shown in Fig. 4. The plot is not of sigmoid shape but the sharp break point corresponds to the stoichiometry of the Ni-EDTA complex.

Conclusions

The membrane sensor incorporating a thiophene-derivative Schiff base as the ionophore has been used in the preparation of a Ni (II) sensor. The developed

Table 5. Comparison of characteristics of the proposed sensor with some reported sensors

Sensor no.	Working concentration range (M)	Slope (mV/decade of activity)	pH range	Life time (months)	Reference no.
1	1.0×10^{-1}–1.0×10^{-3} M	non-Nernstian	NM*	NM	[5]
2	1.0×10^{-1}–5.0×10^{-5} M	non Nernstian	3.5–6.5	5–6	[6]
3	1.0×10^{-1}–5.0×10^{-5} M	non-Nernstian	3.5–8.0	NM	[7]
4	1.2×10^{-2}–6.3×10^{-4} M	near Nernstian	NM	NM	[8]
5	1.0×10^{-1}–4.0×10^{-5} M	Nernstian	3.0–7.5	2	[10]
6	5.5×10^{-3}–2.0×10^{-6} M	Nernstian	4.0–8.0	1.5	[12]
7	1.0×10^{-2}–1.0×10^{-7} M	near Nernstian	4.0–7.0	3	[14]
8	1.0×10^{-1}–2.0×10^{-6} M	non-Nernstian	2.0–7.0	6	[15]
9	1.0×10^{-2}–5.0×10^{-6} M	Nernstian	3.5–7.5	1	[16]
10	1.0×10^{-1}–5.0×10^{-6} M	Nernstian	3.2–7.9	4	proposed sensor

* *NM* Not mentioned.

sensor is found to have good characteristics in terms of slope, concentration range, detection limit, response time, pH range and shelf life. It is also found to be highly selective over a number of cations. A comparison of the characteristics of the presently developed sensor with that of some of the reported sensors is presented in Table 5. An examination of the Table reveals that the proposed sensor is superior in terms of working concentration range [5–8, 10, 12, 15, 16], slope [5–8, 14, 15], life time [5, 7, 8, 10, 12] and pH range [5–8, 12, 14, 16]. In addition, the developed sensor can be used in the determination of Ni (II) in real samples – wastewater from electroplating plants and chocolates.

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