Chemistry

A DYNAMIC NICKEL SELECTIVE POLY(VINYL CHLORIDE) MEMBRANE BASED ON N-(4-(2-THIENYL)-1,3-THIAZOL-2-YL) THIOUREA AS IONOPHORE

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ABSTRACT

In the present study, N-(4-(2-thienyl)-1,3-thiazol-2-yl)thiourea (ionophore) has been used as an ionic carrier for the fabrication of Ni(II) selective poly(vinyl chloride) membrane electrode. The electrode based on bis-(2-ethylhexyl) sebacate(BEHS) used as plasticizer was found to be the best over other tested plasticizers. The electrode has a wide linear concentration range of $4.0 \times 10^{-8} – 1.0 \times 10^{-1}$ M, fast response time (5s) and wide pH range (2.7 – 8.8). The electrode was successfully used as an indicator electrode for the titration of Ni(II) ion solution with standard EDTA solution.

Keywords: Ion-selective electrode, ionophore, Nickel, potentiometry.

INTRODUCTION

Nickel is essential for human beings and many other organisms. It appears to be involved in carbohydrate metabolism. However, the higher concentration can be toxic for various organisms and plants. Nickel is found in coffee, meat, tea, nuts, even in Coca Cola. Nickel is also used as catalyst in various chemical processes. Therefore determination of nickel is very important particularly in the field of medical, environmental and food industry [1-5].

Ion-selective electrodes based on neutral ionophores are the good analytical tools for the selective determination of ions in various samples since they measure the activity instead of concentration [6,7]. There are few nickel selective electrodes available in the literature, most of them have narrow linear concentration range and higher detection limit or slow response

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mechanism. The main objective of this study is to construct the nickel selective electrode with better response characters. In this research, N-(4-(2-thienyl)-1,3-thiazol-2-yl) thiourea has been used as ionophore for selective determination of nickel. The selectivity of the electrode towards Ni(II) ion over other tested cations was calculated by matched potential method (MPM).

EXPERIMENTAL

Reagents

Reagent grade dimethyl phthalate (DMP), di-isobutyl phthalate (DBP), dioctyl phthalate (DOP), bis-(2-ethylhexyl) sebacate (BEHS) high-molecular weight polyvinylchloride (PVC), tetrahydrofuran (THF) and sodium tetraphenyl borate (NaTPB) were obtained from Sigma-Aldrich (Munich, Germany). The chloride and nitrate salts of cations used were purchased from Merck and Aldrich. All solutions were prepared using doubly distilled de-ionized water.

Ionophore

The heterocyclic compound N-(4-(2-thienyl)-1,3-thiazol-2-yl)thiourea contains strong electron donating atoms and is soluble in water. So, it may bind the metal ions in the solution to form chelates. N-(4-(2-thienyl)-1,3-thiazol-2-yl)thiourea was used as an ionophore for the construction of Ni(II) selective polymeric membrane electrode. The ionophore (Figure 1) was bought from Sigma-Aldrich and used without further purification.
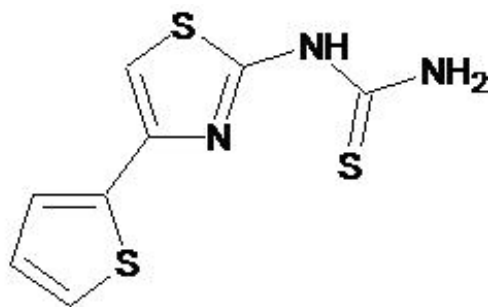

Figure 1: N-(4-(2-thienyl)-1, 3-thiazol-2-yl)thiourea (ionophore)

Preparation of membrane.

The polymeric membrane of ionophore with other membrane components was prepared by reported method [8, 9].The membrane components i.e. ionophore, anionic additive (NaTPB), plasticizers (i.e. DMP, DBP, DOS and BEHS) and PVC powder were dissolved in 5 ml tetrahydrofuran (THF). The solution was mixed well. The resulting mixture was transferred into a glass dish of 5 cm diameter, and the solvent was evaporated slowly until the concentrated mixture was left. A Pyrex glass tube was then dipped into the mixture for about 10s, in order to

achieve a transparent membrane. In the end, the tube was removed from the solution and kept at room temperature for 12h.Later,it was filled with an internal filling solution (1.0×10^{-3} M). The electrode was conditioned for 24h by soaking it in a 1.0×10^{-3} M Ni(II) solution.

All EMF measurements were carried out with the following assembly:

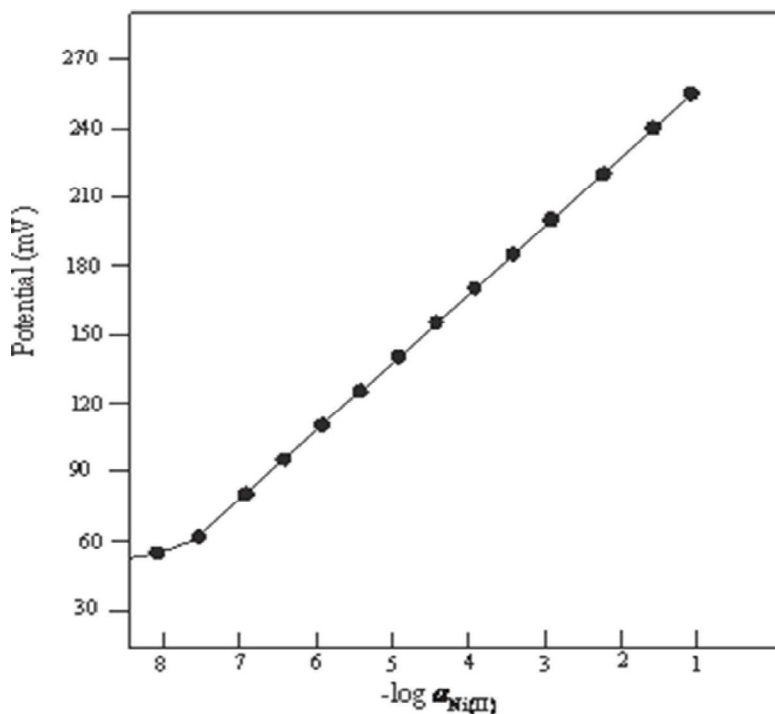**Ag–AgCl 1.0 × 10^{-3} M Ni(II) | PVC membrane: test solution| Ag - AgCl, KCl (satd).**

RESULTS AND DISCUSSION

The composition of membrane electrode is very important to get the optimum response characters. Therefore membranes of various compositions and plasticizers were prepared and their response characters were investigated [10, 11].After several experiments it was observed that the membrane electrode based on N-(4-(2-thienyl)-1,3-thiazol-2-yl)thiourea as ionophore shows the best sensitive response for Ni(II) over other tested cations. This is likely due to quick exchange kinetics between ionophore and Ni(II) ion.

The plasticizer as membrane component plays a significant role in influencing the selectivity and sensitivity of membrane electrode. Therefore the effects of various plasticizers were investigated and the results are summarized in Table 1.

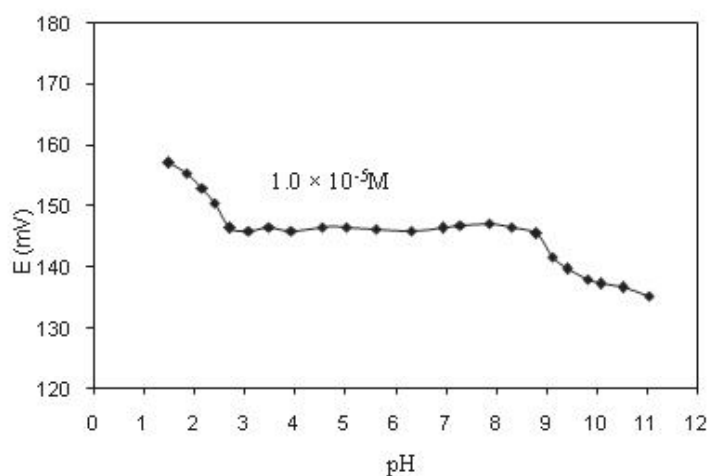**Table 1: Optimization of the membrane ingredients**

Sensor No.	Composition (wt %)				Concentration range (M)	Slope (mV/decade)
	PVC	Plasticizer	NaTPB	Iono-phore		
1	31	DMP, 66	1	2	6.0×10^{-5}-1.0×10^{-1}	24.3 ± 0.3
2	31	DBP, 66	1	2	2.0×10^{-5}-1.0×10^{-1}	24.4 ± 0.5
3	31	DOP, 66	1	2	1.0×10^{-6}-1.0×10^{-1}	25.6 ± 0.3
4	31	BEHS, 66	1	2	4.0×10^{-8}-1.0×10^{-1}	30.2 ± 0.4
5	30	BEHS, 68	0	2	8.0×10^{-8}-1.0×10^{-1}	15.6 ± 0.2
6	30.5	BEHS, 67	0.5	2	6.2×10^{-8}-1.0×10^{-1}	29.8 ± 0.5
7	31	BEHS, 65	2	2	1.0×10^{-7}-1.0×10^{-1}	28.7 ± 0.4
8	30	BEHS, 67	1	2	4.0×10^{-8}-1.0×10^{-1}	30.2 ± 0.4

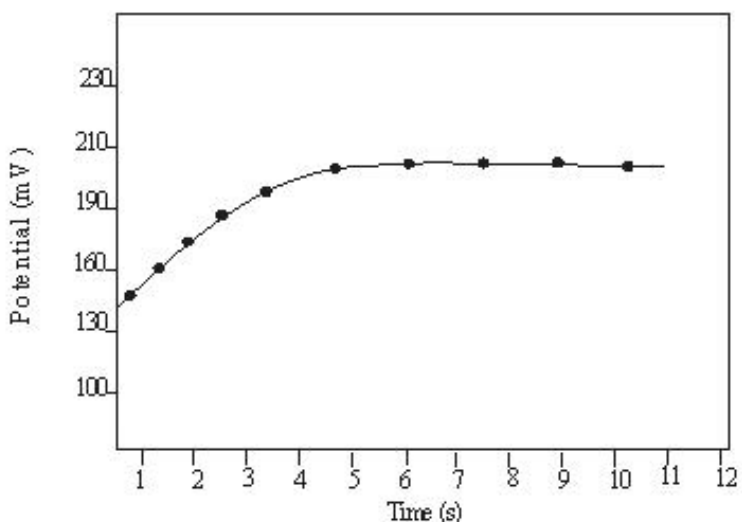**Figure 2: Calibration curve for Electrode No. 4**

The background potential of membrane electrode was investigated in terms of potential response of membrane without ionophore. The electrode without ionophore (No. 5) does not have significant response towards tested ion. The presence of plasticizer provides the suitable environment for the complexation of ligand with metal ions. The Electrodes (No. 1 and 2) based on DMP and DBP as plasticizer have a linear concentration range of the order of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$M, while Electrode No. 3 based on DOP as plasticizer was found to work satisfactorily in the concentration range of $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M. However, the membranes with the composition of 31% PVC, 2% ionophore, 1% NaTPB and 66% BEHS exhibit a Nernstian potential response in the linear concentration range of $4.0 \times 10^{-8} - 1.0 \times 10^{-1}$M for Ni(II) ion. The Electrode No. 4 has a lower detection limit of 1.0×10^{-8} M for Ni(II) ion. The presence of 1% anionic additive (NaTPB) was found suitable for the smooth functioning of the membrane electrode. The lipohilic anionic additive was used to decrease the interference caused by anions. The amount of anionic additive more than 1% interferes in the functioning of membrane electrode due to competition kinetics of additive and ionophore.

The effect of pH on response characters was investigated in the range of 0 – 12. It was observed that the potential of membrane electrode remains same in a pH range of 2.7 – 8.8. Thus, the presence of hydrogen ion or hydroxyl ion does not interfere in the complexation kinetics of ionophore with Ni(II) ion within this range(Figure 3). However significant potential drift was observed beyond this pH range. Thus the Electrode No. 4 can be successfully used for the determination of Ni(II) ion in a pH range of 2.7 – 8.8.

Figure 3: pH effect of the test solution on Electrode No. 4

The static response time of the membrane was measured at 0.001 M concentration (Figure 4.). It was observed that the Electrode No. 4 reached the equilibrium value of potential response in a very short time of about 5s. To investigate the reversibility and reproducibility of membrane electrode, the response time was also calculated by changing the concentration of test solution for lower to higher and then from higher to lower. The average response time for lower to higher concentration was about 5 seconds and for higher to lower concentration it was about 8 seconds.

Figure 4: Response time for Electrode No. 4

The selectivity of membrane Electrode No. 4 towards Ni(II) ion over other interfering ions was investigated by matched potential method (MPM) [12-13]. According to this method, a specified activity of the primary ion (A) was added to a reference solution and the potential is measured. In a separate experiment, an interfering ion (B) was successively added to an identical reference solution (containing the primary ion), until the measured potential matches the one obtained with the primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The results are listed in Table 2. The selectivity coefficients for the all mono, divalent and trivalent ions are smaller than 4.3×10^{-3} and they cannot disturb the function of Ni(II) selective Electrode No. 1.

The response characters of the membrane electrode were also compared with the previously reported Ni(II) selective electrodes (Table 3). The data presented in the Table 3 shows that the proposed electrode is superior to previously reported electrodes.

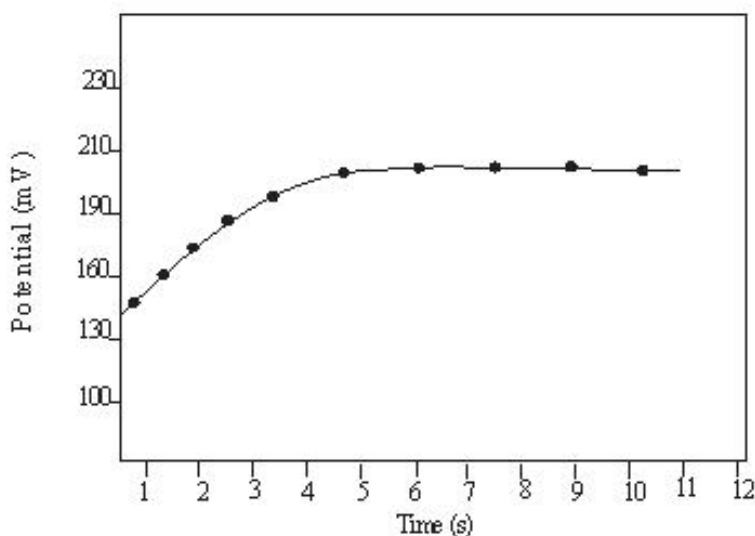**Table 2: Selectivity coefficient value for Ni (II) selective Electrode No. 4**

Interfering ion (B)	$K^{MPM}_{Ni^{2+},M^{n+}}$
Al^{3+}	3.5×10^{-3}
Zn^{2+}	4.1×10^{-3}
Mn^{2+}	4.3×10^{-3}
Co^{2+}	2.6×10^{-3}
Cu^+	2.0×10^{-3}
Cr^{3+}	3.2×10^{-4}
Fe^{3+}	8.3×10^{-4}
Na^+	3.7×10^{-4}
K^+	3.6×10^{-4}
Ca^{2+}	1.4×10^{-4}
Cu^{2+}	2.2×10^{-4}
Cd^{2+}	2.4×10^{-4}
Ba^{2+}	1.7×10^{-4}
Pb^{2+}	1.8×10^{-4}

Table 3: Comparative analysis of proposed electrode (No. 1) with the reported Electrode

Ionophore	Working Conc. range (M)	Slope (mV/decade of activity)	pH range	Response time (sec)	Detection limit (M)	Ref
1-(1H-indol-1-yl)-N-(thiophen-2-ylmethyl) ethanimine	4×10^{-8} -1.0×10^{-1}	30.40 ± 0.3	$2.7 - 8.8$	5	1.0×10^{-8}	This work
1,5-diphenyl thiocarbazone	5.0×10^{-6} -1.0×10^{-2}	29.50 ± 1	4.15-7.8	-	2.8×10^{-6}	[14]
benzylbis (thiosemicarbazone)	1.0×10^{-7} -1.0×10^{-2}	-	-	15	4.0×10^{-8}	[15]
N-[2-thienyl methilidene]-2-aminoethanol (TN)	1.0×10^{-6} -1.0×10^{-1}	29.0 ± 1	4.2-8.3	-	1.0×10^{-6}	[17]
N,N -bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine	2.0×10^{-7} -1.0×10^{-2}	30.0 ± 1	4.5-9.0	<10	8.0×10^{-8}	[18]

ANALYTICAL APPLICATIONS:

The electrode was found to work well under the laboratory conditions and the proposed Ni(II) selective electrode was used as an indicator electrode in the titration of a 1.0×10^{-2}M Ni(II) ion solution with a standard 1.0×10^{-2}M EDTA. The resulting titration curve is shown in Figure 5. The figure has sharp inflation point which indicates that the proposed electrode can be used as an indicator electrode for the determination of Ni(II) ion.

Figure 5: Titration Curve

The proposed Electrode No. 4 was also used for the determination of Ni(II)ions in tap water and river water samples. The results of triplicate measurements are summarized in Table 3. As can be seen from Table 3, the amounts of the Ni(II) ions, which were added to the water sample solutions (0.15-0.5 mg/ml), could be determined by the electrode with relatively good accuracy (Table 4.)

Table 4. Determination of Ni(II) spiked in tap and river water samples by use of the proposed electrode

Sample	Ni(II) added (mg/ml)	Found (mg/ml)	Recovery (%)
River water	0.20 0.45	(0.21[a] ± 0.03) (0.48 ± 0.02)	105 107
Tap water	0.15 0.50	(0.16 ± 0.02) (0.54 ± 0.04)	107 108

Results are based on three measurements

CONCLUSION

A highly selective and sensitive poly(vinyl chloride) membrane electrode has been fabricated for the selective determination of Ni(II) ion. The Electrode No. 4 has a wide linear concentration range of $4.0 \times 10^{-8} – 1.0 \times 10^{-1}$ M with Nernstian slope of 30.2 ± 0.4 (mV/decay of activity). The electrode could be used in a pH range of 2.7 to 8.8 and has a fast response time of about 5 second. The electrode was also used as an indicator electrode for the titration

of Ni (II) ion with standard EDTA solution and for the determination of Ni (II) ion various water samples.

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