

Full Paper

Application of a Hydrazone Derivative in the Construction of a Polymeric Membrane Sensor for Nickel Ions

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Abstract- Based on the results of the complexation reaction between 1-acenaphthoquinone 1-thiosemicarbazone (L) and some metal ions in methanol, it was found that the ligand forms a stable 1:1 complex with Ni²⁺ ions among the range of ions tested. Accordingly, this hydrazone derivative was chosen and evaluated as an ionophore for use in the construction of polymeric membrane sensors with selectivity towards Ni ions. The resulting membrane electrode, under optimal conditions, had a Nernstian slope of 29.5±0.2 mV/decade over a wide concentration window of 1.0×10⁻⁶-1.0×10⁻¹ M, and its limit of detection was as low as 5.0×10⁻⁷ M. The electrode had very good selectivity coefficients for other commonly occurring cations in its response range. The proposed potentiometric sensors possess response times of 10 sec, good reversibility, and are applicable for over 12 weeks after their first use. The response of the membrane sensor was pH-independent in the pH range of 5.0–8.0, and it was used in the analysis of nickel ions concentration in real water samples with satisfactory results. The electrode was also used in the potentiometric titration of nickel ions using a standard ethylenediaminetetraacetic acid (EDTA) solution at pH=6.0.

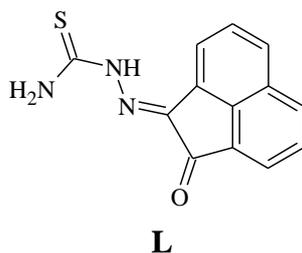
Keywords- Ni-selective electrode; Potentiometry, Sensor; PVC membrane; Hydrazone derivative

1. INTRODUCTION

Nickel has been associated with various health conditions in humans, including dermatitis, asthma, and respiratory system cancer. The element is present in soil and water, due to the widespread applications of its compounds in many alloys and catalysts. Nickel is also an ingredient of urease and is, therefore, an essential element for plants and animals [1-4]. Accordingly, the analysis of this element is key in various food and environmental evaluations. Precise analysis of nickel compounds in various environmental samples is a function of concentration and interferences from the sample matrix. One approach to address these issues is the use of various preconcentration and separation techniques prior to analyses [5-15]. Yet, these steps are either costly and time-intensive or require complex instrumentation. In this light, various methods have been developed to overcome these shortcomings and allow for dependable analyses of different samples.

PVC-membrane ion-selective sensors, based on the application of ionophores are robust analytical tools for the precise analysis of various ionic species in complex matrices. It is the ionophore that determines the selectivity of ion-selective electrodes, which is their key feature. Due to the ability of Schiff's bases in forming stable and selective chelates with metal ions, they are among the most commonly used molecules used as ionophores in cation-selective PVC-based sensors [16-19]. Many recent reports describe the development of selective ion sensors for various metal ions [20-34].

This article describes the development of a polymeric membrane electrode (PME) for Ni^{2+} using 1-acenaphthoquinone 1-thiosemicarbazone, **L** (Scheme 1), as an ionophore with nitrogen, oxygen, and sulfur donors. To evaluate the complexation characters of the ionophore, spectrophotometric analyses were performed. After determining the tendency of the ligand to interact with various ions, it was incorporated in polymeric membranes for potentiometric analysis of Ni^{2+} in different water samples.



Scheme 1. Chemical structure of 1-acenaphthoquinone 1-thiosemicarbazone, **L**

2. Experimental

2.1. Material and instrumentation

Analytical grade dibutyl phthalate (DBP), bis(2-ethylhexyl)sebacate (BES), benzyl acetate (BA), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), methanol, and high relative molecular weight poly(vinyl chloride) (PVC) from Merck was used without further treatment.

All solutions were prepared using double-distilled water and the buffering of solutions was performed using a 0.02 M sodium dihydrogen phosphate buffer. The adjustment of pH was performed using 1 M sodium hydroxide or hydrochloric acid solutions. 1-acenaphthoquinone 1-thiosemicarbazone (L), was synthesized as described in the literature [35,36].

A Jenway 3020 pH-meter and a combined glass electrode were used for pH readings after calibration using Merck standard buffers. The electronic absorption spectra were acquired using a Shimadzu 1650PC double-beam spectrophotometer at constant ± 0.1 °C temperatures.

2.2. Constructing the electrodes

The membranes were prepared through dissolving 5 mg of 1-acenaphthoquinone 1-thiosemicarbazone, 29.0 mg of PVC powder, 62.0 mg of DBP, and 4 mg of NaTPB in 3 mL of tetrahydrofuran. The solution was allowed to become more viscous through the evaporation of the THF, and the resulting oily solution was used for forming the ion-selective membranes. The membranes were next formed through dipping a 5 mm i.d. Pyrex tube was inserted into the viscose solution and kept there for around 10 seconds, to form a 0.3 mm film on its tip. The membrane was allowed to dry, by resting the tube at ambient temperature for one hour, before it was filled with a 1×10^{-2} M solution of Ni^{2+} ion. Eventually, the sensor was conditioned in a 1×10^{-3} M nickel nitrate solution for one day.

2.3. Emf measurements

The determination of the electromotive force was performed using a PME in the below cell:

Ag-AgCl || KCl (3M) | internal solution, (1×10^{-2} mol L⁻¹ Ni^{2+}) PVC membrane | sample solution || Hg-Hg₂Cl₂, KCl (satd) (PME).

3. RESULTS AND DISCUSSION

3.1. Primary studies

The initial studies involved monitoring the complexation of 1-acenaphthoquinone 1-thiosemicarbazone with some cations in methanol through spectroscopy at 20.0 ± 0.0 °C to evaluate the relative stabilities of the different complexes. The maximum absorbance of 1-Acenaphthoquinone 1-thiosemicarbazone occurs at around 255 and 416 nm, while upon adding incremental amounts of Ni^{2+} , the peak decreased (Figure 1). Figure 1 inset illustrates the clear change in the solution color (red to yellow). In the case of tests involving other cations i.e., Hg^{2+} , Cd^{2+} , Zn^{2+} , Al^{3+} , Ag^{+} , Cr^{3+} , Pb^{2+} , Cu^{2+} , Co^{2+} , Mn^{2+} and Fe^{3+} the absorbance maxima of 1-acenaphthoquinone 1-thiosemicarbazone underwent negligible changes. In all cases the ion/ligand mole ratio was 1.0 and the formation constants (K_f) of the complexes were determined using appropriate equations for fitting the absorbance/mole ratio data [37]. Given the data (Table 1) the distinct color change of the ligand solution after adding the Ni^{2+} ions, L

was concluded as having selectivity for Ni^{2+} ions and was hence evaluated as a potential ionophore for constructing a membrane sensor.

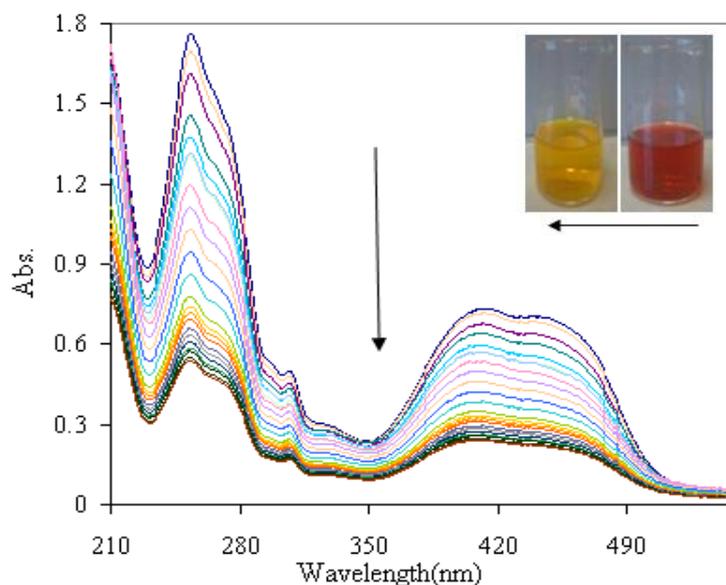


Figure 1. Absorbance of a 1×10^{-5} M solution of 1-acenaphthoquinone 1-thiosemicarbazone in methanol, in the presence of various amounts of Ni^{2+} , the arrow illustrates the direction of absorbance changes while increasing cation concentration. Inset: changes in the color of L solutions upon adding nickel ions

Table 1. The formation constants of 1-acenaphthoquinone 1-thiosemicarbazone– M^{n+} complexes.

Cation	$\log K_f$
Ni^{2+}	6.00 ± 0.01
Hg^{2+}	<2.0
Cd^{2+}	<2.0
Zn^{2+}	<2.0
Al^{3+}	2.51 ± 0.06
Ag^+	2.46 ± 0.10
Cr^{3+}	2.45 ± 0.10
Pb^{2+}	2.86 ± 0.11
Cu^{2+}	2.80 ± 0.11
Co^{2+}	2.55 ± 0.10
Mn^{2+}	2.54 ± 0.11
Fe^{3+}	2.80 ± 0.11

3.2. Potential responses of the sensor

Ionophores possess fast exchange kinetics, further to high complexation constants. These molecules should also be soluble in the membrane solutions. Ionophores should also possess enough lipophilicity, to avoid its leaching into the external solutions. It is well established that

the selectivity of ionophores is a function of the stability constant of their complexes with the target species as opposed to those of other ions, as well as the partition constant between the membrane and test solution [38-42].

The primary tests involved investigating the response of 1-acenaphthoquinone 1-thiosemicarbazone based PVC-membranes with identical compositions for a set of ions (Figure 2). The results indicated that only in the case of Ni^{2+} ion a Nernstian slope of 29.5 was observed, which was attributed to the strong interaction and sensitivity of 1-acenaphthoquinone 1-thiosemicarbazone for nickel ions, and the fast exchange kinetics of the complex.

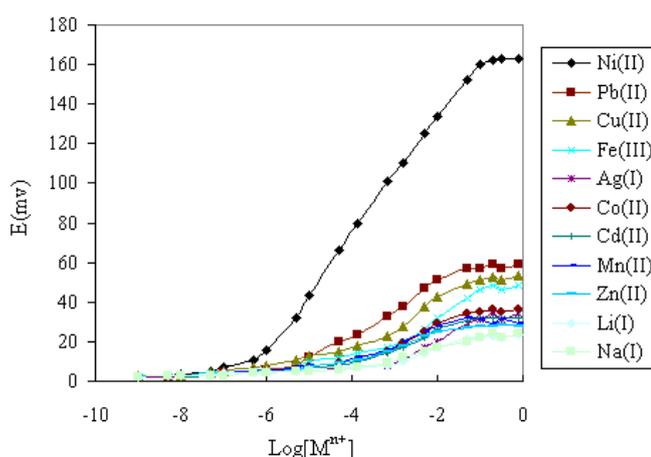


Figure 2. Potential responses of various cation-selective electrodes based on **L**

3.3. Influence of composition

The selectivity and sensitivity of PVC-membrane electrodes is a function of the composition of the membrane including the type and quantity of the membrane solvent and additives used, for any given ionophore. Accordingly, the effects of the composition of the membrane on the behavior of the were studied and the results are presented in Table 2.

To assess the effect of the nature of the membrane solvent (plasticizer) different membranes containing BES, BA and DBP were prepared and their response behaviors were compared (Table 2), indicating that the best sensitivity was obtained in the case of DBP.

The potentiometric response of the electrode to nickel was also a function of ionophore concentration and hence this was also evaluated. The results in Table 2, indicate that the highest sensitivity occurred in the presence of 5%wt. of 1-acenaphthoquinone 1-thiosemicarbazone. Further, incorporation of negatively charged lipophilic additives can improve the selectivity of electrodes based on neutral and charged carriers. This is also known to lower the membrane resistance, further enhancing the selectivity [30-35]. In this regard, sodium tetraphenyl borate (NaTPB) was added to the membrane.

The study of the optimization of the composition of the membranes indicated that the best response could be obtained with membranes containing 29.0% PVC, 62.0%DBP, 5.0% NaTPB

and 5.0% ionophore (**L**) (membrane no. 5) has the best response. Consequently, membrane 5 in Table 2, was considered as the optimal composition with as the best linear response and pH range, sensitivity, as well as, life and response times.

Table 2. Optimization of membrane ingredients of the Ni²⁺ ion-selective electrode based on 1-acenaphthoquinone 1-thiosemicarbazone

Sensor No.	Composition (%wt.)				Slope (mV decade ⁻¹)	Concentration range (M)
	PVC	additive	Plasticizer	Ionophore		
1	34.0	0	DBP, 66.0	0	4.1 ± 0.6	-
2	32.5	0	DBP, 65.0	2.5	18.2 ± 0.4	5.0 × 10 ⁻⁵ -1.0 × 10 ⁻²
3	37.1	3.5(NaTPB)	DBP, 56.4	0	6.7 ± 0.5	-
4	30.5	3.1(NaTPB)	DBP, 63.5	2.9	23.4 ± 0.3	5.0 × 10 ⁻⁵ -1.0 × 10 ⁻²
5	29.0	4.0(NaTPB)	DBP, 62.0	5.0	29.5 ± 0.2	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹
6	29.0	4.0(NaTPB)	BA, 62.0	5.0	24.0 ± 0.5	1.0 × 10 ⁻⁴ -1.0 × 10 ⁻²
7	29.0	3.0(NaTPB)	BA, 63.0	5.0	24.5 ± 0.5	4.0 × 10 ⁻⁴ -1.0 × 10 ⁻²
8	29.0	4.0(NaTPB)	BES, 62.0	5.0	19.4 ± 0.5	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻²
9	29.0	3.0(NaTPB)	BES, 63.0	5.0	20.5 ± 0.6	5.0 × 10 ⁻⁵ -1.0 × 10 ⁻²

3.4. Effect of pH

A 1.0 × 10⁻⁴ M solution of Ni²⁺ was used, and its pH was altered using concentrated acid and base solutions to study the changes in the response of the electrode in different pH response profiles of the PME was examined using a 1.0 × 10⁻⁴ M Ni²⁺ solution and the results can be seen in Figure 3.

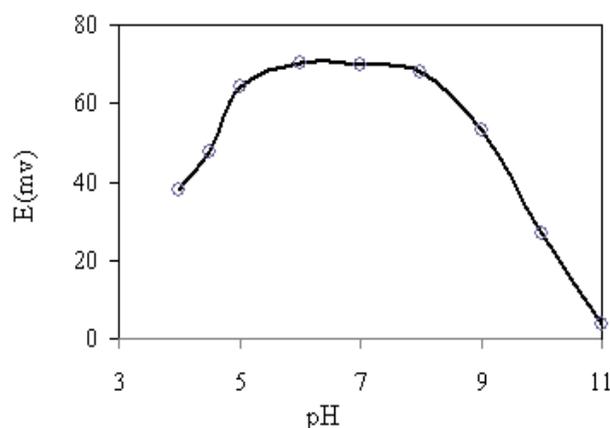


Figure 3. Changes in the potential response of the electrode with the best composition (no. 5, Table 2) in a 1.0 × 10⁻⁴ M solution of Ni²⁺ at various pH values.

It can be seen that the potential response of the electrode in the solution did not considerably change in the pH range 5 to 8. On the two sides of this range, the potential response of the electrode underwent considerable changes. When the solution pH became less than 5, the potential response of the electrode decreased considerably, reflecting the protonation of the donor atoms of the ligand. Over a pH of 8, the response of the electrode also dropped, which could be attributed to the formation of various soluble hydroxide species of Ni^{2+} , which cannot be present in the electrode equilibria. Based on the results, a pH value of 6 was chosen as the optimal value and applied in the rest of the experiments [37-42].

3.5. Response behavior of the sensor

It is well known that the concentration of the internal solution can influence the response of the electrode due to its influence on the internal diffusion potential of the membrane. To evaluate this effect different solutions with three concentrations of 1.0×10^{-4} to 1.0×10^{-2} M were used as the internal solutions and emf-pNi plots were developed. The experiments showed that this factor did not influence the electrode response, yet the intercept of the resulting calibration curves. A 1.0×10^{-2} M solution was used as the internal solution in the rest of the experiments. Also, the optimal time required for conditioning of the electrode in a 1.0×10^{-3} M Ni^{2+} solution was 24 h. After this period the potential response of the electrodes was stable.

The key response characteristics of the electrode were evaluated based on IUPAC recommendations [43]. Plot of the emf response of the optimal electrode in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} (Figure 4) was linear with a response of 29.5 ± 0.2 mV decade⁻¹. The detection limit of the sensor was also determined through intersecting the extrapolated segments at the low end of the calibration curve. The value of the detection limit was found to be around 5.0×10^{-7} M.

Also, the lifetime of the membrane was determined using 4 similar electrodes in the analysis of samples (1 hour per day) over a 3-month period. The results indicated that the response time, slope, or detection limit of the sensors did not change over this period, proving the stability of the constructed sensors.

Another key factor in evaluating an ion-selective electrode is its dynamic response [44-48]. To determine this factor the sensor was used to determine the concentrations of a set of Ni^{2+} solutions each having a 10-fold difference with the previous, and the time required for reaching equilibrium response was determined in the high to low and low to high orders and accordingly the static response times of the electrodes were determined to be less than 10 s over its linear response range. This reflects the rapid complexation-decomplexation kinetics of the complex between 1-acenaphthoquinone 1-thiosemicarbazone and nickel ions [20].

The reversibility of the sensors was also assessed in a similar fashion performing the measurements in the high-to-low sequence and the results are presented in Figure 5. The figure clearly shows there was no memory effect in the response of the electrodes and it had a

reversible behavior. One anticipated incident was that the equilibrium times were longer (about 60 times) than those obtained in low-to-high sequence [20].

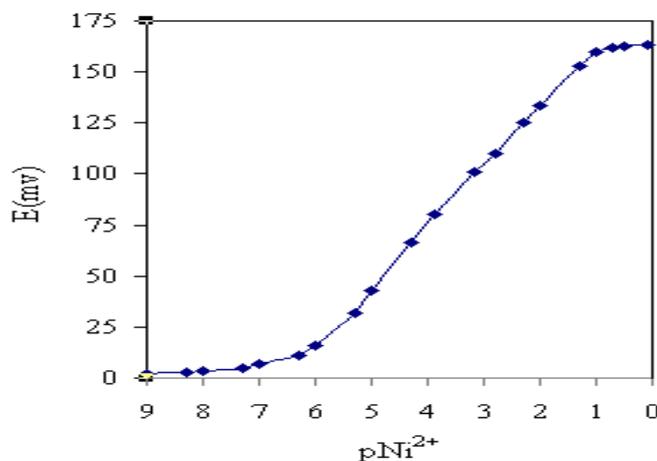


Figure 4. The calibration graph of the Ni^{2+} membrane sensor (membrane no. 5) at pH 6.0

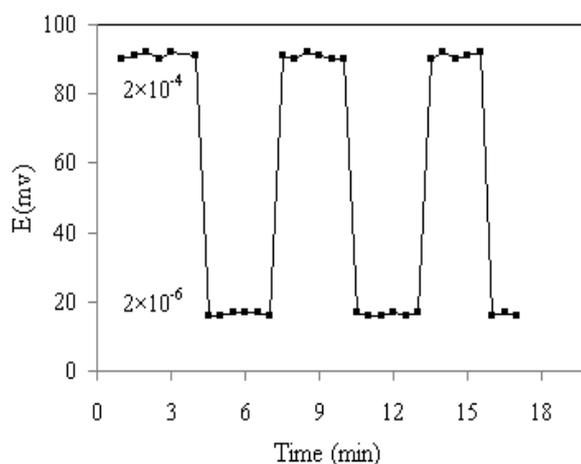


Figure 5. The plot of the potential/time behavior of the Ni^{2+} ion-selective sensor in high-to-low concentration sequence

3.6. Selectivity of the electrode

As the most important factor indicating the properties of an ion-selective electrode, the potentiometric selectivity coefficients of the electrode were also determined. These coefficients show the tendency of the electrode response to change in the presence of an interfering ion (B), compared with the target ion (Ni^{2+}). The selectivity coefficients were determined based on the fixed interference method (FIM) and the separation solution method (SSM) [49-51]. In the fixed interference method, potential measurements are made in solutions, with the activity of the ion to be measured varying in the presence of a background level of the interference. The intercept of the extensions of the response line (slope) with the line defining the plateau in the region of high interference defines a particular intercept activity for the primary ion, a_A . The

FIM selectivity coefficient, $K_{A,B}^{Pot}$, is reflected by the ratio of the activity of the target to that of the ions:

$$K_{A,B}^{Pot} = (a_A / a_B^{Z_A/Z_B})$$

in this equation a_A expresses the activity of target ion A at the limit of detection in the presence of a interfering ion B, and Z_A and Z_B express the charges of A and B. Knowing the activity of $a_A(\text{Ni}^{2+})$ and a_B then permits solving for the selectivity ratio.

According to the second procedure for the determination of the selectivity coefficients, used here, i.e. SSM the determination is based on adjusting the concentration of the concentration of the interfering ion in cell composed of the membrane sensor and a reference electrode. The adjustment is performed using two solutions, one of the target ions in the absence of interfering species (but no B) and obtaining the a_A activity. The second solution contains only the interfering species B (in the absence of the target ion) and hence a_B is obtained, and the concentration of B is increased to reach enough concentration to observe the cell voltage obtained for the pure solution of the target ion (here Ni^{2+}). Using the two a_A and a_B activities producing identical cell potentials $K_{A,B}^{Pot}$ is given by:

$$K_{A,B}^{Pot} = a_A / a_B^{Z_A/Z_B}$$

From Table 3, clearly shows that the developed membrane sensor has distinct selectivity for the target ion, as opposed to the tested cations (i.e. alkali and transition metal ions). The data indicate that none of the tested interfering species is capable has a selectivity coefficient below 10^{-3} . This means these ions cannot seriously influence the response obtained for nickel ions. Also, the selectivity coefficients determined through the two techniques were in good agreement

Table 3. K_{FIM} and K_{SSM} Selectivity coefficients of the developed Ni(II) sensor

Cation	K_{FIM}	K_{SSM}
Pb^{2+}	2.9×10^{-3}	3.3×10^{-3}
Cu^{2+}	3.4×10^{-4}	5.1×10^{-4}
Fe^{3+}	2.1×10^{-4}	9.7×10^{-5}
Ag^+	1.5×10^{-5}	2.7×10^{-5}
Co^{2+}	1.6×10^{-4}	9.7×10^{-5}
Cd^{2+}	1.2×10^{-4}	2.5×10^{-4}
Mn^{2+}	1.1×10^{-5}	5.6×10^{-5}
Zn^{2+}	1.0×10^{-5}	3.3×10^{-5}
Hg^{2+}	2.3×10^{-5}	4.1×10^{-5}
Al^{3+}	2.2×10^{-4}	7.8×10^{-4}
Li^+	8.1×10^{-5}	8.3×10^{-5}
Na^+	8.3×10^{-5}	6.9×10^{-5}

3.7. Analytical Applicability

The sensor with optimal composition was successfully used in some tests under laboratory conditions, including usage as an indicator electrode in the complexation titration of 1.0×10^{-3} M Ni^{2+} solution, with a 1.0×10^{-2} M EDTA solution at pH=6.0 (Figure 6). The resulting titration plot indicates the capability of the sensor in accurately determining the concentration of nickel in the experiment.

The proposed electrode was also used in the analysis of Ni^{2+} concentration in different natural water samples obtained from western of Iran (Table 4). The data given in Table 4 indicates that the concentration of the analyte was accurately determined using the developed sensor, without any sample pretreatment.

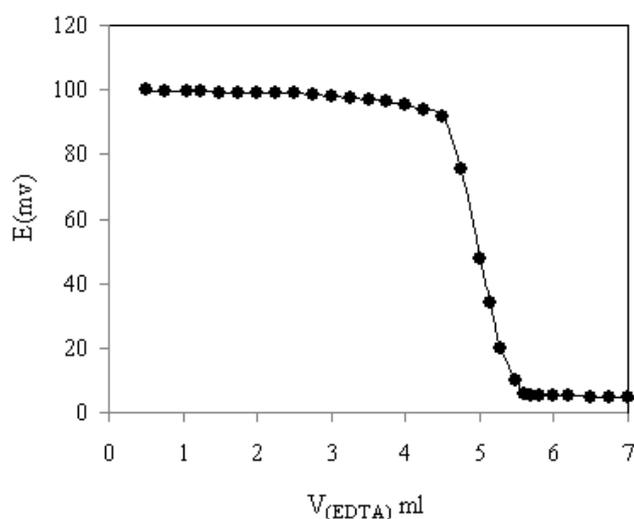


Figure 6. Titration plot obtained for 50.0 mL of a 1.0×10^{-3} M of Ni^{2+} solution using 1.0×10^{-2} M EDTA (pH=6.0), using the developed sensor to potentiometrically determine the endpoint

Table 4. Analysis of Ni(II) content in various samples

Samples	Ni(II) ion (mmol mL^{-1})		
	Added	Found	% Recovery
Spring water of Tgeh Bostan	1.0×10^{-4}	$9.78(\pm 0.07) \times 10^{-5a}$	97.8
Spring well sample	1.0×10^{-4}	$9.81(\pm 0.06) \times 10^{-5}$	98.1

^a% RSD values were obtained through replicate analyses.

3.8. Comparison with other sensors

A comparison of the behavior and properties of (i.e., sensing material, dynamic range, response time, limit of detection, slope, pH range, and coefficients) of the developed sensor

with other reported Ni²⁺ sensors is presented in Table 5 [24-27]. Evidently, the proposed sensor outperforms the formerly reported electrodes and it can be considered as a promising alternative for the analysis of Ni²⁺ solutions.

Table 5. The response behavior of various ionophore-based Ni²⁺ sensors

Characterization	Ref. [24]	Ref. [25]	Ref. [26]	Ref. [27]	This work
Sensing material	Naphthaldehyde-based Schiff base ^a	Ph ₄ Bzo ₂ (12)tetraeneN ₄	NDBBD ^b	Dioxime derivative ^c	Hydrazone derivative ^d
Type of sensor membrane	PVC matrix	PVC matrix	PVC matrix	PVC matrix	PVC matrix
Dynamic range (M)	1.6×10 ⁻⁷ – 1.0×10 ⁻²	3.98×10 ⁻⁶ - 1.0×10 ⁻¹	2.0×10 ⁻⁷ - .0×10 ⁻²	1.0×10 ⁻⁶ – 1.0×10 ⁻¹	1.0×10 ⁻⁶ - 1.0×10 ⁻¹
Response time	10 s	8 s	< 10 s	< 10 s	< 10 s
Detection limit (M)	1.0 ×10 ⁻⁷	2.98×10 ⁻⁶	8.0×10 ⁻⁸	1.6×10 ⁻⁶	5.0×10 ⁻⁷
Slope (mV/decade)	30.0±0.2	29.5	30.0±0.1	29.3±0.2	29.5±0.2
Working pH range	2.5–9.5	2.5–7.7	4.5-9.0	2.0–6.5	5.0–8.0
Method of selectivity determination	FIM	MPM	MPM	FIM	FIM & SSM

^a 3-Hydroxy-N-{2-[(3-hydroxy-N-phenylbutyrimidoyl)-amino]-phenyl}-N- phenylbutyramidine

^b N,N'-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine

^c (2E, 3E)-2H-1,4-benzothiazine-2, 3(4H)-dione dioxime

^d 1-Cenaphthoquinone-1-thiosemicarbazone

4. CONCLUSION

Ni²⁺ is a well-known moderate toxic element. In this work, the use of a new Schiff's base with some donor atoms—containing hydrazone derivative, with the chemical name of 1-cenaphthoquinone-1-thiosemicarbazone for the preparation of a novel Ni²⁺ PVC-based polymeric membrane sensor is described. The proposed potentiometric sensor revealed very good response characteristics in terms of stability, reversibility, dynamic range, detection limit, response time, and selectivity. The proposed sensor was successfully applied to the determination of nickel ions in some real water samples, and as a proper detection system in the potentiometric titration of Ni²⁺ ions with a standard solution of EDTA.

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