Full Paper

Application of a Newly Synthesized Dioxime Derivative to Design and Characterize a Novel Electrochemical Nickel(II)–Selective Sensor

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Abstract- In this work, the suitability of a dioxime derivative, (2*E*,3*E*)-1,4-dihydroquinoxaline-2,3-dione dioxime (H_2L), as a neutral ionophore for preparation of a PVC membrane electrode, is investigated for nickel(II) ion in solution. The prepared membrane exhibits a Nernstian response (28.2 ± 0.1 mV decade^{-1}) for Ni^{2+} ion over a wide concentration range (6.3×10^{-7} to 1.1×10^{-1} M) with a detection limit of 5.4×10^{-7} M. At a working pH range of 4.0–6.5, the proposed membrane electrode revealed very good selectivity for Ni^{2+} ion over a wide variety of other cations. Besides a relatively fast response of <60 s the sensor could be used for at least 3 months without any considerable divergence in potentials. It was successfully applied as an indicator electrode in potentiometric titration of Ni(II) ion with EDTA and in the determination of Ni^{2+} in some water samples.

**Keywords**- Dioxime, Ion–Selective Electrode, Nickel(II), Potentiometry, Sensor

1. INTRODUCTION

The dioxime ligands are known to coordinate metal ions as neutral dioximes [1,2]. The chemistry of the bis–dioximate complexes of transition metal ions has been attracting

continuous attention because of their importance with reference to many chemical roles that they play in coordination chemistry [3–9]. In 1905, Tschugaeff discovered the vicinal dioxime metal complex bis–dimethyl gloximato Ni(II) [10] initiating an area of coordination chemistry which has been widely explored during the past century.

On the other hand, in the past years, a large variety of mainly cation–selective carriers have been synthesized by various research groups and published articles, on ionophore–based ion–selective electrodes (ISEs), are increasingly developed [11–14]. Among various classes of chemical sensors ion-selective electrodes (ISEs) are one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring. The principle of ion-selective electrodes operation is quite well investigated and understood. The increasing use of electrochemical sensors in the fields of environmental, agricultural and medical analysis is stimulating analytical chemists to develop new sensors for fast, accurate, reproducible and selective determination of various species.

Nickel is well known as a toxic element that can cause cancer of nasal lungs, dermatitis, asthma and disorders of central nervous system [15]. Thus, due to the urgent need for selective monitoring of Ni^{2+} in many industrial, environmental and food samples, there have been a number of recent reports in the literature [16–20]. We have recently found out that a dioxime, including a lipophilic moiety can be used as a suitable neutral ionophore in preparation PVC–based Ni^{2+} ion–selective electrode [21]. The results that have been presented in this article show the development of a sensor, based on the newly synthesized (2*E*,3*E*)-1,4-dihydroquinoxaline-2,3-dione dioxime (Fig. 1) to determine Ni(II) ion in solution. Due to highly selective complexation of the ligand with Ni(II) ion and water insolubility of the resulted complex, the developed electrode for Ni(II) ion has a wide working concentration range, fast response time and gives reproducible results.
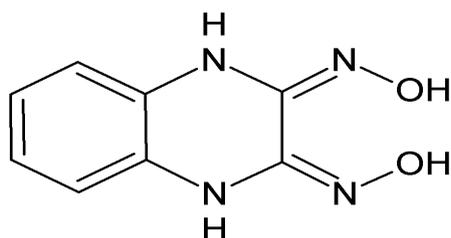
Fig. 1. Chemical structure of H_2L

2. EXPERIMENTAL

2.1. Reagents

Reagent grade bis(2-ethylhexyl) sebacate (DES), tris(2-ethylhexyl) butyl phthalate (TBP), diocthyl phthalate (DOP), dibuthyl phthalate (DBP), sodium tetrakis(*p*-chlorophenyl) borate (NaTPB), tetrahydrofurane (THF), acetonitrile (AN), tetraethyl ammonium perchlorate (TEAP) and high relative molecular weight PVC (all from Merck) were used as received. Nitrate salts of all cations used were of the highest purity available (all from Merck) and used without any further purification. Doubly distilled deionized water was used throughout.

2.2. Apparatus

A Jenway (UK) ion–analyzer 3020 pH/mV meter (capable of reading from three electrodes simultaneously) was used for potential measurements at 25.0 °C. Absorption spectra were recorded on a Shimadzu (Japan) double beam spectrophotometer 1650PC with two 1–cm fused–silica cells. All spectrophotometric measurements were carried out at room temperature (20–25 ºC). The pH data were recorded on the above pH meter. AA 670 Shimadzu (Japan) electro-thermal atomic absorption spectrophotometer (ETAAS) was used for measuring nickel in aqueous solutions.

2.3. Synthesis of Ionophore (H₂L)

H_2L was synthesized and purified as described elsewhere [22]. In an ice-bath, to a stirring solution of 1,2-phenyldiamin (1.08 g, 0.01 mole) in 50 ml of acetonitrile a solution of dichloro glyoxime (1.57 g, 0.01 mole) in 30 ml acetonitrile was added (~0 °C). After 2 h, a purple precipitate was formed and the solvent was evaporated under vacuum condition. The resulted compound was recrystallized and purified in water-acetonitrile mixture (1:3) four times. The residue was the brown crystals of (2*E*,3*E*)-1,4-dihydroquinoxaline-2,3-dione dioxime with melting point of 239–240 °C. The yield of the reaction was about %93 and the spectral characteristics of the product were confirmed by IR, ^{1}H–NMR and Mass. IR spectra of H_2L showed new absorption bands at 2500–3500 (*v* O–H), 1640 (*v* C=N) and 980 (*v* N–O) cm^{-1}. The ^{1}H–NMR spectra of H_2L exhibited D_2O-exchangeable signals for the N–OH and NH protons at 10.13 and 9.46 ppm, respectively, while the aromatic protons appear at 6.71–7.18 ppm. From ^{13}C–NMR spectra of H_2L, the following characteristics were exhibited. The chemical shifts of oxime groups (C=N–OH) appeared at 138.45 and three signals at 125.90, 121.03, and 114.57 were found for benzene carbons. The mass spectra of H_2L revealed a molecular ion peak at m/z = 192.

2.4. Electrode Preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 50 mg of powdered PVC, 100 mg of plasticizer DES, 1 mg of additive NaTPB, and 2 mg of

ionophore H_2L in a 5 mL glass backer. The mixture was then completely dissolved in 3 mL of freshly prepared THF. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d. on top) was dipped into the mixture for ~5 s so that a transparent membrane of ~0.1 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for ~1 h. The tube was then filled with an internal solution (1.0×10^{-2} M $Ni(NO_3)_2$). The electrode was finally conditioned for 10 h in a 1.0×10^{-2} M, $Ni(NO_3)_2$ solution. Two silver/silver chloride electrodes were used as the internal and external references. The amounts of various ingredients, concentrations of equilibrating solution and time of contact were optimized to provide a membrane that was reproducible, noiseless and stable potentials.

2.5. Electromotive Force (Emf) Measurements

All Emf measurements were carried out with the following assembly:

Ag/AgCl, KCl(sat'd.) | Internal solution (0.01 M $Ni(NO_3)_2$ | PVC–membrane | Sample solution | Ag/AgCl, KCl(sat'd.)

3. RESULT AND DISCUSSION

3.1. Preliminary spectrophotometric studies

In preliminary experiments, in order to find a clue about the stability and selectivity of resulted complexes in a non-aqueous solvent, the complexation of H_2L with Ni(II) metal ion and some other cations such as Ag^+, Mg^{2+}, Al^{3+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} and Pb^{2+} was investigated spectrophotometrically in the presence of TEAP (0.05 M) in AN. Standard stock solutions of the ligand (1.0×10^{-3} M) and each cation (1.0×10^{-3} M) were prepared in AN. There were no changes in absorption of the ligand solution during the titration by the solution of the mentioned cations except for the case of Ni(II) ion. According to the spectra reported in Fig. 2 titration of the ligand solution (2.0×10^{-5} M, 3 mL) was carried out by addition of microliter amounts of the standard solution of the metal ion, followed by recording the absorbance intensity of the solution on wavelength range 300 – 550 nm.

As is obvious from Fig. 2 a new absorption band at about 423 nm is observed upon addition of increasing quantities of Ni(II) ion to H_2L, whereas the absorption intensity changes as a function of the $[Ni^{2+}]/[H_2L]$ molar ratio (Fig.3) at the λ_{max}= 423 nm. These changes could be attributed to the complexation between the ligand H_2L and Ni(II) ion. From the inflection point in the absorbance/molar ratio plot at $[Ni^{2+}]/[H_2L]$ value about 1, it can be inferred that a 1:1 $[Ni^{2+}]/[H_2L]$ complex is formed in AN solution. For evaluation of the stability constant from the absorbance versus $[Ni^{2+}]/[H_2L]$ molar ratio data, a computerized non-linear least-squares curve-fitting program KINFIT [23] was used (Fig. 3). The resulting formation constant value, obtained from the computer fitting of the

absorbance/molar ratio data (denoted as "**x**") to a theoretical model (denoted as "**o**") including a 1:1 form, was calculated as $(1.32\pm0.01)\times10^7$. Good agreement was observed between the experimental and theoretical data (denoted as "=").

Thus, based on the selectivity of H_2L for Ni(II) over other preliminary tested ions as well as its high lipophilic character, the ligand was expected to act as a suitable ionophore for Ni(II) ion in a PVC membrane electrode.
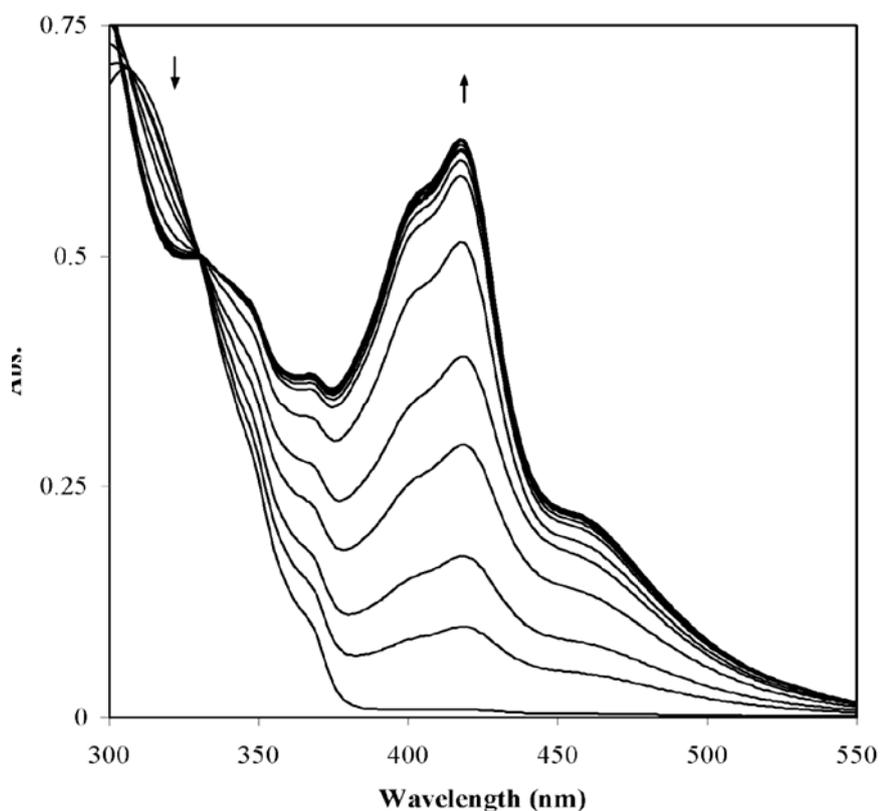
Fig. 2. Absorption spectra of titration of H_2L 2.0×10^{-5} M, with 1.0×10^{-3} M of Ni(II) ion solution in AN, at 25.0 °C
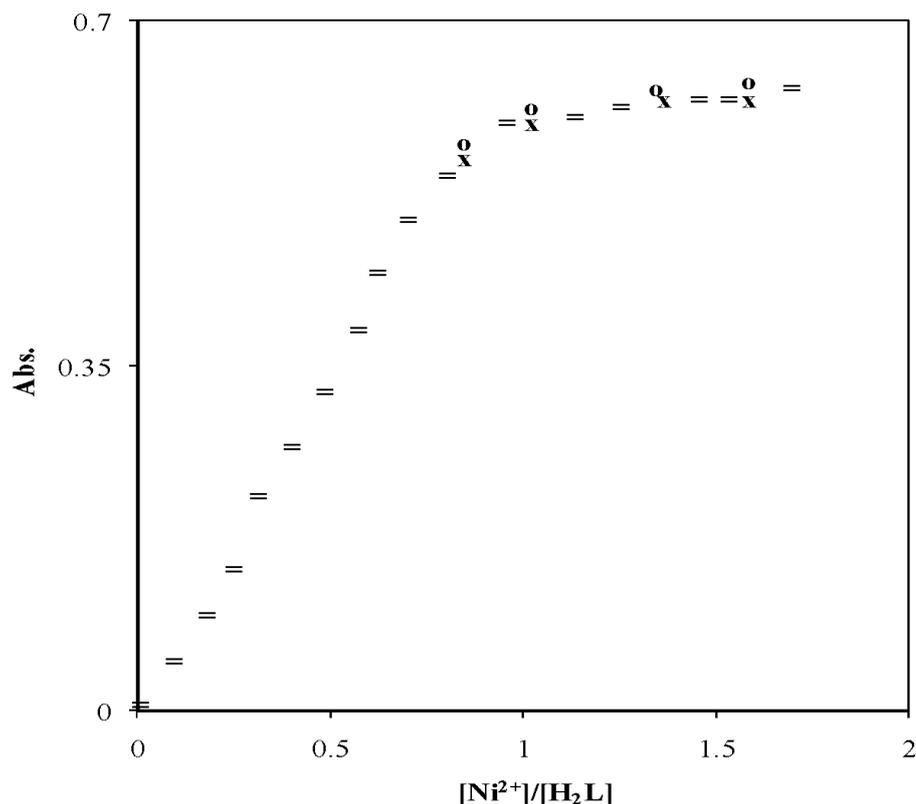
Fig. 3. Absorbance/mole ratio data of titration of H_2L with Ni^{2+} in AN. Theoretical curve fitting data (**o**) are best fitted on experimental data (**x**). The (=) signs show the good fitting of experimental and theoretical data
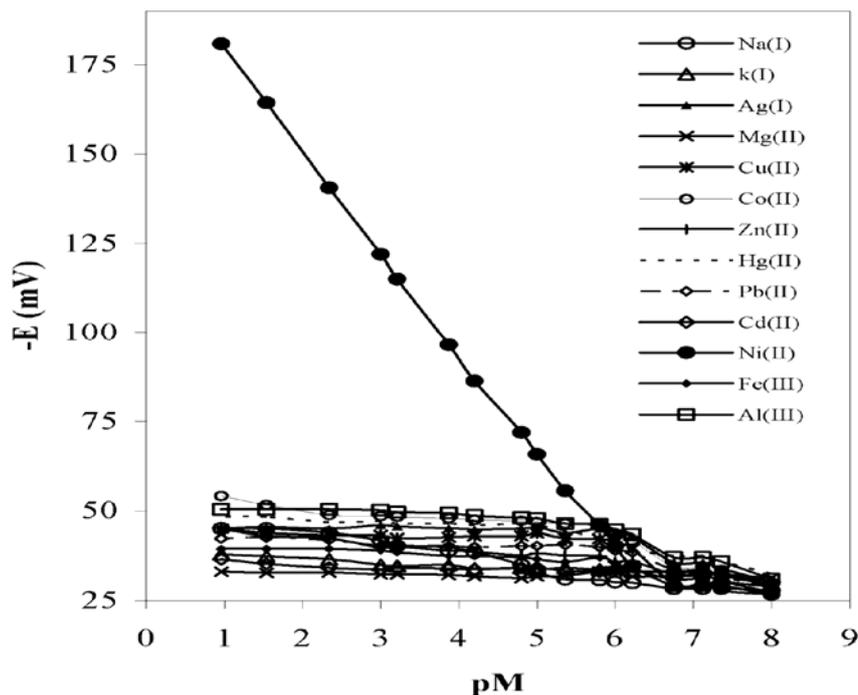
3.2. Membrane Composition

An ion-selective membrane is the key component of all potentiometric ion sensors. It establishes the preference with which the sensor responds to analyte in the presence of various interfering ions from the sample. In conventional ISEs, ion-selective membrane is in electrical contact with inner reference electrode through inner reference solution. Because of the critical role of the nature of the compounds in preparing PVC membrane electrodes, it is well understood that performance characteristics for the ionophore–incorporated PVC membrane may be very dependent on electrode composition and the nature of the solution of which the electrodes are composed [24–27]. Thus, different aspects of the composition of membranes based on H_2L for Ni(II) ion were optimized and the results are summarized in Table 1. The potentiometric response of the membrane ion–selective electrodes based on neutral ionophores is greatly influenced by the polarity of the membrane medium, which is defined by the dielectric constants of the major membrane components [28,29]. The influence of the nature of plasticizer on the response of the electrode was studied on electrodes containing four types of plasticizers including different dielectric constants, DOP,

TBP, DBP, and DES. As shown in Table 1 (Nos. 1–4), DES resulted in the widest working range. As expected, the amount of ionophore was found to affect the PVC membrane performances (Nos. 4–9). The effect of amount of PVC was also examined, Table 1 (Nos. 4, 10, 11). It is well known that incorporation of lipophilic additives can significantly influence the performance characteristics of a membrane sensor [25–31]. Presence of additives may also catalyze the exchange kinetics at the sample–membrane interface [32]. In addition, we examined the influence of NaTPB, as suitable lipophilic additive, on the response characteristics of the proposed PVC membrane. The presence of this additive improved the response performances of the electrode to detection of the target ion. In order to see the response of the blank membrane (without the ionophore), the attraction of the membrane toward the analyte was also determined, as shown by No. 5. As is obvious, there is no considerable response from the membrane with such composition. From Table 1, membrane No. 4 with a PVC/DES/H_2L/NaTPB amounts (mg) of 50:100:1:1 (32.9% PVC, 65.8% DES, 0.65% H_2L, and 0.65% NaTPB) resulted in Nernstian behavior of the membrane electrode over the widest concentration range. This electrode was used in subsequent potentiometric measurements.

The electrode shows a Nernstian response for the cation in the range of 6.3×10^{-7}–1.1×10^{-1} M (Fig. 4). The potential responses of some of the most sensitive electrodes based on H_2L are also shown in Fig. 4 as is obvious from this Fig, among different cations tested, Ni(II) with the most sensitive response seems to be suitably determined with the electrode. This is due to the selective behavior of the PVC membrane system against Ni^{2+} in comparison to the metal ions tested.

3.3. Effect of Internal Solution

Based on the generally adopted ion–selective response formalism [13], the internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable. Thus, the influence of the concentration of internal solution of the PVC electrode was studied as follows. Three similar membranes were prepared under optimal membrane composition (No. 4, Table 1), and each electrode was filled with an internal solution of varying Ni(II) concentrations of 1.0×10^{-1}, 1.0×10^{-2}, and 1.0×10^{-3} M. The electrodes were then conditioned for 10 h by soaking in a 1.0×10^{-2} M Ni(NO$_3$)$_2$ solution. Finally, the Emf versus pNi plot for each electrode was constructed in a pNi range of 0.0-8.0. It was found that the variation of the concentration of the internal solution does not cause any significant difference in the corresponding potential response, but the working range was a bit longer for the case 0.01 M. Thus, a 0.01 M concentration of the reference solution is quite appropriate for the electrode system.

Fig. 4. Potentiometric responses of various Ni(II)–selective electrodes (No. 4, Table 1)

Table 1. Optimization of membrane ingredients

	Composition (mg)				Performances		
No.	H_2L	NaTPB	PVC	Plasticizer (100 mg)	Slope (mV/decade)	DL (M)	Linear working range (M)
1	1	1	50	DOP	34.0	1.1×10^{-4}	$3.2\times10^{-4} - 2.1\times10^{-1}$
2	1	1	50	DBP	39.9	2.8×10^{-4}	$3.3\times10^{-4} - 1.1\times10^{-1}$
3	1	1	50	TBP	32.9	2.4×10^{-4}	$4.4\times10^{-4} - 2.0\times10^{-1}$
4	1	1	50	DES	28.2	5.0×10^{-7}	$6.3\times10^{-7} - 1.1\times10^{-1}$
5	0	1	50	DES	22.4	3.1×10^{-2}	$5.1\times10^{-2} - 1.0\times10^{-1}$
6	0.5	1	50	DES	33.2	2.5×10^{-4}	$4.1\times10^{-4} - 1.1\times10^{-1}$
7	1	0.5	50	DES	29.4	7.6×10^{-5}	$2.3\times10^{-4} - 1.2\times10^{-1}$
8	2	2	50	DES	28.2	3.3×10^{-5}	$4.9\times10^{-5} - 2.0\times10^{-1}$
9	0.5	0.5	50	DES	28.1	8.2×10^{-6}	$6.4\times10^{-5} - 7.1\times10^{-2}$
10	1	1	35	DES	25.3	8.7×10^{-5}	$1.2\times10^{-4} - 1.0\times10^{-1}$
11	1	1	65	DES	22.1	1.3×10^{-5}	$2.2\times10^{-5} - 1.3\times10^{-1}$

3.4. Effect of pH of the Test Solution

The influence of the pH of a test solution on the potential response of the membrane was studied using a 50.0 mL portion of a 5.0×10^{-4} M solution of $Ni(NO_3)_2$. Its pH was adjusted by drop–wise addition of a 0.1 M solution of either HCl or NaOH, and the Emf of the electrode was measured at each pH value, in a pH range of 0.0–10.0. The results are shown in Fig. 5 As seen, the potential remained constant from pH 4.0 to 6.5, beyond which the potential changed considerably. At low pHs, the potential increased, indicating that the membrane sensor responds to hydrogen ion, while the drastically decrease in potential at higher pH values could be due to the formation of some hydroxyl complexes of Ni(II) in the solution. pH=5 of citric acid/citrate system (0.1 M) was used as a proper buffer for subsequent studies.
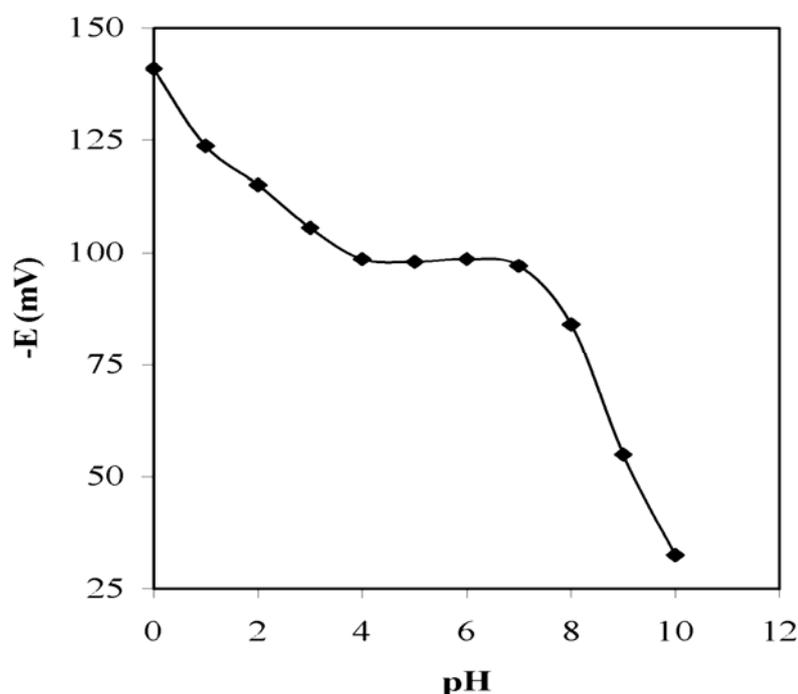
Fig. 5. Effect of the pH of the test solution on the potential response of the Ni^{2+}–selective electrode (No. 4, Table 1) in the presence of 5.0×10^{-5} M of Ni(II) ion

3.5. Response Characteristics of the Membrane Electrode

The critical response characteristics of the proposed Ni(II)–selective electrode were investigated according to IUPAC recommendations [33–35]. From Fig. 6, the practical response time of the membrane electrode (in the presence of Ni(II) 1.0×10^{-5} M) thus obtained was <60 s (for reaching >%95 of its equilibrium potential). This is most probably due to the relatively fast exchange kinetics of complexation–decomplexation of Ni(II) ions

with H_2L at the test solution–membrane interface. This real response time (60 s) was used for subsequent potential measurements.

The practical reversibility required for the Ni(II) sensor, to reach a potential within ±1 mV of the final equilibrium value, after successive immersion of two different concentration of Ni(II) ion solutions, 1.0×10^{-5} and 1.0×10^{-3} M, was measured (Fig. 7). Potentials stayed constant for more than 6 min, after which no divergence within the resolution of the potentiometer (i.e., 0.1 mV) was recorded. The standard deviations of 3 replicate measurements series are ±0.77 and ±0.23 (%), respectively. The sensing behavior of the membrane remained unchanged when the potentials recorded either from low to high concentrations or vice versa. The electrode response was regenerated after simply washing of the electrode by distilled water.

The Emf response of the membrane electrode at varying Ni(II) concentrations (Fig.4) depicts a rectilinear range from 6.3×10^{-7} to 1.1×10^{-1} M with a Nernstian slope of 28.2 ± 0.1 mV decade^{-1}.

The practical detection limit (DL) of the sensor was 5.0×10^{-7} M, as determined from the intersection of the two extrapolated segments of the calibration plots at its lower part.

The time of contact and concentration of equilibrating solution were optimized so that the membrane electrode generated stable and reproducible potentials at relatively short response times. The stability and lifetime of the Ni(II) sensor were tested over a period of 3 months. During this period, the electrode was in daily use over extended period of time (1 h per day) and no significant deviation observed on the optimized response characteristics of the electrode.
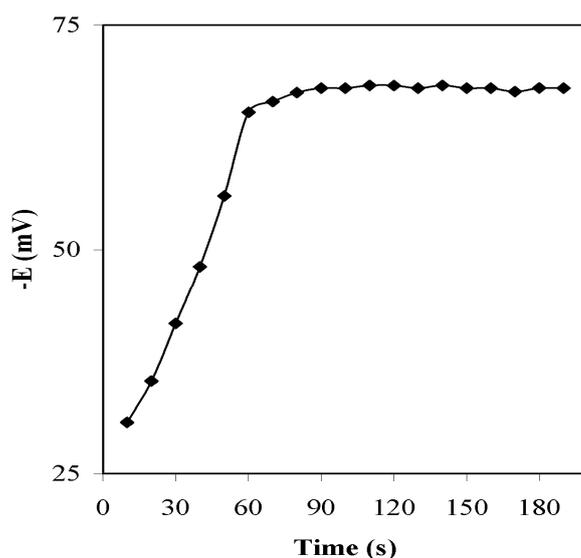
Fig. 6. Practical response time determination by plotting of potential against time, from the moment of addition of Ni(II) (1.0×10^{-5} M) solution, for the Ni(II)–selective electrode (No. 4, Table 1)
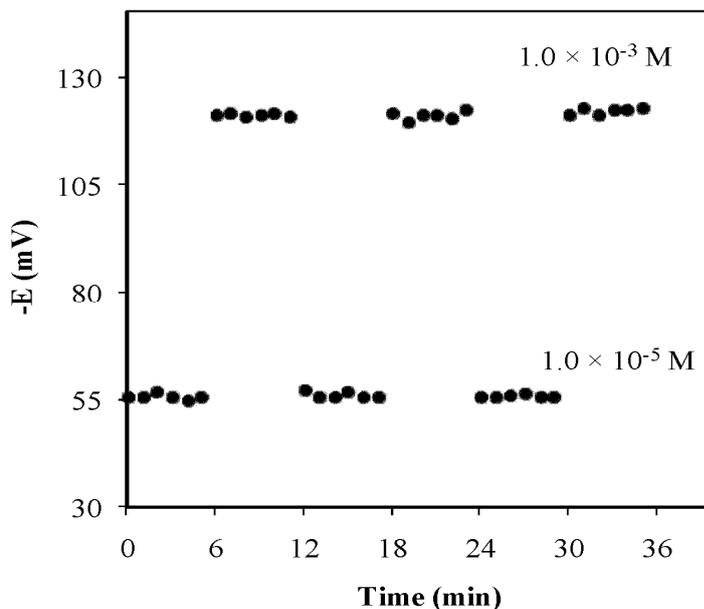
Fig. 7. Dynamic response of the proposed Ni^{2+}–selective electrode (No. 4, Table 1) for reversibility after successive immersion of two different concentration of Ni(II) ion solutions, 1.0×10^{-5} and 1.0×10^{-3} M, at pH 5

3.6. Selectivity Coefficients

However, a membrane truly selective for a single type of an ion and completely non-selective for other ions does not exist. For this reason the potential of such a membrane is governed mainly by the activity of the primary (target) ion and also by the activity of other secondary (interfering) ions. To investigate the selectivity of the membrane electrode proposed, fixed interfering ion method (FIM) was used [32–37]. The Emf of a cell comprising an ion–selective electrode (No. 4, Table 1) and a reference electrode (Ag/AgCl) is measured for solutions of constant activity of the interfering ion, a_B, and varying activity of the primary ion, a_A, with a fixed concentration of 0.01 M of the interfering ion. The Emf values obtained are plotted *vs.* the logarithm of the activity of the interfering ion. The intersection of the extrapolated linear portions of this plot indicates the value of a_A that is used to calculate $K_{A,B}^{pot}$ from the following equation:

$$K_{A,B}^{pot} = \frac{a_A}{a_B^{(z_A/z_B)}} \qquad (1)$$

where z is the charge of ion. This equation regardless of its simplicity and ease of use for mono–valance ions gives the results higher than those expected. The selectivity coefficients were evaluated and the results are summarized in Table 2.

From Table 2, it is readily seen that the proposed Ni(II) ion–selective electrode is quite selective with respect to the common cations tested. Table 2 also shows that, for all diverse

ions used, the selectivity coefficients are small enough indicating that they would not significantly disturb the functioning of the Ni(II) ion–selective electrode.

Table 2. Selectivity coefficients, $K_{A,B}^{pot}$, of various interfering ions

| M^{n+}	$K_{A,B}^{pot}$	M^{n+}	$K_{A,B}^{pot}$
Na^+	2.2×10^{-1}	Pb^{2+}	3.8×10^{-3}
K^+	2.3×10^{-1}	Zn^{2+}	2.1×10^{-3}
Ag^+	3.2×10^{-1}	Fe^{3+}	1.8×10^{-3}
Mg^{2+}	4.6×10^{-3}	Al^{3+}	3.4×10^{-3}
Cd^{2+}	2.2×10^{-3}	Hg^{2+}	3.5×10^{-3}
Co^{2+}	3.5×10^{-2}		
Cu^{2+}	5.2×10^{-2}		

3.7. Application

The proposed membrane electrode for Ni(II) ion was found to work well under laboratory conditions. The electrode was used as an indicator electrode in successful titration of 20 mL of Ni(II) (1.0×10^{-4} M) with EDTA solution (1.0×10^{-2} M). The resulting titration curve for the titration of Ni(II) ion solution with EDTA is shown in Fig.8 indicating that the amount of Ni(II) can be accurately determined with the electrode.

It should be noted that not only this electrode is suitable for the direct determination of Ni(II) ions, but also it is useful as an indicator electrode in titration of Ni(II) with a suitable chelating or precipitating agent. The proposed sensor was also used to determine the concentration of Ni(II) in different real samples including wastewaters from three electroplating industries in Tehran (Iran), water samples of a spring and well from a village near the city. The obtained results comprised with those measured by ETAAS and summarized in Table 3. As seen, the results from the electrode are well confirmed by ETAAS.

Table 3. Determination of Ni(II) concentration in real samples (n=6, replicates)

Sample	Concentration of Ni(II) (M)	
	ETAAS	Proposed sensor
Wastewater (1)	$(2.33\pm0.02)\times10^{-2}$	$(3.80\pm0.11)\times10^{-2}$
Wastewater (2)	$(3.66\pm0.02)\times10^{-2}$	$(8.49\pm0.12)\times10^{-2}$
Wastewater (3)	$(8.46\pm0.03)\times10^{-2}$	$(8.49\pm0.12)\times10^{-2}$
Well	$(1.26\pm0.04)\times10^{-6}$	$(1.29\pm0.15)\times10^{-6}$
Spring	$(1.36\ 0.04)\times10^{-6}$	$(1.43\pm0.15)\times10^{-6}$
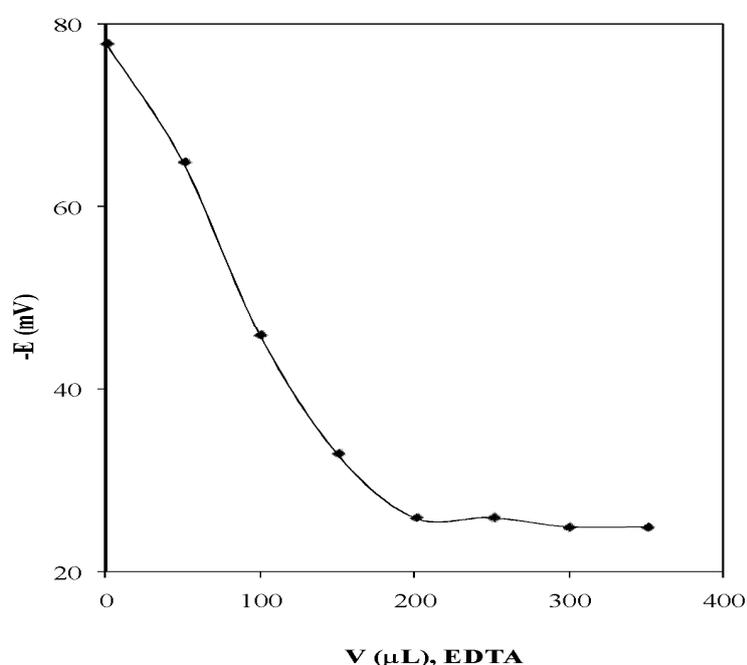
Fig. 8. Potentiometric titration curve plot of 20 mL of 1.0×10^{-4} M, Ni(II) ion solution with 1.0×10^{-2} M, EDTA at pH 5.0, using the proposed sensor (No. 4, Table 1) as an indicator electrode

4. CONCLUSION

On the basis of the results obtained in this study, Ni(II) ion–selective electrode which was designed in this work, has many advantages including: easy preparation, wide dynamic range, low detection limit, suitable pH range, good reversibility and reproducibility. The sensor was used successfully to determine the Ni(II) contents of water samples and the titration of Ni(II) with EDTA in aqueous solution. These reasonable characteristics of the

sensor could be attributed to the fact that the sensing element of the sensor reacts well selective and reproducible with respect to Ni(II) ion on the membrane-solution surface.

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