

**(1E,2E) -bis (2-aminophenyl) N<sup>1</sup>,N<sup>2</sup>-dihydroxyethane bis (imidothioate) as a neutral carrier in ion-selective electrode for Ni(II) and its computational studies**

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Received April 2013; Accepted June 2013

**ABSTRACT**

A PVC membrane Ni(II) ion selective electrode has been constructed using (1E,2E)-bis(2-aminophenyl)N<sup>1</sup>,N<sup>2</sup>-dihydroxyethanebis as membrane carrier. The electrode exhibited a good potentiometric response for Ni(II) over a wide concentration range  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-1}$  M with a slope of  $29.4 \pm 0.5$  mV/decade and a working pH range of 6.5-9.0. It had a fast response time of  $\leq 20$  s. The best performance was observed with the membrane having 30.5% PVC, 3.0% ligand, 61.0% acetophenone and 5.5% oleic acid composition.

In this work, the ligand structure studied by ab initio HF calculations using a standard 6-31G\* basis set and LanL2DZ.

**Keywords:** Ion selective electrode; PVC membrane; Ni(II) determination; computational study

**INTRODUCTION**

Ion-selective electrodes (ISEs), especially those with neutral carrier-based solvent polymeric membranes, have been studied for more than three decades, and are now routinely employed for direct potentiometric measurements of various ionic species in environmental, industrial and clinical samples [1-3]. The increasing use of ion sensors in the fields of environmental, agricultural and medicinal analysis is stimulating analytical chemists to develop new sensors for a fast, accurate, reproducible and selective determination of various species. In the last few decades,

considerable efforts have led to the development of selective sensors for alkali and alkaline earth metals and for heavy metals. Among heavy metals, trivalent metals have received less attention in spite of their widespread occurrence in rocks, alloys, food products, sea- and fresh-water, plants and animals [4].

The dioxime ligands are known to coordinate metal ions as neutral dioximes [5, 6]. The chemistry of bis-dioxime complexes of transition metal ions has attracted special attention because of their importance with reference to dioxygen

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carriers [7], catalysis in chemical transformations [8-10], intramolecular hydrogen bonding and metal-metal interaction [11-13].

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 are increasingly developing [14-18].

However, relatively little effort has been focused on the development of Ni<sub>II</sub> ion-selective electrodes. In recent years, the usefulness of aza-crown ethers as neutral carriers in membrane transport of some transition and heavy metal ions is well established [19-20].

In this paper, a new dioxime was used as an ionophore in fabrication of ISE<sub>s</sub> of determination of Ni (II) and its structure was measured by ab initio HF calculations using a standard 6-31G\* basis set and LanL2DZ.

## EXPERIMENTAL

### Materials

(1E,2E)-bis(2-aminophenyl) N<sup>1</sup>, N<sup>2</sup>-dihydroxyethanebis as ligand (Fig.1), tetrahydrofuran (THF), dibutyl phthalate (DBP), acetophenone (AP), oleic acid (OA), high relative molecular weight PVC, chloride and nitrate salts of all other cations and reagents (all from Merck or Fluka) were of the highest purity available

and used without any further purification.

### Instrumentation

A metrohm pH/mV meter, digital pH/mV meter ion analyzer in stirred solution was used. In all instances, an Ag-AgCl / KCl (sat) electrode (Azar electrode company, Urmia, Iran) in conjunction with the respective indicator electrode were included. A Haoke model FK2 circulation water bath was used to control the temperature of the test solution.

### Electrode preparation and potential measurement

A mixture of PVC, oleic acid, acetophenone and ionophore to give a total mass of 100 mg, was dissolved in about 2 mL of THF and the solution mixed well. Membrane composition is listed in Table 1. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained.

A pyrex tube (5 mm id) was dipped into the mixture for about 10s so that a nontransparent membrane of about 0.2 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 2h. It was then filled with internal solution  $1.0 \times 10^{-3}$  M Ni(II), pH=8. The electrode was finally conditioned for 24 h by soaking in a  $1.0 \times 10^{-2}$  M Ni(II) chloride solution, pH =8.

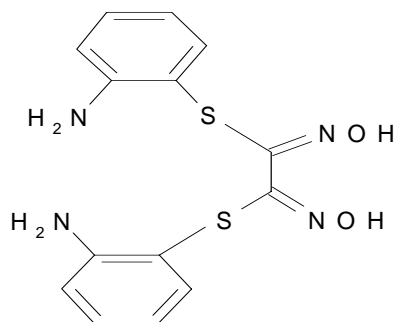


Fig. 1. Structure of (1E,2E)-bis(2-aminophenyl)N<sup>1</sup>,N<sup>2</sup>-dihydroxyethanebis used as ionophore.

The potential measurements were carried out with the following assembly:

Ag-AgCl / 3 M KCl / internal solution ( $1.0 \times 10^{-3}$  M  $\text{CrCl}_3$  +  $1.0 \times 10^{-3}$  M HCl) / PVC membrane / test solution / 3 M KCl / Ag-AgCl

A Metrohm digital research pH meter was used for measuring potential at  $25.0 \pm 1.0^\circ\text{C}$ . Activities were calculated according to the Debye-Huckel procedure [21].

## RESULTS AND DISCUSSION

### Effect of membrane composition on the electrode response

It is well known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of ionophore,

but also significantly on the membrane composition and the properties of plasticizers and additives used [22-25]. Thus, the influences of the membrane composition, the nature and amount of plasticizers and amount of oleic acid as an additive on the potential response of the Ni(II) sensor were investigated.

Among different compositions studied, membrane 6 (Table 1) incorporating 61.0 % PVC, 30.5 % AP, 5.5 % OA and 3.0 % ionophor showed the best sensitivity. The calibration plot is shown in Fig. 2, indicating a linear range from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-1}$  M Ni(II) with a Nernstian slope of  $29.4 \pm 0.5$  mV/decade of Ni(II) concentration.

Table 1. Optimization of the membrane ingredients

NO	Composition, %				Slope	Linear range, M
	Ionophor	PVC	Plasticizer	Additive		
1	-	31.0	63.2(AP)	4.8(OA)	2.7	-
2	1.5	29.0	61.5(DBP)	5.0(OA)	34.6	$1.0 \times 10^{-3}$ - $1.0 \times 10^{-1}$
3	1.8	28.0	65.0 (AP)	5.5 (OA)	27.3	$1.0 \times 10^{-3}$ - $1.0 \times 10^{-1}$
4	2.0	29.0	66.5 (AP)	4.5 (OA)	33.5	$1.0 \times 10^{-3}$ - $1.0 \times 10^{-1}$
5	2.5	27.0	64.0 (AP)	6.6 (OA)	32.8	$1.0 \times 10^{-3}$ - $1.0 \times 10^{-1}$
6	3.0	30.5	61.0 (AP)	5.5 (OA)	29.4	$1.0 \times 10^{-4}$ - $1.0 \times 10^{-1}$
7	4.5	32.0	58.0 (AP)	5.1 (OA)	28.9	$1.0 \times 10^{-3}$ - $1.0 \times 10^{-1}$
8	5.2	30.0	60.0 (AP)	5.0 (OA)	28.0	$1.0 \times 10^{-3}$ - $1.0 \times 10^{-1}$

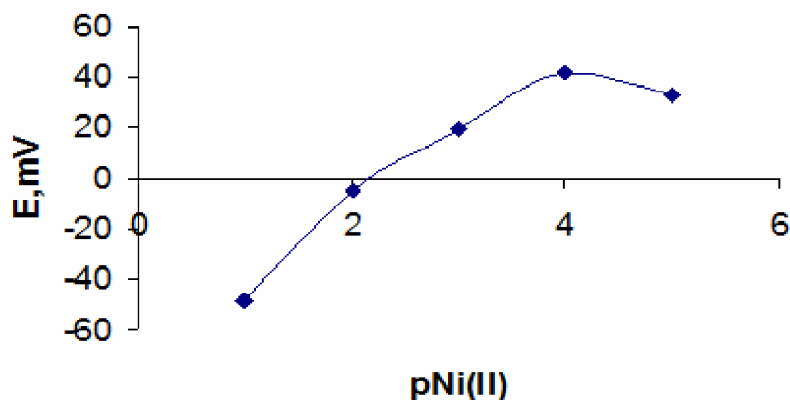


Fig. 2. Calibration plot of the Cr(III)-ISE based on ligand.

### The response time

The response time of an ion selective electrode is one of the important factors especially in connection with the analytical applications. Response time is the time taken by the electrode to achieve a stable and low noise potential. The average time required for the membrane electrode to

reach a potential within  $\pm 1$  mV of the final equilibrium value after successive immersion of Ni(II) ion solutions, each having a 10-fold difference in concentration, was investigated. A potential time plot for the electrode is given in Fig.3. The static response time of the PVC membrane thus obtained was 20s.

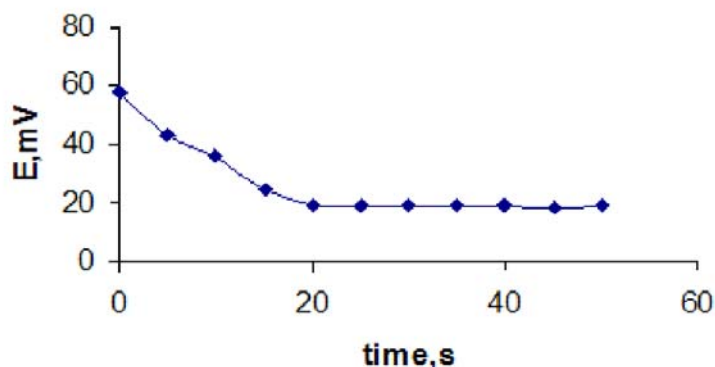


Fig. 3. The response time of Ni(II) -ISE based on ligand for Ni(II) concentration of  $1.0 \times 10^{-4}$  M.

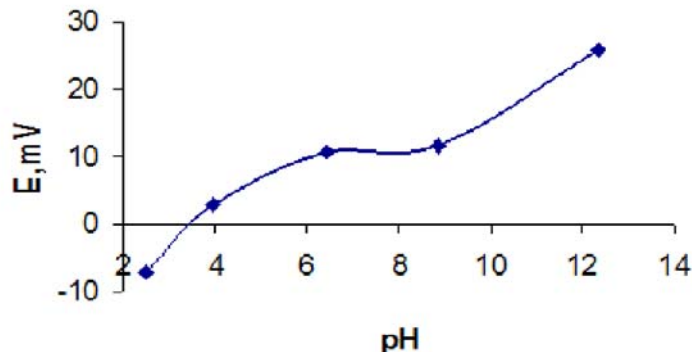


Fig. 4. Effect of pH of test solutions ( $1.0 \times 10^{-3}$ ) on the potential response of the Ni(II)-ISE.

### Effect of pH

The pH dependence of Ni(II) ion selective electrode potential (while the nickel ion concentration was  $1.0 \times 10^{-3}$  M) was tested over a pH range of 2-12 and the results are presented in Fig.4. The potential response remained almost constant over the pH ranges of 6.5-9.

### Reversibility of the electrode

To evaluate the reversibility of the

electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low (from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-3}$  M) sample concentration and the results are shown in Fig.5. This figure shows that the potentiometric response of the electrode is reversible, although the times needed to reach equilibrium values were longer than of low-to-high sample concentration [26].

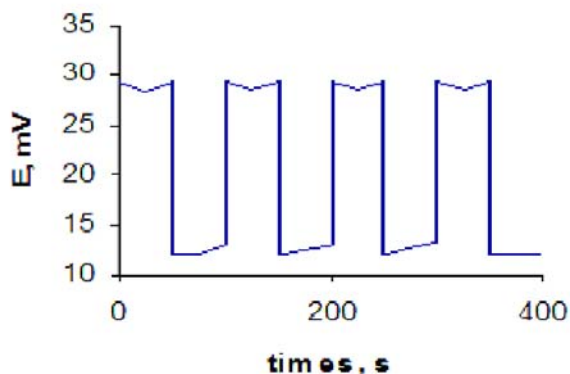


Fig. 5. Dynamic response characteristics of the Ni(II)-electrode for several high-to-low sample cycles.

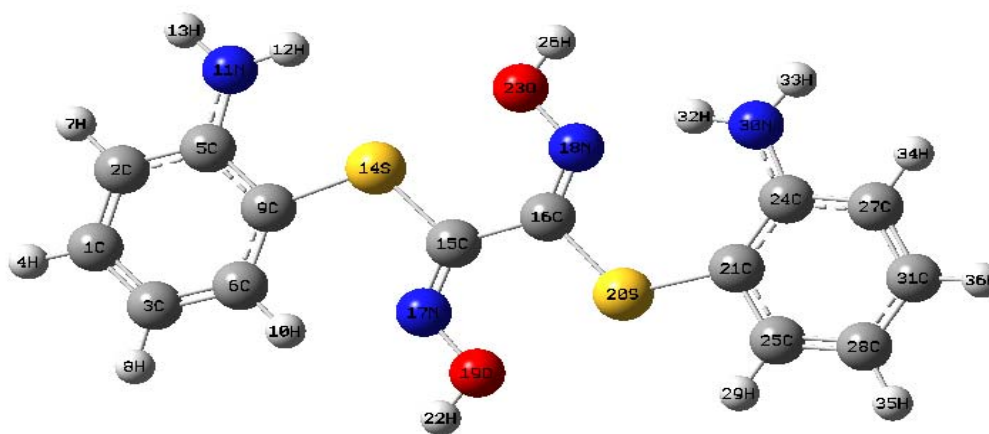


Fig. 6. The ab initio optimized structure of the used dioxime.

Table 2. Calculated energies for ligand in level of theory HF / 6-31G\*

ZPE	$E_{el}$	$E_0$	$G_0$
0.286405	-1700.612965	-1700.326560	-1700.374016

### Ab initio calculations

We performed a full geometry optimization at HF level of theory, using 6-31G\* basis set for dioxime and for formed Ni(II) complex used effective core potential (ECP) standard basis set, LanL2DZ basis set, for Ni(II) and 6-31G\* for all other atoms (Fig.6,7). Stabilisation energy for ligand and its complex were obtained as -1700.326560 Hartree mol<sup>-1</sup>

and -3205.637386 Hartree mol<sup>-1</sup> respectively (Table 2,3). Calculated Cartesian atomic coordinates, bond length, angle and torsion angles of ligand and its complex were obtained. The calculations predicted planar structure for dioxime. Also calculations on complex showed that the Ni(II) complex is as mononuclear complex that Ni was coordinated to N and O [27].

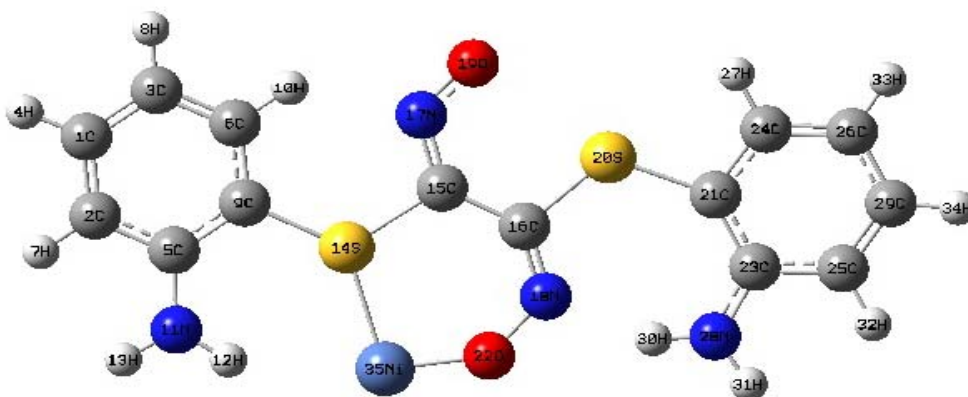


Fig. 7. The ab initio optimized structure of the complex.

Table 3. Calculated energies for complex in level of theory HF / 6-31G\*.

ZPE	E <sub>el</sub>	E <sub>0</sub>	G <sub>0</sub>
0.259359	-3205.896745	-3205.637386	-3205.682670

## CONCLUSIONS

The membrane sensor incorporating imidothioate as the electroactive phase can be used to determine Ni(II) in the wide concentration range. The sensor exhibited good reproducibility over a useful life time about 2 months. This electrode is superior to the existing electrodes with regard to the slope, response time and selectivity over a number of cation [28,29].

## ACKNOWLEDGEMENT

The authors express their appreciation to post-graduate office of Ayatollah Aozma Boroujerdi University for financial support of this work.

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