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Full Paper

Investigating The Effect of Substitution on The Efficiency of Some Hydrazone Ligands in Using Them as Ionophores in The Construction of Membrane Sensors for Cr^{3+} Ions

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Abstract- Chromium is a metallic element that is used in various industries. Because when chromium is placed in the environment, it is possible to be absorbed by humans and other environmental receptors, which is why the control of this element is very important. Ion-selective electrodes are commonly used today to measure a large number of cations and anions, which do not have some of the problems of the other analytical methods. In this study, to design and build a new chromium ion-selective potentiometric sensor, two ligands (E)-4-amino-N'-(5-bromo-2-hydroxybenzylidene) benzohydrazide (LP5) and (E)-4-amino-N'-(2-hydroxy-3-methoxybenzylidene) benzohydrazide (LP7) was used as ionophores. Then, two ligands used as ionophores were compared in terms of performance and efficiency, and finally the best ionophore was selected for further experiments. The potentiometric responses of electrodes for both ligands were without any changes in the pH range of 2.5 to 10. The electrode with LP5 ligand showed a detection limit of 9.8×10^{-8} and the LP7 ligand showed a detection limit of 9.5×10^{-8}. As a result, the LP7 ligand indicates a favorable selectivity toward the Cr^{3+} ion. The optimal composition of the membrane that led to the desired results was 8% ionophilic, 4% additive, 64% plasticizer, and 24% PVC powder.

Keywords- Ion selective electrodes; PVC-membrane; Chromium (III) ions; Hydrazone ligands; Potentiometric sensor

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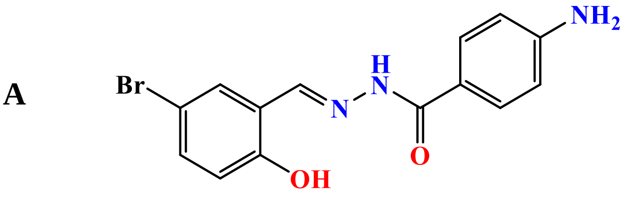
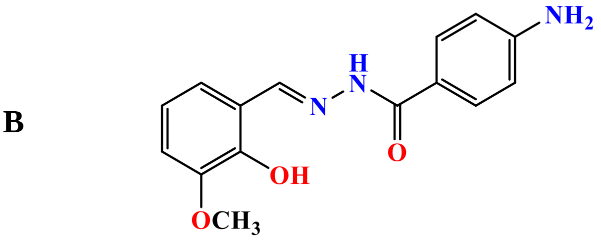
1. INTRODUCTION

Chromium is widely used in many fields such as metal finishing, metallurgy, steel manufacturing, paint, electroplating, wood treatment, and alloy manufacturing industries [1,2]. Metal ions can be both essential and toxic to living organisms depending on the concentration [3]. Chromium is essential for human health in small amounts due to its effect on insulin, carbohydrate, fat, and protein levels which should be kept at certain ranges for human physiology to function properly [4,5]. However, it is toxic at high concentrations. Therefore, it is of great importance to determine the chromium levels in industry and environmental samples. Up to now, several analytical methods of Cr^{3+} determination have been applied in the field such as inductively coupled plasma–atomic emission spectroscopy (ICP–AES) [6], atomic absorption spectrometry (AAS) [7], high-performance liquid chromatography (HPLC) [8], UV–visible spectrophotometry [9], and x-ray diffraction (XRD) [10]. These techniques have some limitations in terms of certain properties such as high energy consumption, the requirement of trained personnel, high cost, time consumption, complex use, and the requirement of sample pretreatment [11,12].

An ion-selective electrode (ISE) also known as a specific ion electrode is a sensor that converts the activity of a specific ion dissolved in a solution into an electrical potential. Ions selective electrodes are used in analytical chemistry and biochemical/biophysical research where measurements of ionic concentration in an aqueous solution are required. Ion-selective electrodes have a wide concentration range. It is highly selective to a particular ion. Ion-selective electrodes are unaffected by the color or turbidity of the solution. ISE has many advantages compared to other techniques, including its relatively inexpensive and easy-to-operate, wide concentration measurement range, and measures activity instead of concentration, it is particularly useful in biological, medical, and agricultural applications [13,14].



(*E*)-4-amino-*N*'-(5-bromo-2-hydroxybenzylidene)benzohydrazide



(*E*)-4-amino-*N*'-(2-hydroxy-3-methoxybenzylidene)benzohydrazide

Figure 1. A) Chemical structure of LP5; B) Chemical structure of LP7

In the present study, we have constructed a potentiometric Cr(III)–selective electrode based on two hydrazone ligands (Figure 1). The ability of these two ligands to be used as ionophores in the construction of membrane electrodes was compared to the potentiometric performance properties of this developed electrode and its applicability in real samples was further investigated.

2. EXPERIMENTAL SECTION

2.1 Synthesis of ionophores

2.1.1. Synthesis of (E)-4-amino-N'-(5-bromo-2-hydroxybenzylidene) benzohydrazide (H_2L^1) (LP5)

For the synthesis of H_2L^1, 0.665 g of 5-bromo-2-hydroxybenzaldehyde (3.307 mmol) and 0.500 g of 4-Aminobenzoic hydrazide (3.307 mmol) were added to the round bottom flask containing 15 mL methanol. The mixture of the reaction was placed in an oil bath under reflux condition for 8 hours (see Scheme 1a). After a while, white precipitates were obtained. The flask containing the product was cooled to RT and after filtration, the precipitates were washed with cold methanol. Yield: 92.3% (1.02 g) M.p. 258-261 °C [15].

2.1.2. Synthesis of (E)-4-amino-N'-(2-hydroxy-3-methoxybenzylidene) benzohydrazide (H_2L^2) (LP7)

H_2L^2 was synthesized by the reaction of 2-hydroxy-3-methoxybenzaldehyde (0.805 g,5.292 mmol) with 4-aminobenzoic hydrazide (0.800 g,5.292 mmol) in 20 mL methanol at 65 °C (see Scheme 1b). The reaction was continued for 6 hours and after checking the completion of the reaction by TLC, the obtained white precipitates were filtered, washed with cold methanol and dried at RT. Yield: 93.4% (1.41 g) M.p. 158-162 °C [16].

2.2. Reagents and materials

Reagent grade nitrophenyl octyl ether (NPOE), dioctyl phthalate (DOP), benzyl acetate (BA), sodium tetraphenylborate (STPB), potassium tetrakis (p-chlorophenyl) borate (KTCPB), DTB18C6, tetrahydrofuran (THF) and high relative molecular weight PVC (all from Aldrich) were used as received. Triply distilled deionized water was used throughout.

2.3. Fabrication of PVC Chromium (III) membrane sensor

Membrane solution was prepared by thoroughly dissolving 5 mg of ionophores, 33 mg of PVC powder, 60 mg of BA plasticizer, and 2 mg NaTPB additive in 2 mL of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm o.d.) [17-26] was dipped into the mixture for 10 s so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for 24 hours. The tube was then filled with 1.0×10^{-3} M Cr^{3+} as an internal solution. A silver-silver chloride electrode was used as the internal reference electrode.

2.4. Emf Measurements

The emf measurements with the polymeric membrane electrodes (PME) were carried out with the following cell assembly:

Ag-AgCl | KCl (3 M) |internal solution, 1.0×10^{-3} M Cr^{3+}|PVC membrane |test solution| Ag-AgCl

A double-junctions silver/silver chloride electrode containing a 3 M KCl solution was used as the internal reference electrode.

3. RESULTS AND DISCUSSION

3.1. Optimization of membrane composition

In ion-selective electrodes, the sensitivity and selectivity of the electrode towards the desired ion depends on the components of the membrane and its percentage composition. In this study, in order to achieve a favorable Nernst gradient and high selectivity, parameters such as the amount of ion carrier, the type and amount of plasticizer, and the amount of additive should be changed to obtain the most suitable percent composition for the membrane.

The amount of ionophores present in the membrane plays a key role in the efficiency of the electrode, because the amount of this substance has an effect on the number of sites available for the interaction of the complex with the desired ion.

Values less than the optimal value will reduce the binding sites for the formation of the complex and therefore the desired response will not be obtained. In the case of values higher than the optimal values, it causes the electrode response to be unfavorable.

At this stage, by keeping the amount of other constituents constant, the optimal amount of LP5 and LP7 ligands, which were used as ionophores, was determined, then the final percentage of 8% was selected, the results of which are shown in Table 1 and 2 are given.

The addition of lipophilic salts such as sodium tetraphenylborate reduces the anionic disturbance by preventing the anions from approaching the membrane and also reduces the electrical resistance of the membrane. The effect of the amount of NaTPB salt in the membrane was investigated in the presence of both types of LP5 and LP7 ionophores, and then the final percentage of 5% was selected, the results of which are given in Table 1 and 2.

Another important factor in ion selective electrodes is plasticizer. Depending on whether the plasticizer is polar or non-polar, it has an effect on the formation constant of the main ion complex with friendly ions against interfering ions and ultimately has a great effect on the selectivity of the membrane. In this project, two types of plasticizers, Benzyl acetate and Ortho nitrophenyl octyl ether, were investigated in the presence of both ionophores LP5 and LP7.

Benzyl acetate was selected with a final percentage of 65%, the results of which are shown in Tables 1 and 2.

Table 1. Optimization of membrane ingredients for LP5

Membrane	Composition (٪)				Slope (mV/decade)
	PVC	Plasticizer	LP5	STPB,Additive	
1	35	BA,65	-	-	~0
2	30	BA,65	-	5	6.2
3	27	BA,65	5	3	9.5
4	29	BA,65	5	8	8.1
5	24	BA,65	4	8	12.5
6	24	NPOE,65	6	8	11.9
7	23	BA,65	5	8	14.5
8	22	BA,65	5	8	17.4
9	28	BA,60	5	8	14.4
10	32	BA,55	5	8	12.8

Table 2. Optimization of membrane ingredients for LP7

Membrane	Composition (٪)				Slope (mV/decade)
	PVC	Plasticizer	LP5	STPB,Additive	
1	35	BA,65	-	-	~0
2	30	BA,65	-	5	4.5
3	27	BA,65	5	3	10.9
4	29	BA,65	5	8	8.3
5	24	BA,65	4	8	17.2
6	24	NPOE,65	6	8	14.9
7	23	BA,65	5	8	18.1
8	22	BA,65	5	8	19.8
9	28	BA,60	5	8	16.4
10	32	BA,55	5	8	13.1

After the optimization process, the composition of the final percentage of the components of the membrane was determined. The obtained data are given in Tables 1 and 2.

According to the results obtained in Table 1 and 2, membrane number 8, with a combination of 8% ionophore, 5% additive, 65% plasticizer, and 22% PVC powder, the electrode made with ionophore LP5 has a Nernstian response of 17.4 mV per decade and the electrode made with ionophore LP7 shows a favorable Nernst response of 19.8 mV per decade.

3.2. Calibration curves and limit of detections:

Using the optimal conditions, the calibration curves for LP5 and LP7 were drawn. The results can be seen in Figures 2A and 2B.

As can be seen in Figure 2, the range of linearity of the curve in both electrodes is in the range of 1×10^{-1} to 1×10^{-7} M, and the detection limit for LP5 and LP7 ligands is 8.9×10^{-8}, and 9.5×10^{-8} M, respectively. Response characteristics of the Chromium ion-selective electrodes are listed in Table 3.

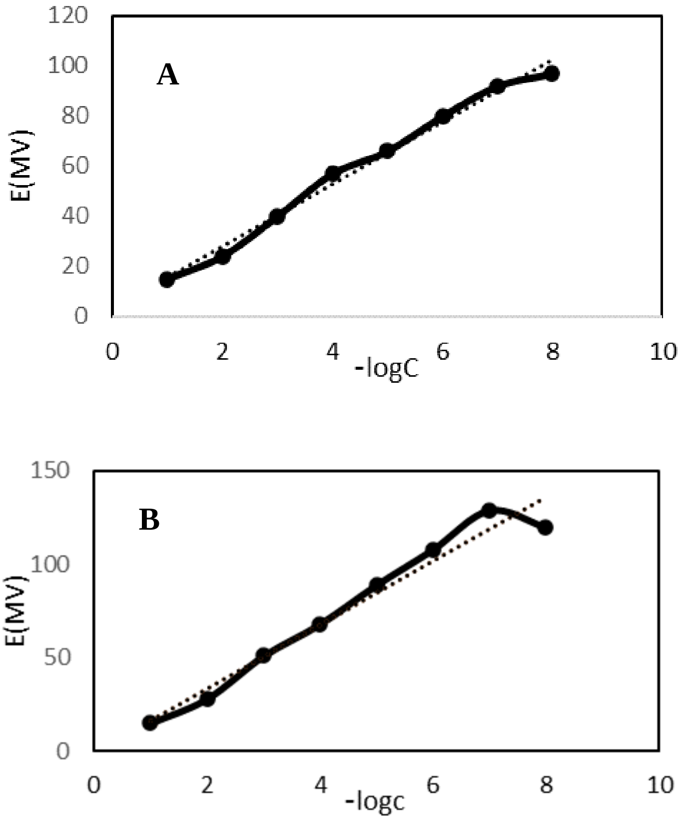


Figure 2. A) Calibration graph for the LP5 PME electrode; B) Calibration graph for the LP7 PME electrode

3.3. Effect of Internal Solution

The influence of internal solution concentration on the PME potential response was investigated. The Cr^{3+} concentrations were changed from 1.0×10^{-4}-1.0×10^{-2} M and the emf-p Cr plots were obtained. It was found that the concentration of the internal solution has a negligible effect on the potential response of the electrode (Figure 3). It should be noted that a change in internal solution concentration is expected to change the potential difference in the internal solution/membrane interface, and consequently, the overall emf of the cell assembly [22].

Table 3. Response characteristics of the Chromium ion-selective electrodes

Electrode	Slope (mV/decade)	Linear range (M)	LOD (M)	Response time (s)	Lifetime (week)
LP5	17.4	1.0×10^{-7} - 1.0×10^{-1}	9.8×10^{-8}	65	12
LP7	19.8	1.0×10^{-7} - 1.0×10^{-1}	9.5×10-8	60	12

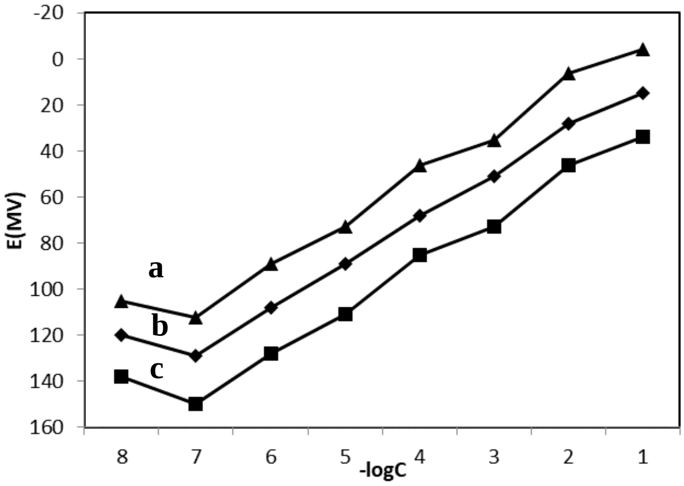


Figure 3. Effect of the internal solution. a: 10^{-2} M, b: 10^{-3} M, c: 10^{-4} M Cr^{3+}

3.4. Effect of pH

The potential response dependence of the BA plasticized prepared membrane sensors on the pH solution over wide 1.0-14.0 ranges, using dilute HCl and/or NaOH was investigated in the presence of 1.0×10^{-3} M Cr^{3+} ions (Figure 4). As shown in Figure 4, the potential remains constant from pH 2.5 to 10 for both electrodes. The observed large decrease in potential at higher pH values could be due to the formation of some hydroxy complexes of Cr^{3+} in the solution. At low pH, the potential decreased, indicating that the ionophores were protonated [23-28].

3.5. Dynamic response time

Dynamic response time is an important factor in analytical applications. The static response time of the electrode tested by measuring the average time required to achieve a potential within ±1 mV of the final steady state potential upon successive immersion of a series of Cr^{3+} ions, each having a tenfold difference in concentrations, was within <60 s for PME, for concentrations 10^{-3}M Cr^{3+} (Figure 5).

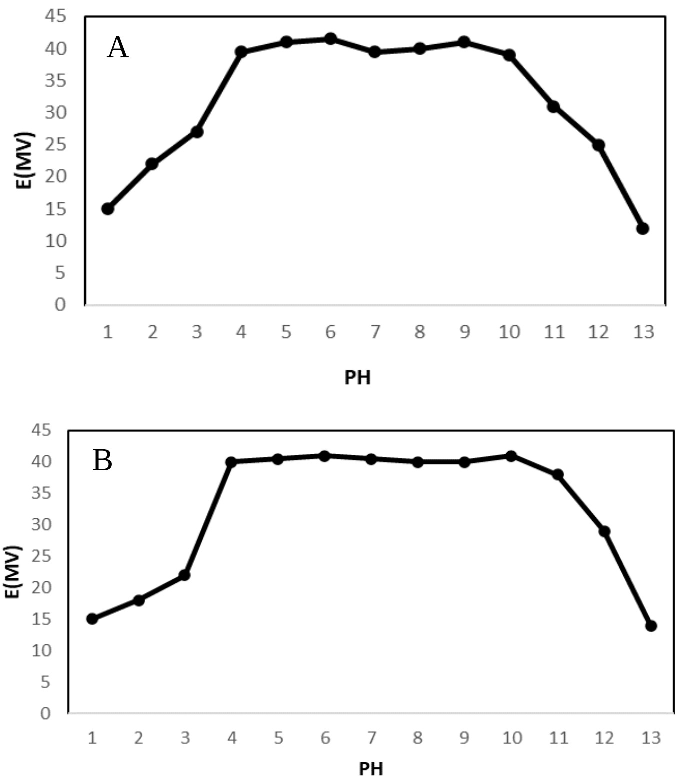


Figure 4. A) Influences of pH of the test solution on the potential response of the LP5 electrode in the presence of 1.0×10^{-3} M Cr^{3+}; B) Influences of pH of the test solution on the potential response of the LP7 electrode in the presence of 1.0×10^{-3} M Cr^{3+}

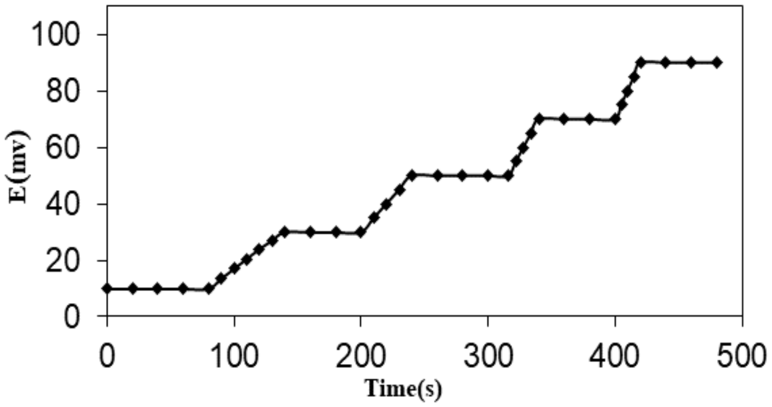


Figure 5. Typical dynamic response of the proposed electrode for step change concentrations from low to high : From 1.0×10^{-6} to 1.0×10^{-2} M Cr^{3+}

3.6. Selectivity Coefficients

The influence of interfering ions on the Cr^{3+} ion selective membrane electrode potential response is usually described in terms of the selectivity coefficient [29-31]. Potentiometric selectivity coefficient, $K_{Ba,M}^{pot}$, describing the preference by the membrane for an interfering ion M^{n+} relative to Cr^{3+}, were determined by the separated solutions method [32,33] as follows. The emf-pM^{n+} plots were obtained for the Chromium and the interfering ions separately, using the proposed electrode systems. Then by using a pair of values of primary (a_A) and interfering (a_B) ion concentrations at which the electrode takes the same potential in separate solutions (i.e., isopotential concentrations) and equation $K_{A,B}^{pot}$= ln $a_A/a_B^{3/z}$(where z is the charge of interfering ion), the selectivity coefficient was determined.

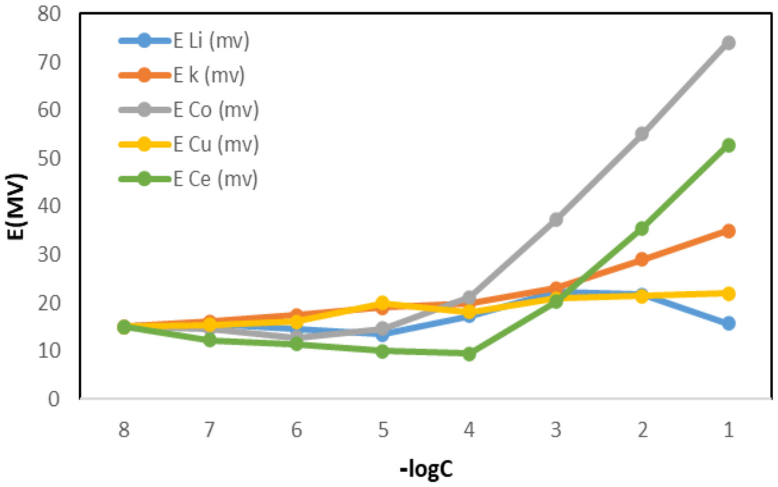


Figure 6. Selectivity coefficient of various interfering ions

The results of investigating the interference effect of other cations (in electrode with LP7) are shown in Figure 6 and the results of calculating the selectivity coefficients are given in Table 4. The results of the table show that the presence of other cations in the tested solution does not have much effect on the performance of the membrane electrode.

Table 4. Selectivity coefficient of various interfering ions

Interfering ion	Selectivity coefficient
Cd^{2+}	2.5×10^{-2}
Ce^{3+}	8.2×10^{-3}
Ni^{2+}	7.3×10^{-3}
Al^{3+}	6.9×10^{-4}
Co^{2+}	5.5×10^{-3}
Cu^{2+}	3.6×10^{-4}
Li^{+}	5.8×10^{-4}
K^{+}	1.0×10^{-3}

4. CONCLUSION

This work introduces two ligands (E)-4-amino-N'-(5-bromo-2-hydroxybenzylidene) benzohydrazide (LP5) and (E)-4-amino-N'-(2-hydroxy-3-methoxybenzylidene) benzohydrazide (LP7) as ionophores to make chromium selective electrodes. After using both LP5 and LP7 ligands as ionophiles in the construction of the PVC membrane sensor and optimizing and checking the properties of the constructed electrode, it was found that both ligands can be used for detecting Cr^{3+} ions. However, the LP7 ligand is more suitable for the manufacture of chromium membrane electrodes which is probably due to the presence of an electronegative bromine atom in the structure of the LP5 ligand. The detection limit of the electrode with LP7 ligand was 9.5×10^{-8} M and for the LP7 ligand was of 9.8×10^{-8} M.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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