Design and Construction of High-Sensitive and Selective Zinc(II) Electrochemical Membrane Sensor Based on N,N-bis (2hydroxy -4-metoxybenzaldehyde)-2,6-di amino pyridine

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In this work, a novel Zn (II) membrane sensor based on N, N-bis (2hydroxy -4-metoxybenzaldehyde)-2, 6-di amino pyridine (L1) is presented. The electrode shows a good selectivity for Zn (II) ions with respect to most common cations including alkali, alkaline earth, transition and heavy metal ions. Conductance study of L1 to Zinc and some other metal ions were carried out and confirmed selectivity toward Zn (II) ions. The electrode comprises 7 % L1, 29 % PVC, 60 % NPOE and 4 % NaTPB. The sensor displays a linear dynamic range between 1.0×10^{-7} and 1.0×10^{-1} M, with a nice Nernstian slope of 29.5 ± 0.5 mV per decade and a detection limit of 7.9×10^{-8} M. The potentiometric response is independent of pH in the range of 4.5–10. The proposed sensor posses the advantages of short response time, low detection limit and wide linear dynamic range in comparison with former ones. The electrode can be used for at least four month without any considerable divergence in the potentials. It was used as an indicator electrode in the potentiometric titration of Zn (II) ions with EDTA. It was also applied for determination of Zn^{2+} in some soil samples and in electroplating industrial samples.

1. INTRODUCTION

Ion selective electrodes have shown to be very effective tools for the analysis of a wide variety of cations, anions, and molecules. They are one of the selective methods for monitoring and determination of rare earth elements. They offer advantages of low cost, portability, selectivity, and simple operatory. They also provide an analysis method without destruction of sample. Also, they can be used incomplex matrix of samples [1-6].

Zinc ion is an important divalent cation in biological systems, and plays important roles in a human body, influencing DNA synthesis, microtubule polymerization, gene expression, apoptosis, immune system function, and the activity of enzymes such as carbonic anhydrase and matrix metalloproteinase [7]. Moreover, zinc ion is also a contributory factor in neurological disorders such as epilepsy and Alzheimer's diseases [8]. Zinc is also essential to the senses of taste and smell and for growth and development. The zinc deficiency wasmarked by dwarfism or severe growth retardation, as well as, can result in metabolic changes such as impaired immune response, abnormal taste and abnormal dark adaptation.

The foods with high content of protein are abundant source of zinc, such as shellfish, meals, liver and milk which is a good source for infants. Zinc is a relatively non-toxic element; however, it can be toxic if consumed in large quantities. For example, zinc is a metal pollutant of environment, significant concentrations of which may reduce the soil microbial activity causing phytotoxic effect [9, 10] and also a common contaminant in agricultural and food wastes [11]. A high zinc intake is known to produce copper-deficiency anemia by inducing the intestinal cells to synthesize large amounts of a protein that captures copper in a non-absorbable form [12]. Determination of zinc in excretive organ of the human body such as hair can reflect the cumulative status of this essential element in the body evaluating the nutrient status [13]. Thus, the determination of trace amounts of zinc is currently of great interest in many scientific fields, including medicine analyses and environmental monitoring.
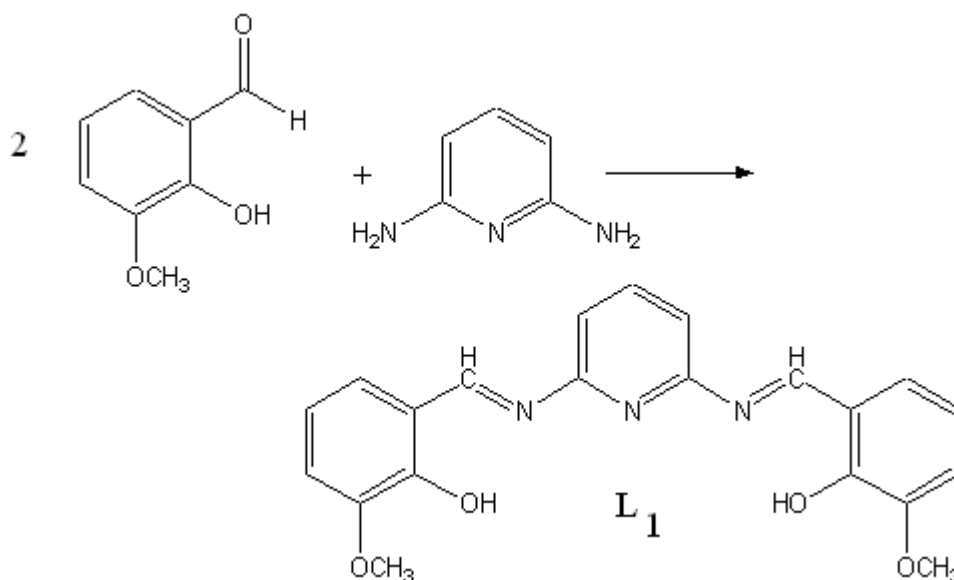

Figure 1. Structure of ligand (**L₁**)

Though several analytical techniques such as UV–Vis spectroscopy [14], potentiometry [15] and flame atomic absorption spectrometry [16], inductivity coupled plasma atomic emission spectroscopy (ICPAES) [17] and fluorescence methods [18, 19] have been reported for zinc ion assay in various samples. The available detection methods of Zn^{2+} are still limited due to its 3d104s0 electron configuration not giving any spectroscopic or magnetic signals. Among these techniques, the ion-

selective electrodes (ISEs) are relatively simple, fast and inexpensive. Due to the critical importance of selective Zn^{2+} ion determination, especially, in biological, industrial and water samples, there are a number of reports on the preparation of Zn^{2+} ion-selective electrodes based on a variety of ionophores [20-27]. In this work, we report the use of N, N-Bis (2-hydroxy-4-methoxybenzaldehide)-2,6-diaminopyridine (L_1), as an excellent ionophore for preparation of a highly Zn(II) ion selective electrode (Fig. 1).

2. EXPERIMENTAL

2.1. Reagents

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight poly vinyl chloride (PVC) were purchased from Merck and Aldrich, and used as received. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P2O5. Triply distilled de-ionized water was used throughout.
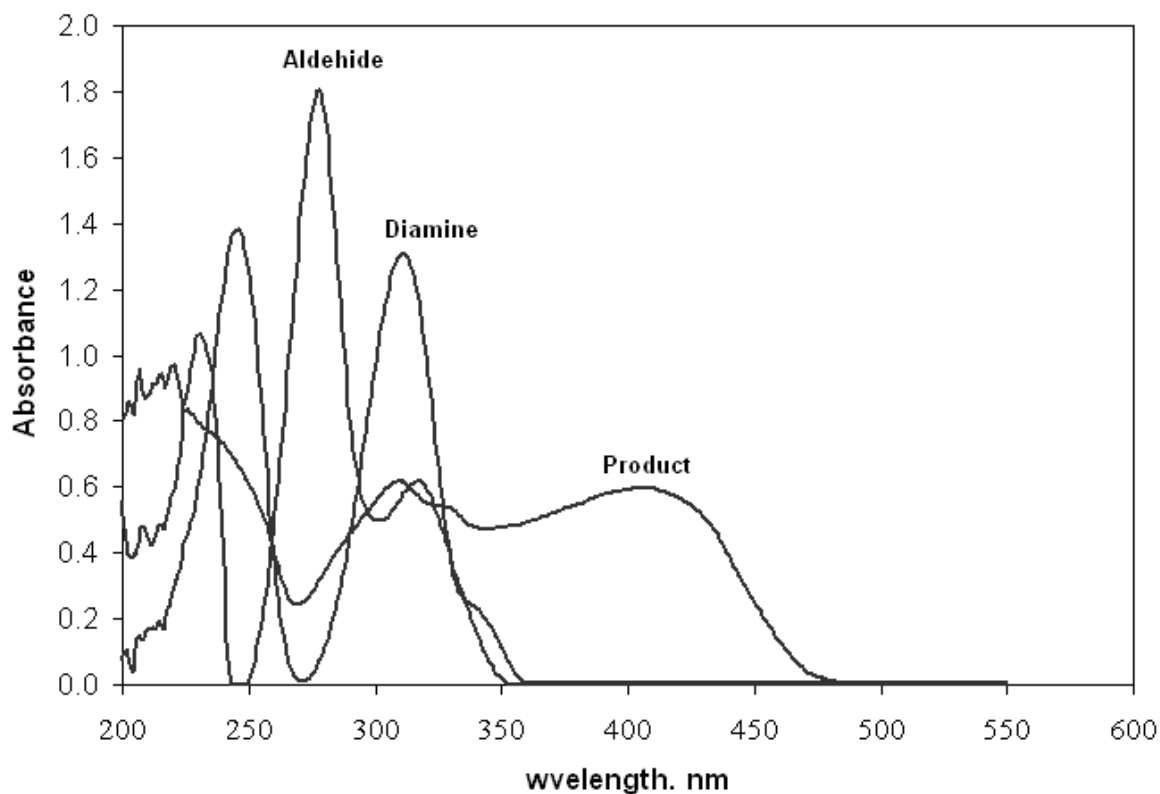
2.2. Synthesis of ligand

Figure 2. The electronic spectrum of product (L_1) and starting materials.

The Schiff base N, N-Bis(2-hydroxy-4-methoxybenzaldehyde)-2,6-diaminopyridine (**L₁**), have synthesized from reaction of 2,6-diaminopyridine and 2-hydroxy-4-methoxy benzaldehyde (Fig. 1). The yield of reaction was about 75%. For remove of water from reaction system the Dean Stark method have used. The synthesis of product has tested with TLC to confirm the pure product without any starting materials as impurity.

The HNMR data: The peaks about 4 ppm is related to protons of OCH_3 groups (the peaks area is 3 and slight difference in chemical shifts). The peaks about 6-8 ppm are related to aromatic ring protons. The peak about 9.5 ppm with area of 2 is related to protons of OH groups and the peak about 11 ppm is related to Imine proton that it appear in down field because it is near the electronegative nitrogen atom.

IR (selected bands; in cm^{-1}): 807m, 965m, 1100m, 1120w, 1250m, 1425m, 1560m, 1650s, 3000w, 3560w.

The UV-Vis spectrum of product and starting materials (aldehyde and diamine) is shown in Fig. 2. The sharp band about 400 nm in Schiff base (the product) shown that the product have been synthesized, because this band is not in any of the starting materials.

Elemental analysis for $C_{21}H_{19}N_3O_4$: calc: C, 66.84; H, 5.04; N, 11.14. Found: C, 66.39; H, 5.23; N, 11.33%.

2.3. Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 29 mg of powdered PVC, 60 mg of plasticizer NPOE, 4mg of additive NaTPB, and 7mg of ionophore L_1 in 4mL of fresh THF. The resulting 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 (3–5mm o.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3mm thickness was formed. The tube was then pulled out from the mixture and kept at the room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3}M of Zn $(NO_3)_2$). The electrode was finally conditioned by soaking in a 1.0×10^{-2}M Zn $(NO_3)_2$ solution for 24 h [3-6]. A silver/silver chloride wire was used as an internal reference electrode.

2.4. The emf measurements

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

Ag–AgCl|3M KCl|internal solution, 1.0×10^{-3}M Zn($NO_3)_2$| PVC membrane |test solution |Hg – Hg₂Cl₂, KC1 (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ∘C. Activities were calculated according to the Debye–H˝uckel procedure [28].

3. RESULTS AND DISCUSSION

3.1. Preliminary Studies

In preliminary experiments, the complexation of L_1 with several metal ions, including Pb^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+}, was studied spectrophotometrically in order to obtain a clue about the stoichiometry and stability of resulting complexes. In this method , at first 2 ml of sample of ligand solution (concentration 5.0×10^{-5} M) in Toluene solvent into the quartz cell was poured and it's spectrum is depicting in about 200 – 600 nm by double beam Shimadzu spectrometer equipped by computer. Then, different volumes of metal ion solutions in Toluene solvent at concentration 1.3×10^{-3} M was added by 10 µl Hamilton syringe and after mixing by a thin tube, the solution absorption was measured .This process continued until several of solution absorption fixed or decrease. the measured absorption diagram is depicting in complex λ_{max} or liquid λ_{max} ,then the experimental data with calculated data of KINFITT software is fitted and the complex formation constants determine by this fitted diagrams. The resulting formation constants are shown in table 1.

Table 1. Some of metal ions complex formation constants logarithm

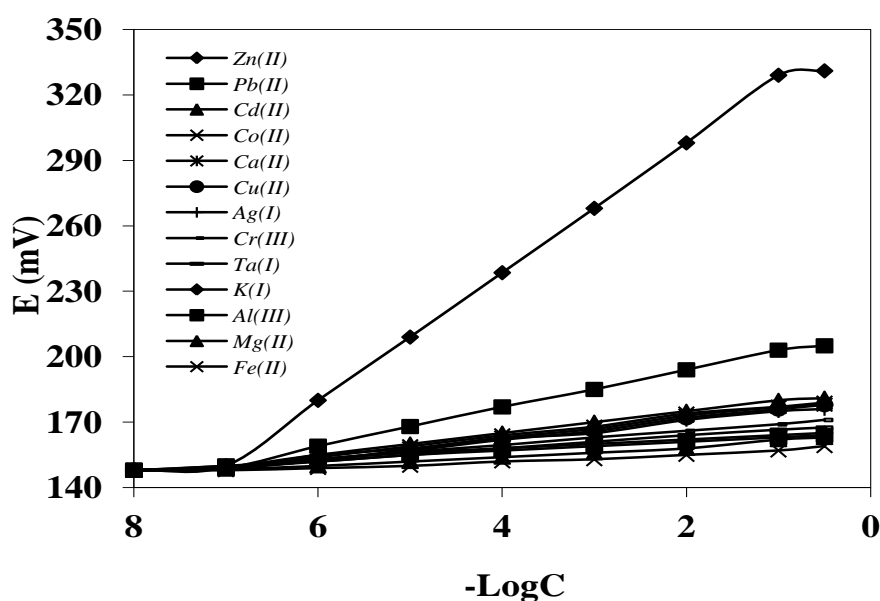| ions	formation constant (log k_1)	formation constant (log k_2)
Pb^{2+}	4.0286±010018	2.9997±0.0016
Hg^{2+}	3.5141±0.0001	3.3669±0.0001
Cd^{2+}	3.6613±0.0005	2.9832±0.0007
Zn^{2+}	4.6539±0.0048	3.8469±0.0036
Cu^{2+}	3.3356±0.0023	3.1586±0.0011

Figure 3. The potential responses of various ion-selective electrodes based on L_1

As seen, in the case of Zn^{2+} addition of the cation to the ligand solution caused the formation of relatively stable complex with the ligand. In the case of other metal ions examined, formation constants are smaller, emphasizing the formation of weak complexes between these cations and the ligand. The results thus obtained revealed the much higher selectivity of L for Zinc ion over other cationic species studied except with lead ion, which is expected to have some minor competition with Zinc ion for the ligand.

In preliminary experiments, it was found that, while the use of an ionophore-free PVC membrane resulted in no measurable response with respect to Zn^{2+} ion, the addition of L_1 shows a Nernstian response for the cation in the range of $1.0 \times 10^{-7} - 1.0 \times 10^{-1}$ M (Fig. 3). Meanwhile, the ligand L_1 was also used as a neutral carrier to prepare PVC membrane electrodes for a variety of metal ions. The potential responses of various ion selective electrodes based on L_1 are also shown in Figure 3. As seen, except for the Zinc ion-selective electrode, in all other cases, the slope of the corresponding potential-pM plots was much lower than the expected Nernstian slopes of 59, 29.5 and 19.5 mV per decade for mono-, bi- and trivalent cations, respectively.

Thus, several parameters were investigated in order to evaluate the performance of the Zinc (II) ion-selective electrodes based on ionophore L_1 in terms of membrane composition, calibration curve slopes, reproducibility, linear range, limit of detection, response time, selectivity and sample analysis.

3.2. Membrane Composition

Table 2. Optimization of membrane ingredients

No.	Composition (%)				Slpoe mV/decade	Concentration range M	D.L (M)
	PVC	Plasticizer	L	Additive			
1	30	NPOE,70	-	-	~3.2	1.0×10^{-4}-1.5×10^{-2}	-
2	30	NPOE,67	3	-	15.4	2.0×10^{-5}-4.0×10^{-2}	9.5×10^{-6}
3	30	DBP,67	3	-	11.1	4.3×10^{-5}-1.8×10^{-2}	1.8×10^{-5}
4	30	BA,67	3	-	10.2	1.1×10^{-5}-1.0×10^{-2}	9.6×10^{-6}
5	30	DOP,67	3	-	7.5	1.0×10^{-4}-2.5×10^{-2}	8.4×10^{-5}
6	28	NPOE,67	5	-	18.3	9.6×10^{-6}-7.0×10^{-1}	7.6×10^{-6}
7	26	NPOE,67	7	-	19.2	5.5×10^{-6}-1.0×10^{-2}	3.2×10^{-6}
8	24	NPOE,67	9	-	16.1	2.3×10^{-6}-1.0×10^{-2}	1.5×10^{-6}
9	26	NPOE,62	7	OA,5	21.8	1.0×10^{-6}-5.0×10^{-1}	9.3×10^{-7}
10	26	NPOE,57	7	OA,10	23.4	1.0×10^{-6}-5.0×10^{-1}	9.5×10^{-7}
11	26	NPOE,52	7	OA,15	22.5	1.0×10^{-6}-3.3×10^{-1}	8.9×10^{-7}
12	30	NPOE,60	7	KTpClPB,3	25.5	8.5×10^{-7}-1.0×10^{-2}	6.8×10^{-7}
13	29	NPOE,60	7	KTpClPB,4	27.9	5.0×10^{-7}-1.0×10^{-2}	3.6×10^{-7}
14	28	NPOE,60	7	KTpClPB,5	26.3	9.1×10^{-7}-2.6×10^{-2}	8.5×10^{-7}
15	30	NPOE,60	7	NaTPB,3	27.2	1.5×10^{-7}-2.0×10^{-1}	9.9×10^{-8}
16	29	NPOE,60	7	NaTPB,4	29.5	1.0×10^{-7}-1.0×10^{-1}	7.9×10^{-8}
17	28	NPOE,60	7	NaTPB,5	28.4	1.0×10^{-7}-4.0×10^{-1}	9.1×10^{-6}

It is well-known that the sensitivity, sensitivity and the linearity of the ion-selective electrodes not only depend on the nature of ionophore used but also significantly on the membrane composition and the properties of plasticizers and additives used [29-34]. Thus, the effects of membrane composition and the nature and the amount of plasticizer and additive on the potential response of the Zn ion-selective electrode were investigated and the results are summarized in Table 2.

It is reported that the response characteristics of ion selective electrodes are largely affected by the nature and amount of plasticizer used [29-34]. This is due to the influence of plasticizer on dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [29, 30]. As it is seen from Table 2, among four different plasticizers used, NPOE with the highest polarity in the series resulted in the best response slope and linearity.

As it was expected, the amount of ionophore L was also found to affect the PVC-membrane sensitivity (Nos. 6 − 8). As it is obvious from Table 2 (Nos. 6 − 8), optimization of amount of ionophore in the membrane was performed in the absence of any additive. The calibration slope increased with ionophore content up to a value of 7%. However, further increase in the amount of L resulted in diminished calibration slope of the electrode (e.g. No. 8), presumably due to some inhomogenities and possible saturation of the membrane [29].

The sensitivity of the PVC-membrane is quite low in the absence of a proper lipophilic additive (Nos. 2 − 8). However, the presence of some 10% OA, and especially 4% NaTPB resulted in increased sensitivity and a more or less Nernstian behavior of the membrane sensor (Table 2, Nos. 10 and 16, respectively), as expected [29-34]. Obviously, the response of lipophilic anions in cations selective membrane electrodes not only diminished the ohmic resistance and enhances the response behavior and selectivity but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrode [32-34]. Moreover, additives may catalyze the exchange kinetic at the sample-membrane interface [31]. From the data presented in Table 2, it is seen that the addition of NaTPB will increase the sensitivity of the electrode response considerably.

As is obvious from Table 2, membrane number 16 with PVC: NPOE: L: NaTPB percent ratio of 29: 60: 7: 4 resulted in the Nernstian behavior of the membrane electrode over a wide concentration range the PME.

3.3. Effect of Internal Solution

The influence of the concentration of the internal solution on the potential response of the PME was investigated. The Zn $(NO_3)_2$ concentrations were changed from 1.0×10^{-4} M to 1.0×10^{-2} M and the emf-pZn (II) plots were obtained. It was found that the concentration of the internal solution has a negligible effect on the potential response of the electrode, except for on expected change in intercept of the resulting plot. A 1.0×10^{-3} M concentration of the references solution is quite appropriate for a smooth functioning of the polymeric membrane system. It should be noted that a change in concentration of the internal solution is expected to change the potential difference on the internal solution/membrane interface and, consequently, the overall emf of the cell assembly.

3.4. Response Characteristics of the Membrane Electrode

Optimum conditioning time for the PME 1.0×10^{-2} M Zn $(NO_3)_2$ solution was found to be 24 h. They then generate stable potentials when placed in contact with Zn^{2+} solutions.
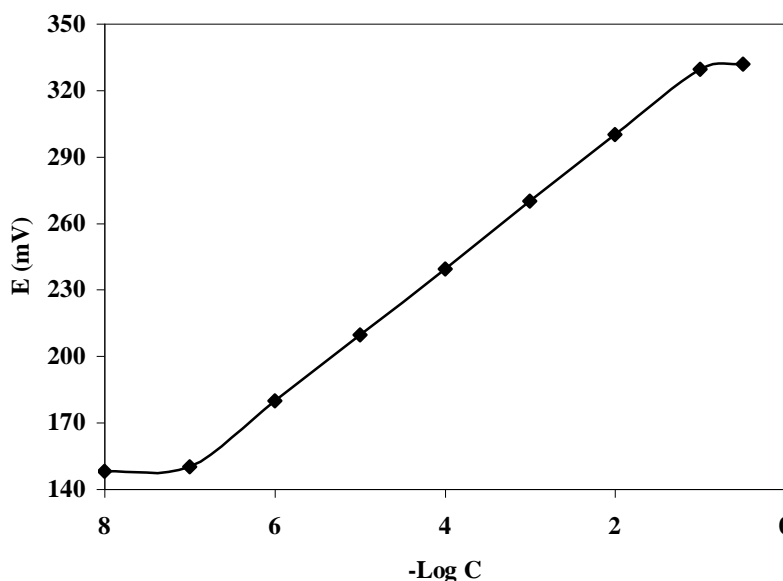

Figure 4. Calibration curve of Zn^{2+} Ion selective electrode Linearity range $1 \times 10^{-7} - 10^{-1}$ M

The critical response characteristics of the proposed electrodes were assessed according to IUPAC recommendation [35]. The emf response of the polymeric membrane electrode (Fig. 4) indicates their Nernstian behavior over a wide concentrations range. The slopes and linear ranges of the resulting emf-p Zn^{2+} graphs are given in Table 3. The limits of detection, defined as the calibration of Zinc ion obtained when the linear regions of the calibration graphs are extrapolated to the baseline potentials, are also included in Table 3.

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

	Slope (mVdecade^{-1})	Linear range (M)	LOD (M)	Electrode Lifetime (months)	Response time (s)
Zn (II) electrode	29.5 ± 0.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$	7.9×10^{-8}	4	<40

For analytical applications, the response time of a membrane sensor is on important factor. 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 Zn^{2+} ions, each having a tenfold difference in concentrations, was within <40 s for Zn^{2+} concentrations $< 10 \times 10^{-3}$ M(Fig. 5).

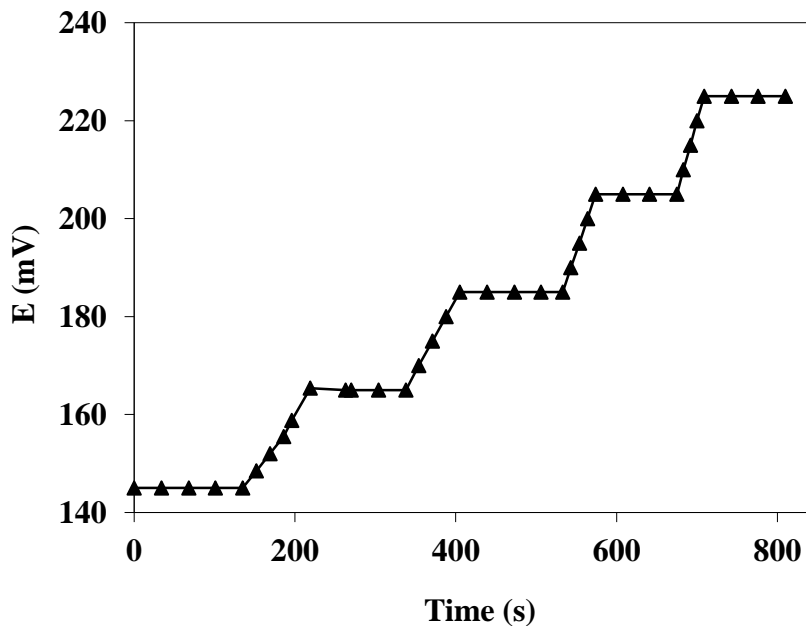Furthermore, the prepared electrode could be used frequently for at 4 months, without any measurable divergence.

Figure 5. Dynamic response time of the proposed sensor for step changes in the concentration of Zn^{2+} (M): A) 1.0×10^{-6}, B) 1.0×10^{-5}, C) 1.0×10^{-4}, D) 1.0×10^{-3}, E) 1.0×10^{-2}.
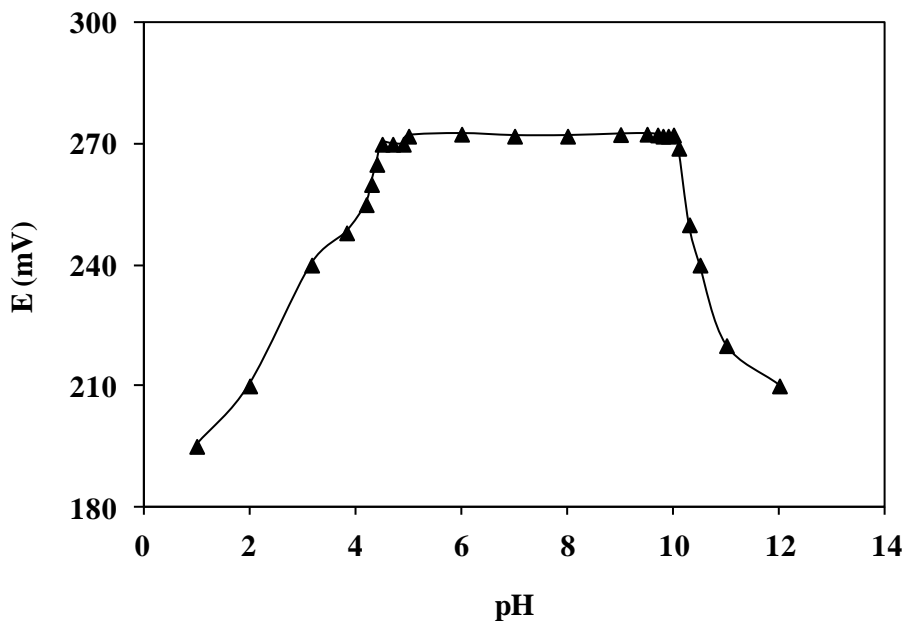
3.5. Effect of pH of the Test Solution

Figure 6. Influences of pH of the test solution on the potential response of electrode in the presence of 1.0×10^{-3} M Zn^{2+}.

The influences of the pH of the test solution on the potential response of the electrode in the presence of 1.0×10^{-3}M Zn^{2+} ion are shown in (Fig.6). The results are depicted as can be seen; the potential remains fairly constant in the pH range of 4.5-10 (the pH of the solutions was adjusted by either HCl or NaOH solutions). As can be seen, the potential remains constant from to beyond which it changes considerably. At higher pH values hydroxy complexes of Zn^{2+} can be formed on the other hand, at lower pH values the decrease in potential is due to the protontions of ionophore.

3.6. Selectivity Coefficients

The influence of interfering ions on the potential response behavior of the ion selective membrane electrodes is usually described in terms of the selectivity coefficient [36]. Potentiometric selectivity coefficient, $K_{Zn,B}^{Pot}$, describing the preference by the membrane for an interfering ion relative to Zn^{2+}, were determined by separated solutions method [37] To determine the selectivity coefficients by the separated solution method, [38-41] the emf-pM^{n+} plots were obtained for the Zn^{2+} and the interfering ion (over a pM^{n+} range of 2-6), separately, using the proposed electrode system. 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 (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 $K_{A,B}^{Pot}$ was determined.

The resulting values are listed in Table 4. It is interesting to note that there is a satisfactory agreement between the trends observed for the selectivity coefficients reported in Table 4 with the data shown in Figure 3.

Table 4. Selectivity coefficient of various interfering ions

Interfering Ion	Selectivity coefficient	Interfering Ion	Selectivity coefficient
Pb(II)	3.5×10^{-4}	Ta(I)	4.3×10^{-5}
Cd(II)	9.7×10^{-5}	K(I)	2.5×10^{-5}
Co(II)	8.4×10^{-5}	Al(III)	9.1×10^{-6}
Ca(II)	8.1×10^{-5}	Mg(II)	1.2×10^{-5}
Cu(II)	7.6×10^{-5}	Fe(II)	8.8×10^{-6}
Ag(I)	7.0×10^{-5}	Mn(II)	7.1×10^{-6}
Cr(III)	6.1×10^{-5}		

The selectivity coefficient patterns presented in Table 4 - clearly indicate that the electrodes are highly selective to Zn^{2+} over other cations tested, the selectivity coefficient are on the order of 10^{-5} or lower (except Pb^{2+}), which seems to indicate that these cations have negligible impact on the functionality of the Zn^{2+} .

3.7. Comparison with the pervious works

Table 5. Comparison of the characteristics of the proposed sensor with those of the previously reported Zn^{2+} sensor

Ionophore	L.O.D (M)	Dynamic range (M)	Slope (mV decade^{-1})	Ref
Bzo2Me2Ph2(16)hexaeneN4	$2.24×10^{-6}$	$2.8×10^{-6}$-$1.0×10^{-1}$	28.5	23
N,N-Bis(acetylacetone)ethylenediimine	$8.9×10^{-7}$	$1.0×10^{-6}$-$1.0×10^{-1}$	30	21
DBDA15C4	$3.0×10^{-5}$	$5.0×10^{-5}$-$1.0×10^{-1}$	22	22
5,10,15,20-Tertraphenyl-21H,23H-porphine	-	$6.2×10^{-6}$-$1.0×10^{-1}$	29	24
1,13-diaza- 2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione	$5.0×10^{-5}$	$9.0×10^{-5}$-$1.0×10^{-1}$	30	25
Thiazolidin-4-one	$8.5×10^{-7}$	$1.0×10^{-6}$-$1.0×10^{-2}$	29.3	26
N,N′-phenylenebis (salicylideaminato)	$2.6×10^{-7}$	$5.0×10^{-7}$-$1.0×10^{-1}$	29.4	27
N,N-bis (2hydroxy -4- etoxybenzaldehyde)-2,6-di amino pyridine	$7.9×10^{-8}$	$1.0×10^{-7}$-$1.0×10^{-1}$	29.5	Present work

In Table 5 linear dynamic range, slope and detection limit of different Zn^{2+} ion-selective electrodes based on different ionospheres are compared with those of this work. The data show that the proposed sensor is comparable and has a lower limit of detection, a wide dynamic range of application when compared with other sensors [20–27].

3.8. Analytical Applications of the Sensor

Table 6. Comparison of results from the determination of the Zn^{2+} in synthetic and real samples by the proposed method and that of ICP

Sample	Zn^{2+} content (pM)[a]	
	This method	ICP
Synthetic solution		
Sample 1	5.12 ± 0.06	5.09 ± 0.01
Sample 2	6.54 ± 0.05	6.52 ± 0.03
electroplating industrial Wastewater		
Sample 1	2.45 ± 0.05	2.43 ± 0.02
Sample 2	2.91 ± 0.07	2.88 ± 0.03

[a] Average of three determinations ±S.D

The optimized Zn^{2+} selective electrode was found to work well under laboratory conditions. To assess the applicability of the proposed electrode to real samples, an attempt was made to determine zinc content of synthetic solutions and electroplating industrial wastewater samples.

For synthetic solution, two solutions of Zn^{2+} in the presence of different concentration of other ions were prepared. In the case of electroplating waste water, 1.0 ml of each sample was taken and diluted to 50.0 ml by acetic acid/sodium acetate buffer (pH 4.0) and distilled water. The zinc content of

the sample solutions was determined by the proposed zinc selective electrode using the calibration method. The results are summarized in Table 6. As it is seen from Table 6, the results determined with the proposed electrode are in good agreement with those obtained by inductivity coupled plasma atomic emission spectroscopy (ICP-AES) method.

Table 7. Galvanized steel corrosion study with proposed sensor

Alloy in contact with galvanized steel piece	steel	copper	tin	aluminum
Zinc corrosion (Ref. 42)	low	high	medium	low
Zinc content (pM)[a]				
Determined by Porposed sensor	<7	4.07±0.04	6.30±0.05	<7
Determined by Icp	<7	4.05±0.03	6.26±0.03	<7

[a] Average of three

Galvanized light steel profiles are an economical, fire resistant, high quality and simple alternative to classic construction methods. Zinc coating is used to protect steel against corrosion. When steel meets another metal in the presence of an electrolyte such as water, one of the metals will corrode. The rate of zinc corrosion reaction by different metals is different as table 7 [42]. To test this issue with proposed sensor, a 5cm × 5cm piece of some metal was placed in contact with a same size piece of iron coated with zinc, in 250 ml of water for 2 month. Then the amount of zinc in the water was measured by both proposed sensor and ICP and the results are presented in Table 7. As can be seen on the table, results of both measurements match with each other well and also changing process of zinc amount in different metals, which are in contact with metal coated with zinc, is in accordance with the values predicted in mentioned reference [42].

4. CONCLUSIONS

A Zinc selective polymeric membrane electrode (PME) based on N, N-bis (2hydroxy -4-metoxybenzaldehyde)-2,6-di amino pyridine is constructed. The sensor showed advanced performances with a relatively fast response time, a lower detection limit of 7.9×10^{-8} mol L^{-1}, the potential responses across the range of 1.0×10^{-7}-1.0×10^{-1} mol L^{-1}. This can be related to the presence of three intermediately soft N-donor atoms in its structure, and also to the size of the semi-cavity formed as a result of the arrangement of the different parts of the ligand around the desired ion in the solution. Another determining property which leads to the applicability of L_1 as a proper ion carrier, is the relatively fast ion exchange kinetics that governs the formation of its complexes, at least those with Zn(II) ions. The best PVC membrane electrode performance was achieved by a membrane composition of 7 % L1, 29 % PVC, 60 % NPOE and 4 % NaTPB.

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