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Synthesis of 3-((6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)imino)indolin-2-one as an Excellent Ionophore to the Construction of a Potentiometric Membrane Sensor for Rapid Determination of Zinc

Ali Sharifi,[1] Leila Hajiaghababaei,[1,*] Saeed Suzangarzadeh[1] and Mohammad Reza Jalali Sarvestani[2]

[1]*Department of Chemistry, Yadegar-e-Imam Khomeini(RAH) Shahre rey Branch, Islamic Azad University, Tehran, Iran*

[2]*Young Researchers and Elite Club, Yadegar-e-Imam Khomeini(RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran*

*Corresponding Author, Tel.: +98-21-55229200 (Off); Fax: +9821339022

E-Mail: lhajiaghababaei@yahoo.com

Abstract-   3-((6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)imino)indolin-2-one was used as a neutral ion carrier in the PVC membrane to construction of a new zinc ion selective electrode. The sensor shows a good Nernstian response for Zn^{2+} over a wide concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 27.12 mV per decade. The limit of detection of the sensor is 8×10^{-6} mol L^{-1}. The sensor has a relatively fast response time (~5 s) and a useful working pH range of 4.4-8.0 and it can be used without any divergence in Nernstian response for 60 days with high reproducibility. Interference of some cations was also evaluated and it exhibits an appropriate selectivity. Finally it was used as an indicator electrode in potentiometric titration of Zn^{2+} with EDTA and in direct determination of Zn^{2+} in rice and in zinc enriched soufflé cake samples. The results indicate that this electrode is sensitive for determination of Zn^{2+} ion.

1. INTRODUCTION

Zinc is a hard bluish color metal and 24th most abundant element in the earth's crust and its common oxidation state is +2 [1]. Zinc is considered to be a very necessary nutrient for humans and other living organisms in trace amounts [2], this vital mineral acts as a cofactor for more than 70 different enzymes [3], Zinc heals the wounds, increases normal growth and hydration of the skin and it helps maintain a sense of taste and smell it also improves the immune system and synaptic plasticity [4-8]. Zinc is an essential element for the production and moving of the retinal-binding protein [9]. Zinc deficiency leads to dermatitis, hair loss, depression, anxiety, diarrhea and weight gain [10-15]. The sulfate salt of zinc is used as an auxiliary drug in the treatment of wounds, acne, ear granulomatosa, rheumatoid arthritis, anosmia, acrodermatitis enteropathica and zinc deficiency [16-20]. However, zinc can be too harmful in its large doses and causes several problems such as anemia, nausea, vomiting, pain, zinc chills, pulmonary edema, gastric ulcer, low blood pressure and renal failure [21-27]. Therefore zinc determination in clinical and environmental analyzes has a great importance. There are several methods for determination of zinc such as atomic absorption spectroscopy (AAS) with flame and graphite furnace atomizers, striping voltammetry, neutron analysis activation, inductive-coupled plasma-mass spectrometry (ICP-MS), UV-Visible spectrophotometry, polarography and complexometry methods [28-35]. The most of the mentioned methods are time consuming and elaborate and involve sophisticated and expensive equipment that might not be available in most analytical laboratories, in addition most of them require sample pre-treatment and infrastructure back up, which results in destruction of the sample matrix and high-skill operators are required to perform sample treatment and working with these complex instruments.

On the other hand, potentiometric ion selective electrodes offer several advantages over other methods of analysis. The most significant features of this technique are the speed with which the samples can be analyzed, low cost, simplicity, portability of the device, wide working range, sample non destruction, good precision, online monitoring, high selectivity and ability to be used in colored and opaque samples. The increasing use of ion selective electrodes in the various fields has generated increasing interest in the development new sensors [36-50] to the fast and accurate determination of various species. Despite the fact that, a lot of ISEs have been designed for determination of various species such as anions, cations and drugs, research in this direction is still ongoing to improve the parameters affecting the ISEs, including working range, response time, working pH range, detection limit, life time and selectivity, to increase their application in routine analyzes [51].

Therefore, in this study 3-((6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)imino)indolin-2-one was synthesized in two ways (Conventional method and Microwave method). The Microwave method has more yield and purer product. Finally, for the first time 3-((6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)imino)indolin-2-one   was

used as an excellent ionophore in the construction of a liquid membrane ion selective electrode for potentiometric determination of zinc ions.

2. EXPERIMENTAL

2.1. Apparatus

Melting points were determined by using an Electrothermal IA9300 Bamstead apparatus and were uncorrected. The FT-IR spectra were recorded on a Bruker, Tensor 27 instrument using KBr disks. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker 500 MHZ spectrometer with $(CD_3)_2SO$ as solvent using tetramethylsilane (TMS) as an internal standard, the chemical shift values are in δ. Mass spectra were obtained with a Finnigan-MAT-8430 Electron impact ionization-mass spectrometer (70 eV) (in *m/z)*. Microwave reactions were carried out in microwave oven with a 2500 W power (Micro-Synth, Milestone).

A corning ion analyzer 250 pH/mV meters was used for potential measurements at 25.0±0.1 ℃. Two Ag/AgCl reference electrodes (Azar-Electrode, Iran) were used as the internal and external reference electrode.

2.2. Reagents and Materials

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), high relative molecular weight polyvinyl chloride (PVC) and tetrahydrofurane (THF) were purchased from Merck and used as received. Hydrazine hydrate(80%), carbondisulfide, pyruvic acid and isatin were purchased from Merck. 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one (Fig. 1 a) was prepared according to the literature procedure [52]. Nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout.

2.3. Synthesis of Ionophore

The Schiff base of 3-((6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)imino)indolin-2-one (Fig. 1 c) was synthesized in two ways, as follows:

2.3.1. Conventional Method

To a suspension of isatin (Fig. 1 b) (6 mmol) in absolute ethanol (20 ml), was added triazin (Fig. 1 a) (3 mml). The suspension was heated until a clear solution was obtained. 10 drops of conc. sulphuric acid were added and the solution was refluxed for 6 h on a water

bath. After cooling, the precipitated solid filtered off and recrystallized from ethanol. Brownish-Yellow crystal was obtained (yield 80%, m.p. 200-202°C). (Fig.1).
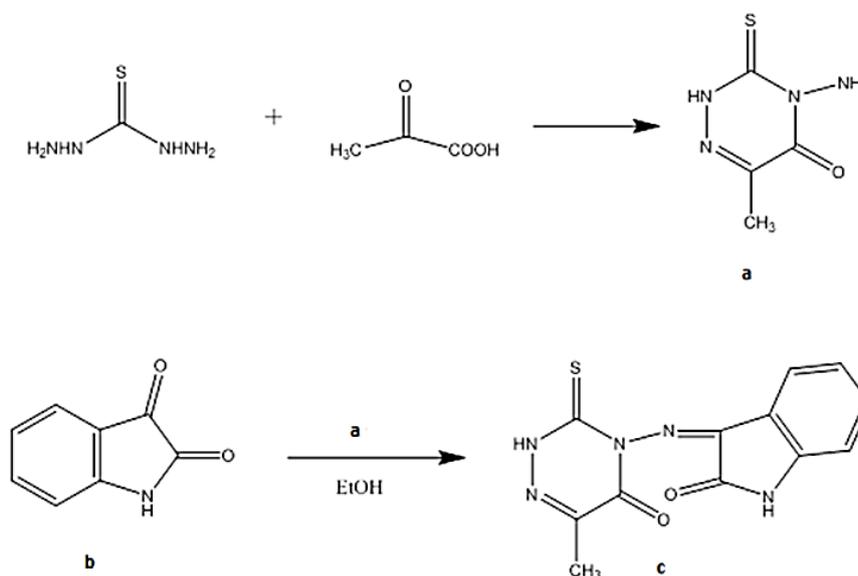

Fig. 1. Schematic illustration of the synthesize of Schiff base of 3-((6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)imino)indolin-2-one

2.3.2. Microwave method

In a high pressure Teflon reactor equipped with a magnetic stir bar and an optical fiber (for controlling the reaction temperature), a mixture of isatin (3 mmol), triazin (3 mmol) and with 4–5 drops of DMSO exposed to microwave irradiation at 80 °C (400 W) for 4 min using a Micro-Synth lab station reactor. Then, the reaction mixture was allowed to cool down, and the resulting solid was filtered off, and recrystallized in ethanol (yield 96%, m.p. 200-202 °C). IR (KBr cm^{-1}): 3291.04; 3216.11; 3068.35; 2970.06; 1700.30; 1608.21; 1540.85; 1498.92; 1379.55; 1269.24; 753.40. ^{1}H NMR: (DMSO-d$_6$) δ ppm, 2.50 (3H, s); 6.87- 8.43 (4H, m, aromatic), 10.70 (1H,s, NH indole ring), 14.42 (1H,s, NH triazin ring). ^{13}C NMR: (DMSO-d$_6$) δ ppm, 20.27, 121.83, 122.23, 123.06, 128.52, 131.56, 132.73, 141.23, 145.03, 149.64, 169.01, 169.42. MS: m/e (relative intensity): 43(33.55); 90(46.45); 145(32.26); 218(25.81); 272(9.68); 287(45.16).

2.4. Electrode Preparation

The general procedure to prepare the PVC membrane was as followed [53-56]: different amounts of the ionophore along with appropriate amounts of additive (NaTPB) were weighed. Afterward, known amounts of plasticizer and PVC were added to the mixture. The mixture was dissolved in 2 mL of tetrahydrofurane (THF), and the solution was blended well. The resulting mixture was transferred to a glass dish of 2 cm diameter. The solvent was

evaporated slowly and until an oily concentrated mixture was obtained. A sampler tip (3-5 mm o.d.) was dipped in to the mixture for about 5 s so that a transparent membrane of about 0.3 mm thickness was formed. The sampler tip was then pulled out from the mixture and kept at room temperature for about 24 h. afterward the sampler tip was filled with an internal filling solution (1.0×10^{-3} mol L^{-1} $Zn(NO_3)_2$) solution. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} Zn $(NO_3)_2$ solution.

2.5. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Ag-AgCl, KCl (satd.)│internal solution, 1.0×10^{-3} mol L^{-1} $Zn(NO_3)_2$│PVC membrane│ sample solution│Ag-AgCl, KCl (satd.)

These measurements were preceded using calibration of the electrodes with several standard solutions. Activities were calculated according to the Debye- Huckel procedure.

3. RESULTS AND DISCUSSION

3.1. Membrane Composition Effect on the Potential Response of the Sensor

Despite the fact that the nature of ionophore plays an essential role in the degree of sensitivity and selectivity of the sensor but other factors such as the amount of ionophore, the amount of ionic additive, the type of plasticizer and polymeric matrix and their ratio to each other have an important impact on the sensor's response too [57-58]. For this reason, it is necessary to examine the effect of the membrane ingredients. For this purpose in this study, different membrane compositions, as shown in table 1, were tested. As can be observed, the membrane with the composition of 28% PVC, 14% ionophore, 2% NaTPB and 56% NB (no.13) was the optimum one in the development of this sensor.

The Zn^{2+} ion extraction into the liquid membrane is a result of the high concentration of the ligand in the membrane. From table 1, it was obvious that in the absence of ionphore (no. 1, 11), the response of the recommended electrode was low (slope of 6.50 ± 0.4 and 8.20 ± 0.4) which show significant effect of the ionophore. The sensitivity of the electrode response increases with increasing ionophore content until a value of 14% is reached. It shows the affinity of the ionophore to Zn^{2+} ion. Further addition of ionophore will, however, result in diminished response of the sensor (no. 10, 16), most probably due to some in homogeneities and possible saturation of the membrane [36].

The second factor which helps the extraction of the Zn^{2+} ion is plasticizer. Plasticizer acts as a membrane solvent allowing homogeneous dissolution and diffusional mobility of the ion-pair inside the membrane [59]. The plasticizer should be water- immiscible liquid of low vapor-pressure, compatible with PVC and no functional groups which can undergo protonation reactions. The selectivity of such electrode can be significantly influenced by the

choice of the membrane solvent. Nature of the plasticizer has a noticeable effect on analytical responses e.g. slope, linear domain and selectivity of PVC membrane electrodes [60-62]. Here, two plasticizers with different polarity (dielectric constant) were tested, dibutyl phthalate (DBP with DC of 6.4) and nitrobenzene (NB with DC of 35.7) as listed in table 1. After the evaluation of two solvent mediators, it was observed that NB is the effective solvent mediator (no. 16) and provided an effective Nernstian response. This is due to the high dielectric constant of NB which facilitates the better extraction of Zn^{2+} with a relatively high charge density from water to an organic layer of the membrane.

Table 1. The optimization of the membrane ingredients

Membrane No.	Composition (%)					Slope (mV decade^{-1})
	Ionophore (%wt)	NaTPB (%wt)	NB (%wt)	DBP (%wt)	PVC (%wt)	
1	0	0	-----	70	30	6.50±0.4
2	8	2	-----	60	30	12.80±0.3
3	10	2	-----	58	30	14.77±0.4
4	13	2	-----	60	25	18.76±0.4
5	14	2	-----	56	28	19.28±0.2
6	14	3	-----	55	28	18.20±0.2
7	14	2	-----	57	27	16.40±0.4
8	14	2	-----	62	22	17.63±0.4
9	16	1	-----	55	28	12.65±0.3
10	16	2	-----	56	26	13.90±0.5
11	0	0	70	-----	30	8.20±0.4
12	14	0	56	-----	30	21.33±0.3
13	14	2	56	-----	28	27.12±0.3
14	14	2	62	-----	22	17.63±0.4
15	13	2	60	-----	25	18.76±0.4
16	16	2	56	-----	26	19.03±0.5

The effect of the presence of ionic additive was also evaluated. In fact, the presence of these lipophilic anions in a cation-selective membrane, which is based on a neutral carrier, leads to a decrease in Ohmic resistance. In addition, these anions improve selectivity, sensitivity and linear range in most cases. Here, a NaTPB addition of 2% as an additive led to the slope increase of the potential sensor response from the value of 21.33±0.3 mV per decade (no. 12) to the value of 27.12±0.3 mV per decade (no. 13). Actually, it helps to the ion exchange of the analyte from aqueous solution to organic layer of the membrane.

3.2. Internal Solution

The concentration of the internal solution $Zn(NO_3)_2$ of the electrode was varied from 1.0×10^{-2} mol L^{-1} to 1.0×10^{-4} mol L^{-1} and the potential response of the Zn^{2+} selective electrode was obtained (Fig. 2). It was found that the change in the concentration of the internal solution does not significantly affect the response of the sensor, except for an expected variation in the intercept of the resulting Nernstian plot. A 1.0×10^{-3} M concentration $Zn(NO_3)_2$ solution is perfectly suitable for proper functioning of the electrode system.
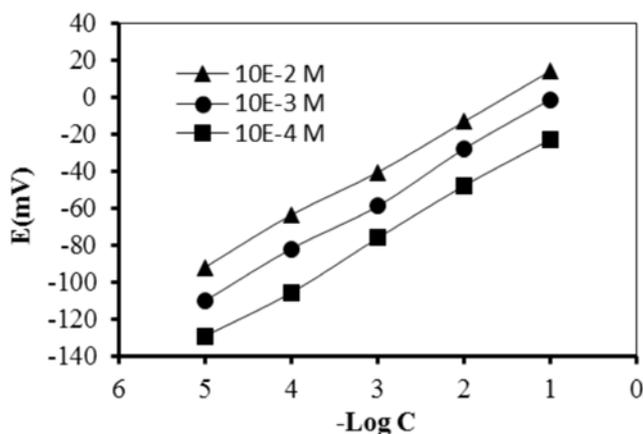

Fig. 2. The effect of internal solution concentration on the electrode response

3.3. pH Effect on the Electrode Response

In order to investigate the influence of the pH on the potential response of the Zn^{2+} sensor, at first a Zn $(NO_3)_2$ solution with 1.0×10^{-4} mol L^{-1} concentration was prepared and its pH was adjusted by concentrated NaOH and HCl solutions in the range of 2.0 to 9.5. In agreement with the resulting data (Fig. 3), the potential remained constant despite the pH change in the range of 4.4 to 8.0, indicating the applicability of this electrode in this specific pH range.

On the contrary, relatively noteworthy fluctuations in the potential *vs.* pH behavior took place below and above the formerly stated pH limits. In detail, at pH values higher than 8.0 the potential fluctuations might be due to the formation of Zn^{2+} ion hydroxy complexes in the solution. On the other hand, the potential oscillations below the pH value of 4.4 were attributed to the partial protonation of the employed ionophore. If H$^+$ concentration is much more than Zn^{2+}, then H$^+$ ions can compete with Zn^{2+} ions for making complex with ionophore. In pH between 4.4-8.0, H$^+$ concentration is not enough for competing with Zn^{2+} ions (because ionophore has more trend to Zn^{2+} ions in compare to H$^+$ ions), but in below pH of 4.4, H$^+$ concentration is enough to overcome on Zn^{2+} and employed ionophore can be protonated.
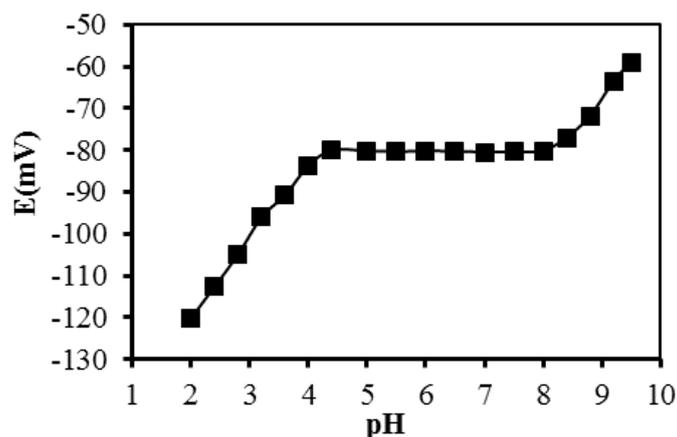
Fig. 3. The effect of the pH on the potential response of the zinc sensor

3.4. Response Time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurements were performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effort on the experimental response time of a sensor [63]. In this work, dynamic response time was obtained by changing the Zn^{2+} concentration in solution, over a concentration range 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}.
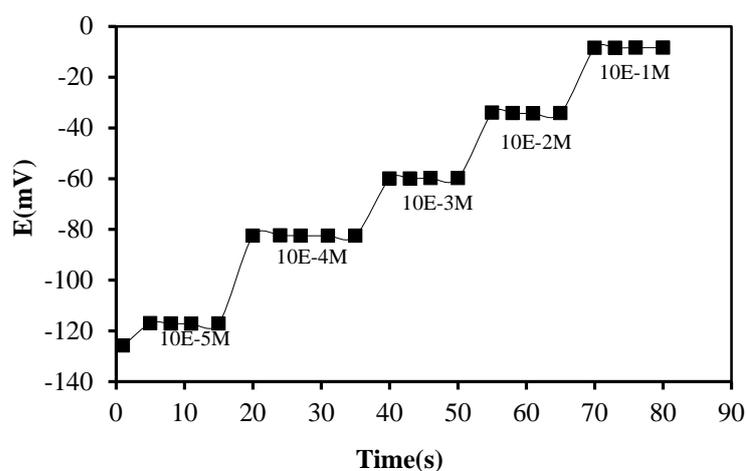

Fig. 4. Dynamic response time of cadmium ion electrode for step changes in concentration of Zn^{2+} over a concentration range from 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}

The actual potential versus time traces is shown in Fig. 4. As can be seen, in whole concentration range the electrode reaches its equilibrium response in a relatively short time ($\sim$5 s). This is most probably due to the fast exchange kinetics of complexation-decomplexation of Zn^{2+} ion with the ionophore at the test solution-membrane interface.

3.5. Measuring Range and Detection Limit

The measuring range of an ion-selective electrode includes the linear part of the calibration graph as shown in Fig. 5. The applicable measuring range of the proposed sensor is between 1×10^{-5} and 1×10^{-1} mol L^{-1}. In practice, detection limits for the most selective electrodes are in the range of 10^{-5}–10^{-6} mol L^{-1}. In this work the detection limit of the proposed membrane sensor was 8×10^{-6} Mol L^{-1} which was calculated by extrapolating the two segments of the calibration curve.
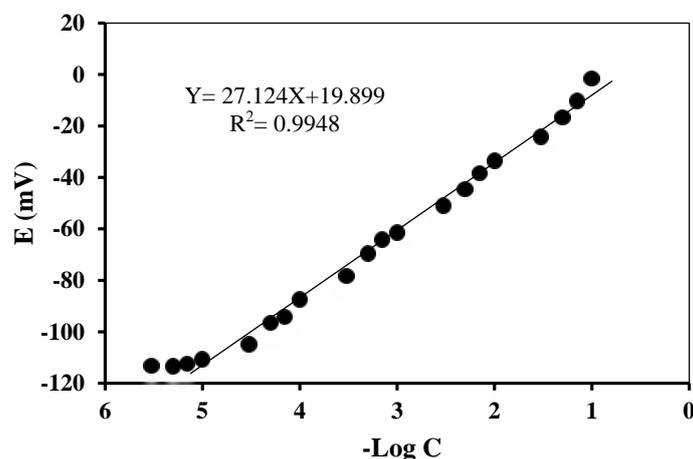

Fig. 5. The calibration curve of the zinc ion sensor

3.6. Selectivity

The potentiometric selectivity coefficients for the Zn^{2+} sensor were evaluated by using the matched potential method (MPM) [64,65]. The resulting values of selectivity coefficients are reported in Table 2. If the obtained K_{MPM} is equal to one, it means that the designed sensor cannot differentiate between the primary and interfering ions. Further, the smaller the value of the selectivity coefficient, the higher is the selectivity of the sensor. As can be observed from the table, the selectivity coefficient values are much smaller than 0.1 which indicates that they exhibit sufficient selectivity towards Zn^{2+} over all the interfering ions studied.

Table 2. The selectivity coefficients of various interfering cations for the membrane

Ion	K_{MPM}
Cu^{2+}	4.7×10^{-4}
Cr^{3+}	5.8×10^{-3}
Cd^{2+}	1.8×10^{-2}
Ag^{+}	1.6×10^{-2}
Co^{2+}	7.3×10^{-2}
Pb^{2+}	4.6×10^{-2}
Hg^{2+}	1.0×10^{-1}
Mn^{2+}	5.2×10^{-2}

3.7. Lifetime

The loss of ionophore, plasticizer and ionic additive from the polymeric film due to the leaching into the sample is the main factor that reduces the life span of ion selective electrodes. The average life time of this category of sensors is usually between 4 and 10 weeks, after this period the Nernstian slope will be decreased and a rise in limit of detection can be observed. For evaluating the lifetime of this sensor, after the conditioning step, the electrodes were frequently recalibrated one time a day for 90 days, and the slope of calibration curve and the linear range were monitored regularly. As can be seen from Fig. 6. The proposed sensors can be used for more than 60 days. There is a slight gradual decrease in the slopes during 60 days, but after it, a considerable change in slope is observed.
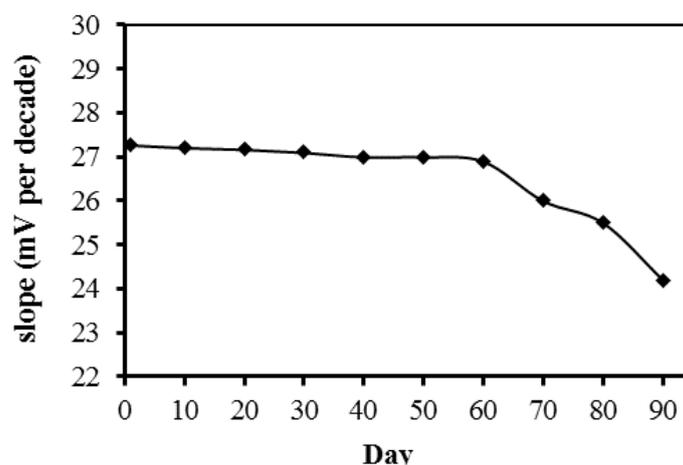
Fig. 6. The lifetime of the Zn^{2+} membrane ion electrode

3.8. Analytical Application

Ion-selective electrodes tend to be; low in cost, simple to use, rapid in determination, with low interferences from the matrix and can be applied to small volumes. These characteristics make them an ideal choice for environmental and food measurements. The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 25.0 mL of 1.0×10^{-4} mol L^{-1} of Zn^{2+} solution with EDTA 1.0×10^{-2} mol L^{-1}. The resulting titration curve is shown in Fig. 7. As can be seen, the amount of Zn^{2+} ions in solution can be accurately determined with the electrode.
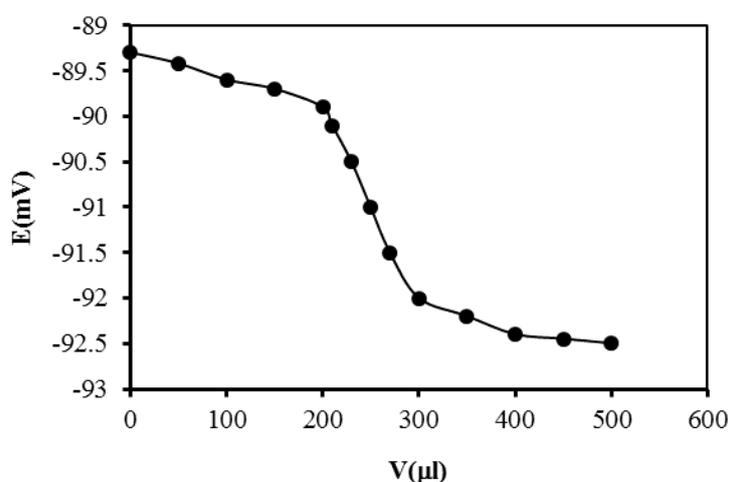

Fig. 7. Potentiometric titration curve of 25 mL 1.0×10^{-4} mol L^{-1} Zn^{2+} with 1.0×10^{-2} mol L^{-1} EDTA, using the proposed sensor as an indicator electrode

Finally, in order to evaluating the applicability of the proposed electrode in real samples an effort was made to determine Zn^{2+} ions in rice and zinc enriched soufflé cake samples. A 1.0 g zinc enriched soufflé cake was taken in a beaker and dissolved in HNO_3 (10 mL) and $HClO_4$ (4 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask.

Table 3. Determination of Zn^{2+} in various samples

Sample	Measured with FAAS (mg L^{-1})	Measured with proposed sensor (mg L^{-1})
Rice	1.31 (1.51) [a]	1.38 (1.29)
zinc enriched soufflé cake	1.04 (2.33)	1.12 (1.19)

[a] %RSD based on three replicate analysis

Also one gram of the grilled rice sample was placed in the oven (500 $^{\circ}$C) for about 4 hours, after cooling the resulting ash was dissolved in HNO_3 (15 mL) and $HClO_4$ (10 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask.

An aliquot of the both sample solution were taken and Zn^{2+} ions were determined by the calibration procedure by proposed electrode and flame atomic absorption spectroscopy (FAAS). The results are given in Table 3. As seen the results obtained by the proposed method and FAAS are in satisfactory agreement.

3.9. Comparison of the proposed Zn^{2+} sensor and some of the best previously reports

The limit of detection, linearity range, working pH range and response time of the proposed Zn^{2+} sensor with some of the best previously reports are compared in Table 4. As is obvious, the results clearly indicate that the proposed sensor is superior to the previously reported ones in terms of response time and in linearity range, detection limit and working pH, proposed sensor is closed to the best previously reports.

Table 4. Comparison of the proposed Zn^{2+} ion sensor and the some previously reports

Ionophore	Detection limit (mol L^{-1})	Linear range (mol L^{-1})	Response time (S)	pH	Ref.
diamide 1,13-diaza- 2,3;11,12;15,18- tribenzo-4,7,10-trioxacyclononaoctane- 14,19-dione)	5×10^{-5}	9×10^{-5} -1×10^{-1}	20	3.0-7.0	[66]
disodium salt of porphyrin 3,7,12,17- tetramethyl-8, 13- divinyl 2,18-porphine dipropionic acid	---	1.3×10^{-5} -1×10^{-1}	10	3.0-7.4	[67]
4-*tert*-butylcalix[4]arene	5×10^{-7}	9.8×10^{-1}-1×10^{-6}	30	2.5-4.3	[68]
2-(2-Hydroxy-1-naphthylazo)-1,3,4- thiadiazole	5.6×10^{-6}	5.6×10^{-6}-1×10^{-1}	10	2.5-6.0	[69]
N-[(ethyl-1 pyrrolidinyl-2)methyl] methoxy-2 sulfamoyl-5 benzamide	7×10^{-6}	1×10^{-5} -1×10^{-1}	20	4.0-6.5	[70]
N-undecyl-Nё- (sodium p- aminobenzenesulfonate)- thio-urea	7.3×10^{-6}	1×10^{-5} -1×10^{-1}	12	4.0-8.0	[71]
tetra(2-aminophenyl) porphyrin	3×10^{-5}	5×10^{-5} -1×10^{-1}	10	3.0-6.0	[72]
thiophene-2-aldehyde semicarbazone	----	1×10^{-6} -1×10^{-1}	15	2.4-6.7	[73]
2,6- diacetylpyridinebis(benzenesulfonylhydr azide)	1.0×10^{-7}	1×10^{-6} -1×10^{-1}	20	4.0-12	[74]
Functionalized NiO nanostructures with 12-crown-4 on nickel foam	0.5×10^{-6}	1×10^{-6} -1×10^{-1}	10	----	[75]
2-(6-chloroquinoxaline-2-yl)hydrazine	8×10^{-6}	1×10^{-5} -1×10^{-1}	5	4.4-8.0	**This work**

Response time is one of the most important characters on construction of ion selective electrodes and the proposed sensor exhibits the shortest response time (5 s) between them. In addition, it should be noted that the proposed electrode in terms of other parameters also have a very close and good response to the best of the previous reports.

4. CONCLUSION

Zinc in trace doses is an essential and vital nutrition for humans and other living organisms, and plays an essential role in many biological processes. On the other hand, this vital mineral, is toxic at high doses and causes many irreparable complications. Therefore, easy, fast, accurate and low-cost determination method for zinc is a great importance in food and environmental analysis. Consequently, in this study, the Zn^{2+} potentiometric membrane sensor was constructed by 3-((6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)imino)indolin-2-one as ionophore. The electrode exhibits a Nernstian response for Zn^{2+} over a concentration range of (1×10^{-5} to 1×10^{-1} mol L^{-1}) with a slope of 27.12 ± 0.3 mV per decade. This electrode was shown a fast response time (~5 s), a low detection limit of 8×10^{-6} M, pH independent potential responses across the wide range of 4.4-8.0 and long life time (60 days). It was used as an indicator electrode in potentiometric titration of Zn^{2+} with EDTA and it was also being applied successfully for the direct determination of Zn^{2+} ions in rice and soufflé cake samples.

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