

## Zinc(II) Selective Electrode based on Polymeric Membrane of 2,6-Diacetylpyridinebis(benzenesulfonylhydrazide) Ligand

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The performance characteristics of polymeric membrane electrodes based on 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) ligand (L) have been prepared for the quantification of zinc(II) ions. Several membranes having different compositions of PVC, plasticizers, and ionophore were fabricated and the best response was observed for the membrane composition L: PVC: DBP in the ratio of 10:30:60 (w/w). It exhibited a very good response for Zn<sup>2+</sup> in a wide concentration range from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M with a slope of  $29.06 \pm 0.1$  mV per decade of Zn<sup>2+</sup> concentration. The detection limit was down to  $1.0 \times 10^{-7}$  M. The working pH range of this sensor was 4-12 with the fast response time less than 20 second. The developed method was applied for the determination of zinc(II) concentration in the wastewater samples and the results were in good agreement with an atomic absorption (AAS) which was obtained here.

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**Keywords:** Zinc(II) selective electrode, 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) ligand, Polymeric membrane electrode, Potentiometry

### 1. INTRODUCTION

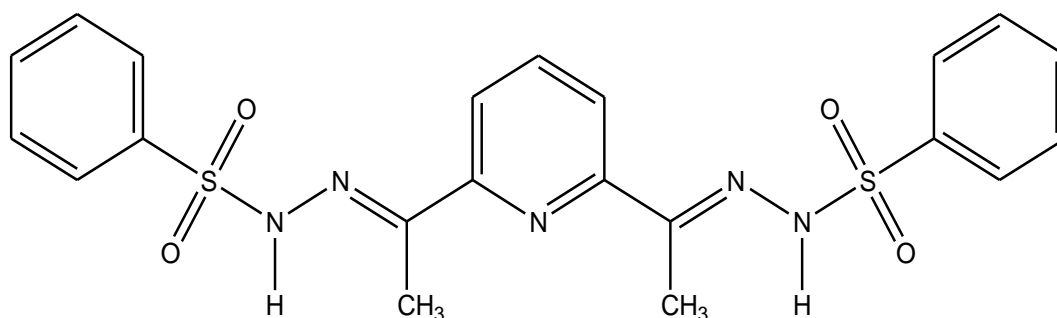
Ion selective electrodes are being widely used in the analytical research as they offer several advantages over other methods of analysis [1]. Ion selective electrodes provide accurate, rapid, portability, good selectivity and low cost analysis [2-4], hence development of ion selective electrode continue to be expanding in areas of analytical research since the 1960s [5]. Ion selective electrodes

exhibit very effective tools for the analysis of a wide variety of cations, anions, and molecules without destruction of sample.

Zinc is an essential element for human body, it is important for DNA synthesis, microtubule polymerization, gene expression, apoptosis, immune system function, and the activity of enzymes [6,7]. Adults need between 8 and 15 mg of zinc per day to maintain health [8]. The uptake of zinc by human above a certain level is known to cause fever, chills, pulmonary manifestation, gastroenteritis, anaemia, renal failure, and internal organ damage. Zinc concentrations are rising in air, water, and soil due to widely used in electroplating, pharmaceutical and paint industries [2]. Excess of zinc can cause environmental pollution. Also significant concentrations of zinc may reduce the soil microbial activity causing phytotoxic effect [9] and which is also a common contaminant in agricultural and food wastes [10]. Therefore, sensitive, accurate and reproducible analytical techniques are required in the determination of zinc in the environment.

Nowadays the available methods that have been reported for low level determination of zinc in the environmental samples include atomic absorption spectrometry (AAS) [11], inductively couple plasma-optical emission spectroscopy (ICP-OES) [12], flame atomic absorption spectrometry (FAAS) [13], inductive couple plasma-mass spectrometry (ICP-MS) [14], potentiometry [15-17], and voltammetry [18]. Among these techniques, potentiometry using the ion-selective electrodes (ISEs) are generally suitable for determination of zinc, due to its relative simplicity, wide linear range, rapid and inexpensive procedure. The ionophore is the key component of ion-selective electrodes (ISEs), which define the selectivity of sensor via selective complex formation with cation of interest [16]. Various numbers of ionophores [4-6, 15,17, 19-26] have been reported in the development of zinc ion-selective electrode. These reported zinc(II) ion-selective electrodes have some limitations such as poor selectivity, narrow working concentration range, low pH range, and long response time. Thus, a better sensor for zinc(II) is required.

In this study, 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) ligand (Figure 1) was used to develop a Zn(II) ion-selective sensor. The 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) ligand was synthesised according to the same procedure outlined by Yusnita et al. [27]. This ligand shows complexation with Zn(II), which indicates high affinity of Zn(II). Thus, PVC based membranes of 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) was desirable to prepare and investigate as a Zn(II) ion-selective sensor.



**Figure 1.** Structure of 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) (L).

## 2. EXPERIMENTAL

### 2.1. Reagents

All reagents used were of analytical reagent grade. High molecular weight poly(vinyl chloride) (PVC) was obtained from Fluka Chemica (Switzerland), dibutylphthalate (DBP), o-nitrophenyl octyl ether (o-NPOE) and dioctylphthalate (DOP) were obtained from Aldrich (Germany), while dioctyl phenyl-phosphonate, 95% (DOPP), tetraethyl methylenediphosphonate (TMDP), tetrahydrofuran (THF) were obtained from Merck (Germany). Hydrochloric acid (HCl), sodium hydroxide (NaOH) and Britton–Robinson buffer solution were used for pH adjustments. A cobalt(II) chloride hexahydrate, copper(II) chloride dehydrate, nickel(II) chloride hexahydrate, manganese(II) chloride tetrahydrate, magnesium chloride hexahydrate, barium chloride dehydrate, calcium chloride dehydrate, cadmium chloride hemi-pentahydrate, potassium chloride and sodium chloride solutions were prepared standardized according to appropriate methods. Stock solutions of zinc ion were freshly prepared by dissolving appropriate amount of zinc(II) chloride in distilled deionized water [28].

### 2.2. Equipments

All solutions were prepared using distilled deionized waters from EASY pure LF, Barnstead (USA). The potential measurement was carried out on a pH/milivoltmeter Orion 720A, Mass (USA). A Ag|AgCl electrode of BaSi, MF-2052 (USA) with a fiber junction was used as a reference electrode. The pH value was determined by using Orion, 915600, Mass. (USA) glass-pH electrode. Metal ion was analysed using atomic absorption spectrophotometer (AAS) from Perkin Elmer (USA).

### 2.3. Preparation of electrode

The PVC membranes were prepared by dissolving with an appropriate amount of PVC, plasticizers and ionophore in 5 ml of THF. In some composition plasticizers of DBP, DOP, DOPP, TMDP and NPOE were added to get membranes of different combination. This solution was vigorously stirred immediately with a glass rod after the addition of THF for an easy dissolution of PVC. When the solution became viscous it was poured into a glass ring with an inner diameter of 3.5 cm which was placed on smooth glass plate. A filter paper was placed on top of the glass plate to prevent dust and air streams from spoiling the mixture. The solution was then allowed to evaporate for 24 hours at room temperature. The resulting membranes of about 0.5 mm thickness were obtained which then cut to size and were glued to one end of a pyrex glass tube with Araldite.

The glass tube was then filled with an aqueous solution of  $1 \times 10^{-2}$  M  $\text{ZnCl}_2$  solution and electrical contact was done by immersing a gold wire in the  $1 \times 10^{-2}$  M  $\text{ZnCl}_2$  solution. The electrodes were conditioned for at least 24 hour in a fresh  $1.0 \times 10^{-4}$  M  $\text{ZnCl}_2$  solution and rinsed well with distilled water when not in use. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized to develop reproducible, noiseless and stable potentials.

## 2.4. Potential measurements

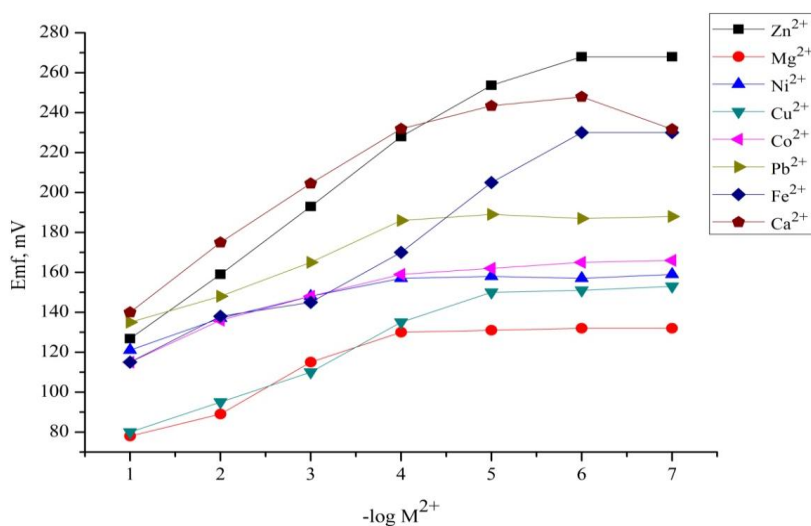
The performance of the electrodes was investigated by measuring the emf of zinc(II) chloride solutions prepared with concentration range of  $1.0 \times 10^{-1}$  to  $1.0 \times 10^{-7}$  M serial solution. Each solution was stirred and the potential was recorded when it became stable and then plotted against logarithm function of Zn(II) ion activity. Compositions of the best-performed membranes are listed in Table 1 along with other characteristics. All potential studies were carried out at  $25 \pm 0.1$  °C temperature by using the following cell assembly set up.

Ag/AgCl;KCl (satd.) | internal solution (0.01 M ZnCl<sub>2</sub>) | membrane | zinc (II) chloride | gold wire

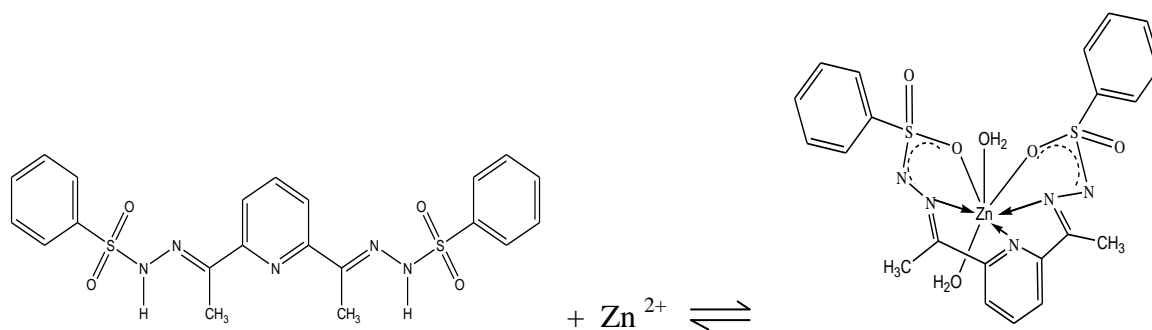
## 3. RESULTS AND DISCUSSION

### 3.1. Optimization of membrane composition

In preliminary experiment, the suitability of the ligand L as an ion carrier for Zn<sup>2+</sup>, PVC membrane ion-selective sensor was tested for variety of metal ions, including alkali, alkali earth, and transition metal ions. The potential response of membrane sensors based on ligand L for various metal ions is depicted in Figure 2. From Figure 2, it can be seen that zinc(II) ion had the most sensitive response with the polymeric membrane based on ligand L. This was due to the emf obtained for Zn<sup>2+</sup> ion was closed to Nernstian equation. However the emf response obtained for zinc(II) ion was higher than those expected by Nernstian equation. The existence of nitrogen and oxygen atoms in the structure of ligand L make the zinc(II) ion possible to form interaction with the ligand L through a lone pair of electron of the nitrogen and oxygen atoms. The possible mechanism that is responsible for the potentiometric response is shown in Figure 3. Therefore, the 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) ligand (L) was selected as a suitable ionophore for Zn<sup>2+</sup> ion-selective electrode.



**Figure 2.** Potential response of membrane sensors based on ligand L for various metal ions.



**Figure 3.** Possible mechanism for potentiometric response.

It is well known that the sensitivity, linearity, and selectivity of the ligand toward zinc(II) ion obtained for a given ionophore depends significantly on the membrane composition. Thus, the influence of the amount of ionophore and the nature and amount of plasticizer and PVC on the potential response of the  $\text{Zn}^{2+}$  sensor were investigated. Several membranes based on 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) ligand with different compositions have been prepared and their response characteristics are summarized in Table 1. Table 1 shows that sensor no. 3 having ionophore, PVC, and DBP in the ratio of 10:30:60 (w/w) exhibited the best working concentration range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M with a Nernstian slope of 29.06 mV/decade and detection limit of  $1.0 \times 10^{-7}$  M  $\text{Zn}^{2+}$ . Thus, sensor no. 3 was chosen for further studies.

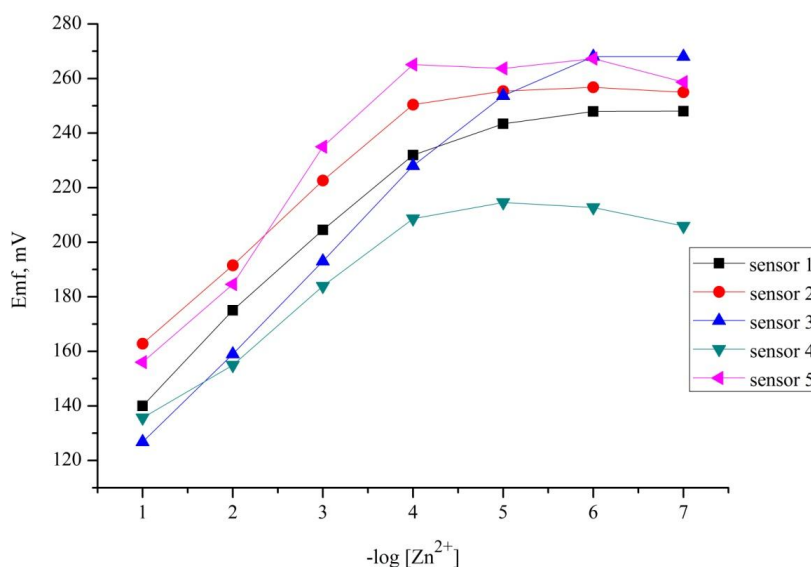
### 3.2. Effect of addition of plasticizer

Plasticizer acts an important component in the electrode performance as it is responsible for ionophore solvation and distribution in the membrane matrix, thus controlling the detection limit, affecting the selectivity and sensitivity and giving the plastic membrane its proper elasticity and strength [29]. The performance characteristics among five different plasticizers (DOPP, DOP, DBP, TMDP and NPOE) were investigated by performing the sensor at varying concentration zinc(II) ion.

The working concentration range for different sensors as evaluated from Figure 4 is given in Table 1. It was apparent that sensors no.3 having membrane with DBP plasticizer and active ionophores, respectively, were the best. This was due to nearly ideal slope at 29.06 mV/decade as compared with the other plasticizers. This sensor exhibited the widest working concentration range of ( $1.0 \times 10^{-1}$  –  $1.0 \times 10^{-6}$  M) and detection limit ( $1.0 \times 10^{-7}$  M). The slopes of this membrane were near Nernstian slope and the working concentration ranges were wide. This indicated that the solvent medium of DBP was probably providing the best complexation environment between zinc ions and its respective carrier. Thus, further studies were carried out with the cells employing sensors no.3.

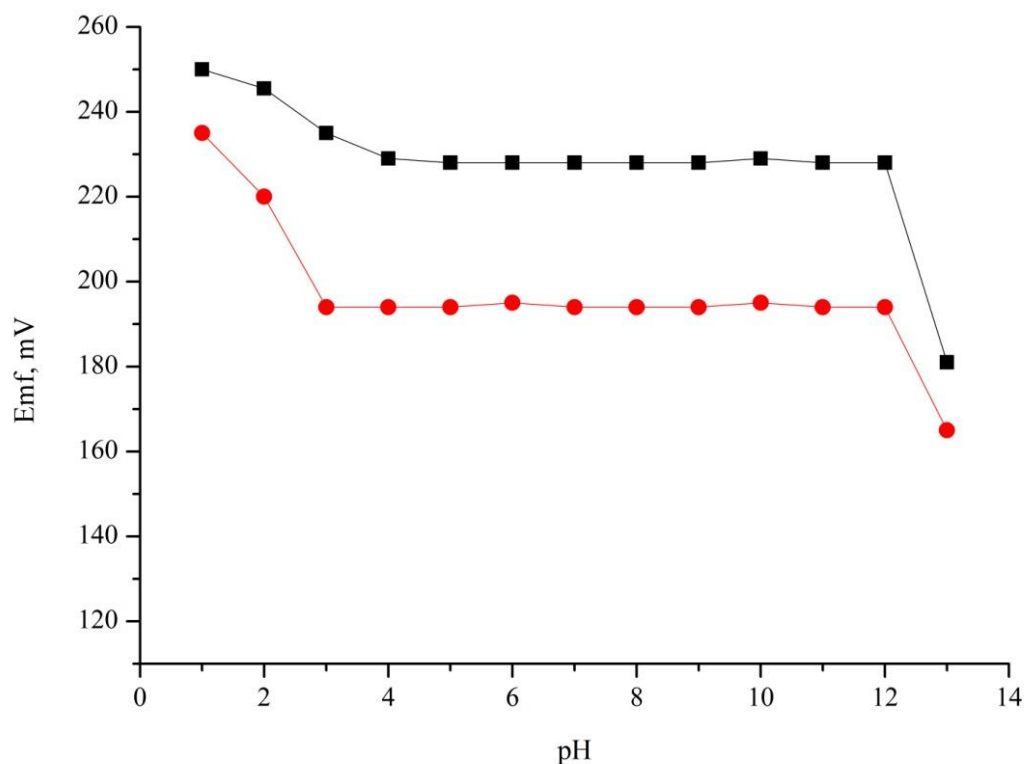
**Table 1.** Optimization of membrane composition based on ligand L and performance in zinc(II) ion-selective electrode

Number	Ion (L)	PVC	Plasticizer	Slope (mV)	Working range (M)	Detection limit (M)
1	10	30	50 (DOPP)	30.52	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$	$1.0 \times 10^{-5}$
2	10	30	60 (DOP)	29.39	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$	$1.0 \times 10^{-4}$
3	10	30	60 (DBP)	29.06	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$	$1.0 \times 10^{-7}$
4	10	30	60 (TMDP)	24.8	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$	$1.0 \times 10^{-5}$
5	10	30	60 (NPOE)	38.35	$1.0 \times 10^{-1} - 1.0 \times 10^{-5}$	$1.0 \times 10^{-4}$

**Figure 4.** Variation potential membrane sensors based on ligand L for different membrane composition and plasticizer, respectively with  $Zn^{2+}$  concentration.

### 3.3. Effect of pH

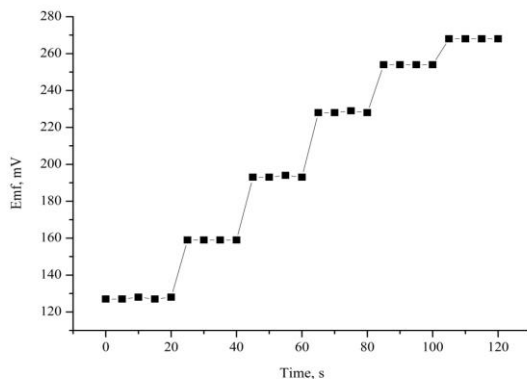
The pH dependence of membrane sensor no.3 was evaluated with a solution containing  $1.0 \times 10^{-4}$  M zinc(II) ions over a pH range of 1.0–13.0. The pH of the solution was varied over the range 1.0–13.0 by the addition of 0.1 M Britton- Robinson Buffer or 0.1 M NaOH solution and the emf reading was plotted against the pH values. As shown in Figure 5, the potentials were independent of pH in the range 4.0–12.0. At the lower pH, the significant change in potential response was observed, it can be related to the presence of  $H^+$  ion which resulted in a loss of their complexing ability with zinc(II) ions [4,14,15]. On other hand, the observed potential drifted at a higher pH due to hydrolysis of  $Zn^{2+}$  [16,26]. Thus, the above range may be taken as the working pH range of this sensor.



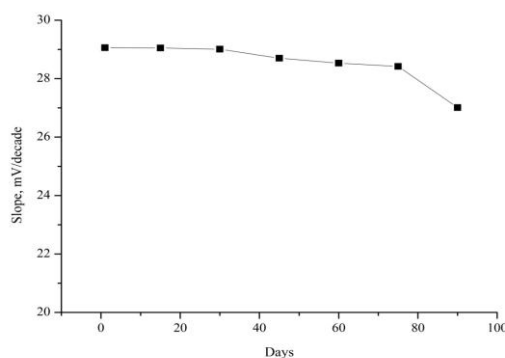
**Figure 5.** Effect of pH on the performance of sensor no.3

#### 3.4. Response time and lifetime of the electrode

The response time of membrane sensor is one of the important factors in deciding the applicability of ion-selective electrode. In this work, the dynamic response time of the sensor was recorded by fast stepwise changing of the  $Zn^{2+}$  concentration from  $1.0 \times 10^{-6}$  M to  $1.0 \times 10^{-1}$  M. The average time required for the electrodes to produce a potential response within  $\pm 1.0$  mV of the final equilibrium value after successive immersion in a series of zinc(II) ion solution and increase in concentration was recorded. The static response time thus obtained was less than 20 seconds over the entire concentration range (Figure 6) and the potentials stayed constant for more than 5 minutes, after which only a very slow divergence was recorded. The result measured was plotted by the calibration graph at 25 °C. It was observed that the response time decreasing when proceeding from diluted solutions to concentrated solutions. This can be explained due to the enhancement of the ion fast exchange process between zinc(II) ions with the ionophore at the test solution- membrane interface at higher concentrations. Then, in order to determine the lifetimes, the performance of electrode was recorded from time to time on daily basic over a period of 3 months. The result is summarized in the Figure 7.



**Figure 6.** Dynamic response time of the membrane sensor no.3 for step changes in concentration of  $1.0 \times 10^{-6}$  M to  $1.0 \times 10^{-1}$  M  $Zn^{2+}$  solution.



**Figure 7.** Potential response of membrane sensor no.3 at different time intervals.

### 3.5. Effect of interfering ions on sensor performance

The influence of interfering ions on the response behavior of ion selective membrane electrode is usually described in terms of selectivity coefficient which is expressed as the logarithm of ( $K^{pot}_{A;B}$ ). The selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of primary ions ( $1.0 \times 10^{-2}$  M) and varies concentration of interfering ions ( $1.0 \times 10^{-1}$  –  $1.0 \times 10^{-7}$  M) were used in this method. Then, the selectivity coefficient was calculated by applying the following equation.

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

Where  $a_A$  is the activity of the primary ion ( $Zn^{2+}$ ) and  $a_B$  is the activity of the interfering ions, and  $z_A$  and  $z_B$  are their respective charges on A and B. As can be seen from Table 2, the selectivity coefficients obtained were lower than 1.0 indicating that the electrode is more selective to the analyte than to the interfering ion [30]. Therefore, it is quite obvious from the corresponding table that  $Zn^{2+}$  ion selective electrodes were highly selective than other common cations. In general, the interfering effect of the cations is in the following order:  $Na^+ > Mn^{2+} > K^+ > Ca^{2+} > Cu^{2+} > Cd^{2+} = Ba^{2+} > Co^{2+} > Mg^{2+} > Ni^{2+}$ .



### 3.6. Comparison with the previous work

In Table 3, working concentration range, detection limit, slope, interfering ion, response time and pH range of  $Zn^{2+}$  ion-selective electrodes based on different ionospheres were compared with those of this work. The data show that the proposed membrane sensor is comparable and has lower detection limit, and a wide pH range when compared with previously reported  $Zn^{2+}$  membrane sensor [2,4,6,16,20,31].

**Table 2.** Selectivity coefficient values of  $Zn^{2+}$  ion-selective electrode based on ligand L for several interference ions (membrane sensor no. 3)

Interfering ion	Selectivity coefficient
$Cu^{2+}$	$2.0 \times 10^{-2}$
$Co^{2+}$	$6.3 \times 10^{-3}$
$Ni^{2+}$	$1.0 \times 10^{-4}$
$Mn^{2+}$	$6.7 \times 10^{-2}$
$Mg^{2+}$	$2.5 \times 10^{-3}$
$Ba^{2+}$	$1.0 \times 10^{-2}$
$Ca^{2+}$	$6.2 \times 10^{-2}$
$Cd^{2+}$	$1.0 \times 10^{-2}$
$K^+$	$6.3 \times 10^{-2}$
$Na^+$	$7.0 \times 10^{-2}$

**Table 3.** Comparison of response characteristic of  $Zn^{2+}$  ion-selective electrodes with previous reported electrodes.

Ionophore	Working concentration range (M)	Detection limit (M)	Slope (mV/decade)	Response time (s)	pH range	Ref.
4- <i>tert</i> -butylcalix[4]arene	$9.6 \times 10^{-6} - 1.0 \times 10^{-1}$	$5.0 \times 10^{-7}$	$28.0 \pm 1.0$	30	2.5 – 4.3	2
<i>N,N'</i> -Bis(2-dimethylaminoethyl)- <i>N,N'</i> -dimethyl-9,10-anthracenedimethanamine	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$1.5 \times 10^{-6}$	$30.0 \pm 0.5$	15	3.0 – 7.5	4
<i>N,N'</i> -phenylenebis(salicyli deaminato)	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	$2.6 \times 10^{-7}$	$29.4 \pm 0.2$	<10	3.0 – 7.0	6
6,7:14,15-Bzo <sub>2</sub> -10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N <sub>2</sub> -1,5-O <sub>2</sub>	$5.0 \times 10^{-7} - 1.0 \times 10^{-2}$	$3.3 \times 10^{-7}$	$28.8 \pm 0.3$	10	2.5 – 9.0	16
<i>N,N'</i> -bis(acetylacetone)-ethylenediimine	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	$8.9 \times 10^{-7}$	$30.0 \pm 0.5$	8	3.2 – 7.1	20
3-hydroxy-2-naphthoic hydrazide	$1.8 \times 10^{-7} - 3.6 \times 10^{-1}$	$1.1 \times 10^{-7}$	-	<18	2.3 – 5.4	31
2,6-diacetylpyridinebis-(benzene sulfonylhydrazide)	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	$1.0 \times 10^{-7}$	$29.06 \pm 0.1$	<20	4.0 – 12.0	This work

### 3.7. Analytical application

The analytical applicability of the electrode was evaluated by analysis on zinc(II) ions in different wastewater samples obtained from the nearest industrial area in Selangor, Malaysia. The pH value of sample solution was adjusted by adding 0.1 M HCl solutions to pH 4.0. The results obtained from the triplicate measurement of proposed zinc sensor were compared with the result determined by atomic absorption spectroscopy (AAS) and are given in Table 4. It was found that the data obtained from triplicate measurements is in satisfactory agreement with the results obtained by AAS. Therefore, the sensor can be employed for Zn<sup>2+</sup> quantification in real samples.

**Table 4.** Determination of Zn<sup>2+</sup> ion in water samples (n=3) by membrane sensor no.3 and atomic adsorption spectroscopy (AAS).

Method	Samples		
	Sample 1	Sample 2	Sample 3
Membrane electrode (mg L <sup>-1</sup> )	11.2±0.5	10.6±0.3	10.9±0.4
AAS (mg L <sup>-1</sup> )	10.7±0.4	10.3±0.3	10.4±0.4

## 4. CONCLUSIONS

The plasticized PVC-based membrane sensor incorporating 2,6-diacetylpyridinebis(benzene sulfonylhydrazide) ligand can be used as an electroactive material for determination of zinc(II) ions. The best composition of the membrane sensor was found to be in the ratio of ionophore:PVC:DBP = 10:30:60 (w/w). It can be used to determine Zn<sup>2+</sup> in a wide concentration range 1.0×10<sup>-6</sup> to 1.0×10<sup>-1</sup> M with a detection limit down to 1.0×10<sup>-7</sup> M in pH range 4.0–12.0. This membrane sensor has wide dynamic range, high reproducibility over a period of 3 months, performs good selectivity and relative short response time. The developed membrane sensor was applied successfully for the determination of zinc(II) ion in the wastewater samples.

## ACKNOWLEDGEMENTS

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