# Zinc Selective Liquid Electrode on the Basis of Phenyl Disulfide

**غشاء الزنك الانتقائي السائل المحضر بالاعتماد على Phenyl Disulfide**

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## Abstract:

A Zinc(II) selective electrode based on phenyl disulfide as ionic membrane carrier was prepared. The electrode exhibits a near-Nernstian response for $Zn^{2+}$ ions over a wide concentration range from ($1.0x10^{-5}$-$1.0x10^{-1}$ M) with a slope of 30.1 mV/decade and a limit of detection of $6.2x10^{-6}$ M. The response time measured was 15 second .It was found to be selective and useable within the pH range of (3.0-8.0). The life time of membrane sensor prepared could be used for at least 2 months. The electrode was successfully used as an indicator electrode in potentiometric titration of Zinc ions.

**الخلاصة :**

قطب الزنك (II) الانتقائي حضر بالاعتماد على phenyl disulfide كناقل ايوني في غشاء القطب . أظهر القطب استجابة نيرنستية لايونات $Zn^{2+}$ ضمن مدى تراكيز تراوحت بين ($1.0x10^{-5}$-$1.0x10^{-1}$ M) وبميل نيرنستي مقداره 30.1 mV/decade وحد تحسس مقداره $6.2x10^{-6}$ M . وكان زمن الاستجابة 15 ثانية . تم إيجاد الانتقائية ومدى الدالة الحامضية المناسبة والتي تراوحت ما بين (3.0-80) . وكان العمر الزمني للغشاء المحضر هو شهرين . وتم استعمال القطب بنجاح كقطب دليل في التسحيح الجهدي لايونات الزنك .

**Keywords:** Zinc ion-selective electrode, membrane, response time, life time.

## Introduction:

Zinc is a moderately-reactive bluish-white metal that tarnishes in moist air and burns in air with a bright greenish flame, its carcinogens and mutagens nature the toxicity of zinc arises from its synergistic/antagonistic interaction with other heavy metals, particularly its homologue cadmium [1]. Its compounds are widely used in electroplating, pharmaceuticals, paint, rubber, dye, wood preservatives, ointments and batteries so the waste from these industries need to be frequently analyzed [2]. Common zinc compounds found at hazardous waste sites include zinc chloride, zinc oxide, zinc sulfate and zinc sulfide [3]. Besides, it is also present in high protein foods and its large doses can cause fever, chills, pulmonary manifestation, gastroenteritis, vomiting, nausea, anemia and renal failure [4].

Numerous methods have been proposed for the spectrophotometric determination of zinc in the samples [5-7]. These methods, however, are time consuming, have poor selectivity and also have the disadvantage of high blank values. Other notable methods used for the determination of zinc include AAS [8], ICP-MS [9] and voltammetry [10]. Most of these methods are disadvantageous in terms of cost and the instruments used in routine analysis. Ion-selective electrode (ISE) is one of the most convenient and reliable analysis. Only few zinc selective electrodes are reported in literature and most of them have poor sensitivity, selectivity, long response time and short life time, an electrode was fabricated by incorporating zinc salts of bi(4-octylphenyl)hydrogen phosphate in PVC matrix [11] but the electrode showed serious interference from some metals such as ($Cd^{+2}$ and $Fe^{+2}$). Linnersund and Bhatti [12] tried zinc complex of bis(2-ethylhexyl)phosphate, an extractant, as electroactive material for preparing

$Zn^{2+}$-selective electrodes but it had a very narrow working pH of range 4.5-6.0. Lebedeva and Jansons [13] prepared $Zn^{2+}$-selective electrodes using saturated solutions of Zn-8-hydroxyquinoline in chloroform. Kojima and Kamata [14] used tetrabutylthiuram disulfide as the carrier in PVC based membrane electrode. Zinc orthophosphate and zinc mercuric thiocyanate were used by Rocheleaw and Purdy [15] as electroactive material on a carbon support for the fabrication of $Zn^{2+}$-selective sensors. Another electrode, based on salicylaldoxime-formaldehyde resin, for zinc [16] exhibited a working concentration range of ($3.0x10^{-6}$-0.1 M) with a near Nernstian slope. Crown ether based electrode has also been reported [17] in literature for zinc, it exhibited a working concentration range of ($70x10^{-6}$-0.1 M) with a Nernstian slope of 29.5 mV/decade of activity. An electrode based on 5,6,14,15-dibenzo-1,4-dioxo-8,12-diazacyclopentadecane-5,14-diene showed response for zinc [18], it has a working concentration range of (5.0 µM-100 mM) in the pH range of 1.5-7.0.

In this work, the use of phenyl disulfide (PD) as an ionophore are reported in the construction of a Zinc(II)-PVC membrane electrode and studied the characteristic and properties of selective electrode.

## Experimental Part:

*Materials:*

Reagent grade dibutyl phthalate (DBP), acetophenone (AP), tri-*n*-butylphosphate (TBP), *o*-nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), benzyl acetate (BA), phenyl disulfide (PD), tetrahydrofuran (THF) and high relative molecular weight PVC were all obtained from Alderich Chemical Company. The nitrate salts of the cations used (all from Merck) were of the highest purity available. Doubly distilled deionized water was used throughout. The pH adjustments were made by the addition of (1.0 M) $HNO_3$ and NaOH solutions.

## Apparatus*:*

All potentiometric measurements were carried out with the following assembly:

1. pH-inolab 720 pH/mV meter was used for the potential and the pH measurements.
2. *Ag | AgCl(satd.) | KCl(satd.) | internal solution ($1.0x10^{-1}$ M $Zn(NO_3)_2.6H_2O$) | PVC membrane | test solution | KCl(satd.) | $Hg_2Cl_2$(satd.) | Hg*

## Preparation of Membrane and Electrodes:

The general procedure to prepare the PVC membrane was to mix thoroughly 3.0 mg of ionophore (PD), 60 mg of plasticizer DOP, 30 mg of powdered PVC and 10.0 mg of $Zn(NO_3)_2.6H_2O$ in 9 mL of 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 (8-10 mm) was dipped into the mixture for about 5 second so that a nontransparent membrane of about 0.5 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 12 h. The tube was then filled with internal filling solution (0.1 M $Zn(NO_3)_2.6H_2O$). The electrode was finally conditioned by soaking in 0.5 M $Zn(NO_3)_2.6H_2O$ solution for 48 h. A silver/ silver chloride wire was used as an internal reference electrode, it is shown in Figure 1.

## Selectivity*:*

The selectivity coefficient ($K_{Zn,J}$) of the electrode towards different cationic species ($J^{+n}$) was determined using the mixed solution method [19]. The mixed solution method was used according to the following equation:

$$K_{Zn,J}^{Pot} a_J^{1/Zj} = a_{Zn}(anti\log\frac{E_2 - E_1}{RT/F}) - a_{Zn}$$

where $E_1$ is the potential of a known volume of solution containing $Zn^{2+}$ ions at an activity of $a_{Zn}$, and $E_2$ is the potential of the $Zn^{2+}$solution with a known volume of interfering ions at activity of $a_{Zn}$.

*Precision [20]:*

The mean, is the numerical average obtained by dividing the sum of the individual measurements by the number of measurements.

$$\overline{X} = \frac{\sum X_i}{n}$$

The absolute standard deviation, S.D. describes the spread of individual measurements about the mean and is given as:

$$S.D. = \frac{\sum\left(X_i - \overline{X}\right)^2}{n-1}$$

The relative standard deviation, R.S.D. is reported.

$$R.S.D. = \frac{S.D.}{n} \times 100$$

## Results and Discussion:

Phenyl disulfide (PD) it is shown in Figure 2, the ionophore used to construct a membrane for potentiometric measurements. The results are summarized in (Table 1). Several plasticizers including DOP, DBP, AP, *o*-NPOE, TBP and BA, which are often used with PVC membrane electrodes, were evaluated. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the inophore molecules and the state of ligands [21], it is expected to play an important role in determining the ionselective characteristics. As it is seen from Table 1, among different plasticizers examined, DOP results in the best sensitivity, it is shown in Figure 3.

The dependence of the electrode response (slope and detection limit) on the amount of carrier was also examined and is shown in Figure 4. In the case of the carrier-weight ionselective electrodes. In spite of these considerations, a carrier content of 3.0 mg was chosen as the optimum condition (No. 4, Table 1), because the surface condition of the PVC membrane deteriorated as a result of decreasing and increasing the carrier content (1.0 and 4.0 mg, respectively). The plasticizer/PVC ratio of 1.0-3.0 were examined. The membranes prepared with a plasticizer/PVC ratio of about 2.0 were found to have the best sensitivity [22], with a slope of 30.1 mV per decade over a wide concentration range (Figure 5).

*The concentration range, the slope and detection limit:*

The electromotive force (emf) response of the proposed $Zn^{2+}$ sensor (prepared under optimal membrane ingredients) indicate a rectilinear range from $1.0x10^{-5}$-$1.0x10^{-1}$ M. The slope of the calibration curve were 30.1 mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration curve, was $6.2x10^{-6}$M.

*The effect of internal solution:*

The influence of the concentration of internal solution on the potential response of the $Zn^{2+}$ ion-selective electrode was studied. The $Zn(NO_3)_2.6H_2O$ concentration was changed from $1.0x10^{-3}$ to $1.0x10^{-1}$ M and the emf-pZn plot was obtained. It was found that the variation of the concentration of internal solution does not any significant difference in the electrode's potential response, except for an expected change in the intercept of the resulting near-

Nernstein plots. A 0.1 M concentration of the reference solution is quite appropriate for smooth functioning of the system (Figure 6).

*Response time and stability:*

Optimum conditioning time for the membrane sensor in a 0.5 M $Zn(NO_3)_2.6H_2O$ solution is 48 h. It then generate stable potentials when placed in contact with $Zn^{2+}$ solutions. The response time measured was less than 15 s for $Zn^{2+}$ concentrations $1.0x10^{-2}$ M. It is noteworthy that the equilibrium potentials essentially remained constant for more than 3 min, after which only a very small divergence within the resolution of the pH meter was recorded the membrane sensor prepared could be used for at least 2 months without any measurable divergence.

## The effect of pH:

One of the ions present in aqueous solution is the hydrogen ion. It interferes, in many instances, with the functioning. In view of this, it is necessary to find the optimum pH range where the electrode without interference from the hydrogen ions. pH dependence of the membrane electrode works has been tested by using 0.01 M and 0.001M $Zn^{2+}$ solutions over a pH range 1 to 10 (Fig.7). pH was adjusted by the addition of small drops of hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M). As could be seen from fig.6, the potentials stay constant from pH 3.0 to 8.0. Beyond this pH, a drift in potential is observed which is due to the formation of some hydroxy complexes of $Zn^{2+}$ at higher pH while at lower pH, there could be protonation of (PD) in the membrane which results in a loss of their complexing ability with the metal ion. Thus the working pH range of the proposed assembly may be taken from 3.0-8.0.

## Selectivity:

The important parameter of many potentiometric ion is response to the primary ion in the presence of the other ions presence in solution, which is expressed in terms of the potentiometric selectivity constant ($K_{Tl,J}$). The values obtained for selectivity coefficients by the mixed solutions method with a mixed concentration of interference metal ion ($J^{+n}$) with an activity of aqueous 0.1 M solution of $Zn(NO_3)_2.6H_2O$, are given in (Table 2). It can be seen from these values that the electrode is characterized by a high selectivity towards Zinc ions with respect to alkali, alkaline earth, transition and heavy metal ions [7].

## Analytical Application:

The proposed Zinc membrane electrode was found to work well under laboratory conditions. It was successfully applied to the titration of a $Zn^{2+}$ ion solution with EDTA. During the titration no pH or ionic strength adjustments were made. All titration were performed with $1.0x10^{-3}$ M of $Zn^{2+}$ in 50 mL of sample solution with 0.01 M of EDTA. A typical titration curve is shown in Figure 8. The other titrants led to similar titration curves, the steepness of the potential jump being inversely dependent on the solubility product, as usual. As shown, the amount of $Zn^{2+}$ ions in solution can be accurately determined with the electrode.

## Conclusion:

A PVC-membrane electrode for $Zn^{2+}$ ions based on (PD) as ionophore, was investigated. The optimized formulation of the membrane (*i.e.* 3.0 mg PD, 30 mg PVC, 60 mg DOP, 10.0 mg $Zn(NO_3)_2.6H_2O$) resulted in a linear concentration range of $1.0x10^{-5}$-$1.0x10^{-1}$ M with a slope of 30.1 mV/decade and a limit of detection of $6.2x10^{-6}$ M. The fast response time, wide linear range, fair selectivity coefficients and long lifetime of the proposed sensor are

advantageous over most of the reported $Zn^{2+}$-selective electrodes. The proposed electrode can be used successfully as a sensor in potentiometric titrations.

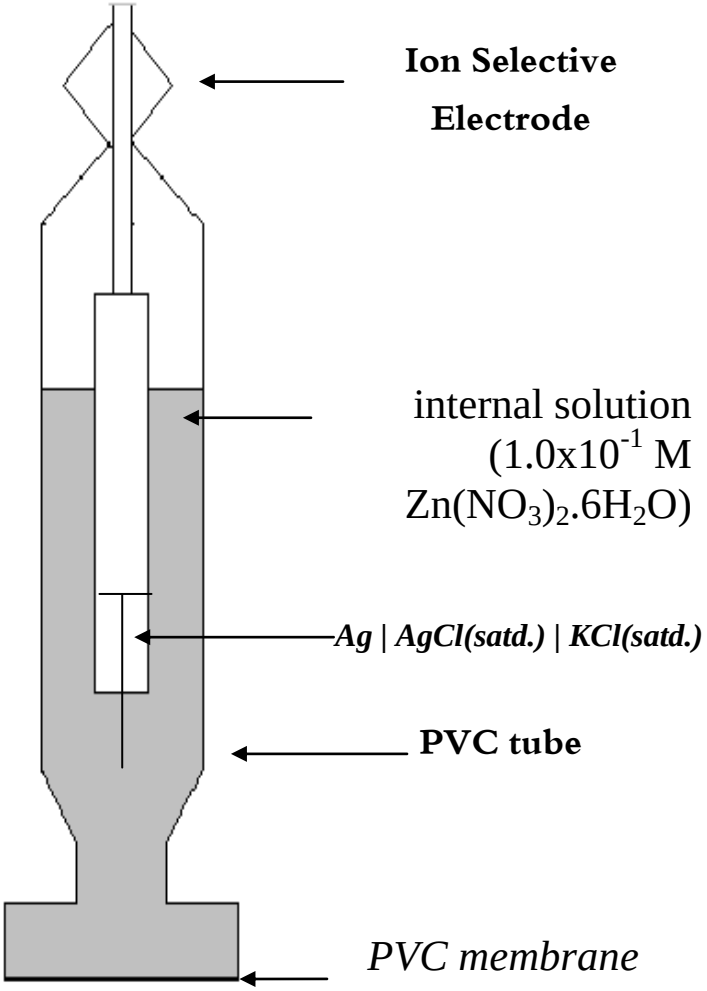


**Figure 1. Structure of Zinc(II)-Selective electrode**

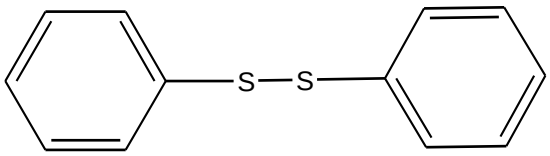


**Figure 2. Structure of Phenyl Disulfide (PD)**

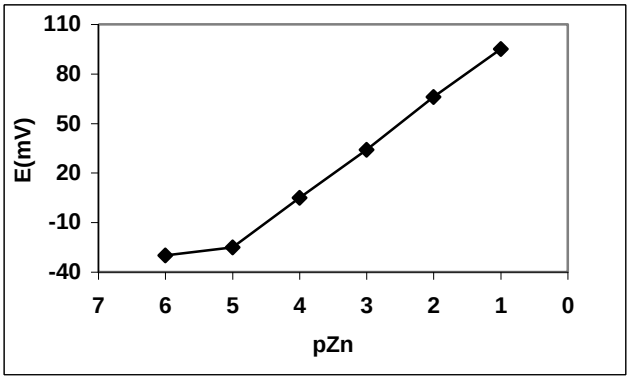


**Figure 3. Calibration Curve of Structure of Zinc(II) selective electrode**

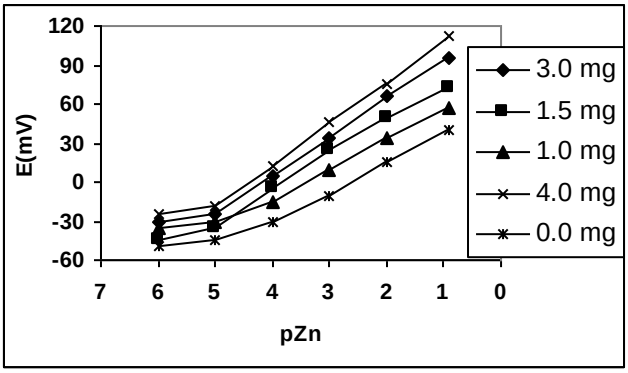


**Figure 4. Effect of the content of (PD) on the response of the membrane**

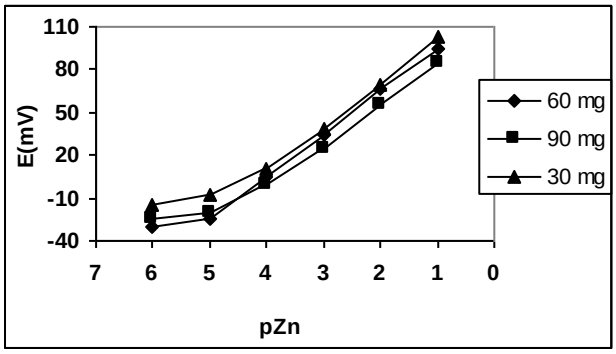


**Figure 5. Effect of the content of (DOP) on the response of the membrane**

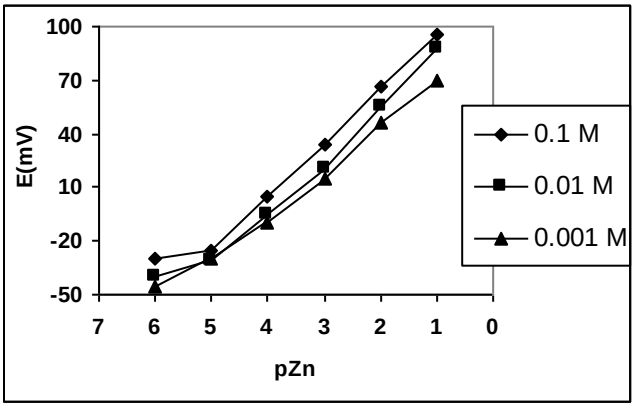


**Figure 6. Effect of the internal solution on the response of the membrane**

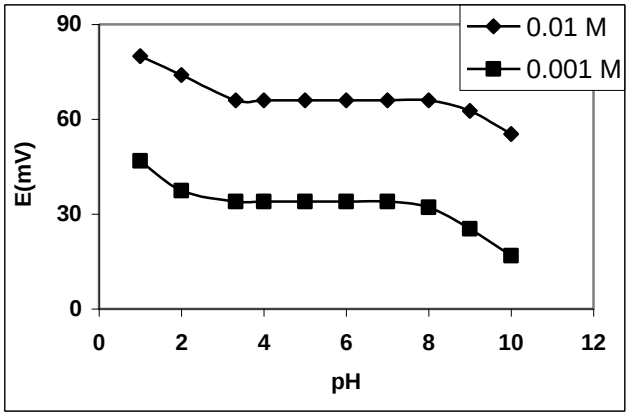


**Figure 7. Effect of pH on the response of Zinc(II) selective electrode based on (PD)**

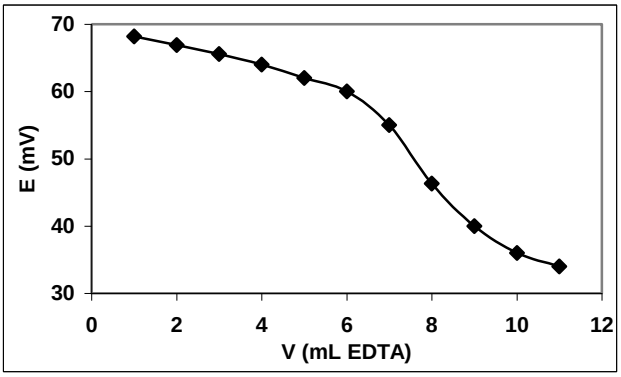


**Figure 8. Titration of $Zn^{2+}$ (0.001 M) in 50 mL of aqueous solution with (0.01 M) EDTA using the Zinc(II) selective electrode**

**Table 1. Optimization of the membrane ingredients**

| Electrode No. | Composition (mg) | | | | | | | | Slope mV/decade |
|---|---|---|---|---|---|---|---|---|---|
| | PD | PVC | DOP | BA | *o*-NPOE | AP | TBP | DBP | |
| 1 | 0.0 | 30 | 60 | - | - | - | - | - | 21.5 |
| 2 | 1.0 | 30 | 60 | - | - | - | - | - | 22.7 |
| 3 | 1.5 | 30 | 60 | - | - | - | - | - | 25.5 |
| 4 | 3.0 | 30 | 60 | - | - | - | - | - | 30.1 |
| 5 | 4.0 | 30 | 60 | - | - | - | - | - | 34.8 |
| 6 | 3.0 | 30 | 30 | - | - | - | - | - | 32.5 |
| 7 | 3.0 | 30 | 90 | - | - | - | - | - | 27.1 |
| 8 | 3.0 | 30 | - | 60 | - | - | - | - | 25.4 |
| 9 | 3.0 | 30 | - | - | 60 | - | - | - | 26.3 |
| 10 | 3.0 | 30 | - | - | - | 60 | - | - | 33.9 |
| 11 | 3.0 | 30 | - | - | - | - | 60 | - | 32.7 |
| 12 | 3.0 | 30 | - | - | - | - | - | 60 | 27.2 |

**Table 2. Selectivity coefficients of various interfering ions**

| Interfering ion | Log $K_{Zn,J}$ | Interfering ion | Log $K_{Zn,J}$ |
|---|---|---|---|
| $H^+$ | -3.15 | $Ba^{2+}$ | -2.30 |
| $Li^+$ | -2.85 | $Fe^{2+}$ | -2.82 |
| $Na^+$ | -2.44 | $Co^{2+}$ | -2.84 |
| $K^+$ | -2.58 | $Ni^{2+}$ | -2.23 |
| $Cs^+$ | -1.99 | $Cu^{2+}$ | -2.85 |
| $Ag^+$ | -4.25 | $Mg^{2+}$ | -1.87 |
| $NH_4^+$ | -1.85 | $Cd^{2+}$ | -2.68 |
| $Tl^+$ | -2.47 | $Hg^{2+}$ | -2.85 |
| $Ca^{2+}$ | -2.95 | $Pb^{2+}$ | -3.54 |

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