

Development Zinc-selective membrane potentiometric sensor based on crown ether.

Zeina Mohammed Kadhum Al-Mossawy
Kerbalaa University /Science college/Chemistry department

الخلاصة

لقد حُضر قطب انتقائي سائل جديد لايون الزنك المعتمد على الايثر التاجي DB18C6 والمذيب الملدن Di-n-octyl phenyl phosphonate (DOPP) وقد حقق القطب الحساس إستجابة نيرنستية لايونات الزنك لمدى $1.7 \times 10^{-2} - 3.1 \times 10^{-4}$ وحدة فعالية وبميل نيرنستي $27.00 \frac{mV}{decade}$. وحد كشف 3.9×10^{-4} وحدة فعالية. وكان زمن الاستجابة حوالي (30 s) ويمكن ان يستعمل لفترة (60 days) على الاقل بدقة قياسات ثابتة. واستعمل القطب بنجاح في تقدير أيونات الزنك مباشرة في المحلول.

Abstract//

A new liquid selective electrode for Zinc ions based on Di-benzo-18-crown-6 as membrane carrier with plasteicezer (DOPP) was prepared. The sensor exhibits a nernstian response for Zn^{2+} range $1.7 \times 10^{-2} - 3.1 \times 10^{-4}$ with nernstian slope $27.00 \frac{mV}{decade}$, and detection limit of (3.9×10^{-4}) activity unit. It has a response time of a bout (30 s) and can be used for at least (60 days) without any divergence. The proposed membrane sensor revealed good selectivity for Zn^{2+} over variety of other metal ions and could be used in pH range of (3-7). It was successfully used for direct determination of Zn^{2+} in solution.

Introduction

The use of ion selective electrodes has gained importance because of their selectivities on specific ions.

After numerous attempts to design a membrane electrode based on various crystalline materials, Pungor and hallos –succeeded in preparing the first workable ion-selective electrode ⁽¹⁾. Then the fields of ion selective electrodes of membrane biochemistry and of electrochemistry are progressing rapidly ⁽²⁾.

Silver salts of spare solubility are used mostly for their preparation. It was found that solid state electrodes prepared from silver halogenides were sensitive to halogenide however these electrodes could also be used for the determination of some cat ions such as mercury ^(3,4) in directly.

It was found that the electrodes made from two sulfide salts such as Ag_2S - PbS . And Ag_2S - CdS were sensitive to lead and cadmium ions respectively ⁽⁵⁾.

The correlation found between the crystalline structure of the sensing material and the potentiometric response made possible the controlled preparation of several precipitate based electrodes such as cadmium, lead and copper selective electrodes.

⁽⁶⁻⁸⁾ Also there is lithium-selective electrodes based on a new series of neutral carriers ^(9,10). We have reported zinc-selective electrodes based on a new series of neutral carriers which exhibit satisfactory selectivity to zinc which the mineral is

present in every part of the body and has a wide range of functions. It helps with the healing of wounds and is a vital component of many enzyme reactions⁽¹¹⁾. Zinc is vital for the healthy working of many of the body's systems. It is particularly important for healthy skin and is essential for a healthy immune system and resistance to infection.

Our body contain a bout (2-3)g of zinc and so a regular supply in diet is required⁽¹²⁾.

While the neutral carriers as in Fig (1) which one of these was used in this work ,named the crown ethers are among the first synthetic complexing agents introduced to bind strongly and selectively to alkali metal ions ^(13,14),they have been used as suitable neutral carriers for the selective transport of alkali metal cat ions throw liquid membrane^(15,16).

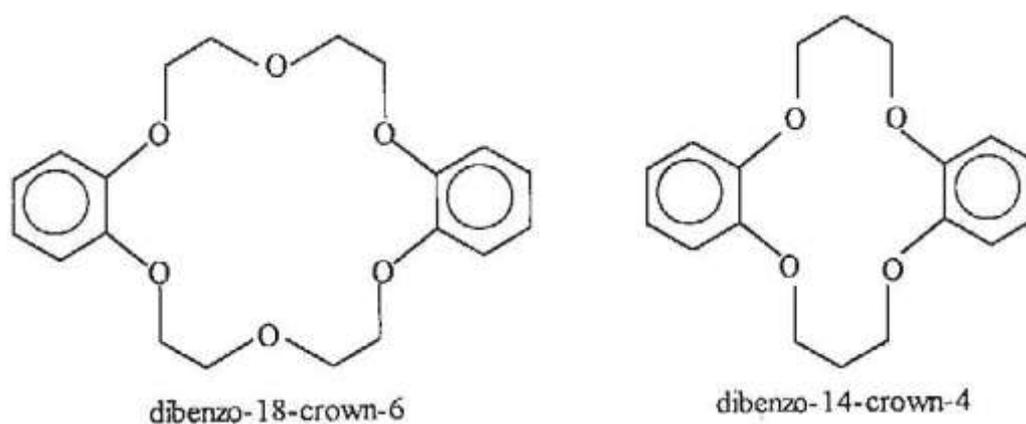


Fig (1) Some types from Crown ethers compounds.

2- Experimental

2-1 Apparatus and reagents

****Apparatus:-**

pH meter Knick-Digital pH, EmV-meter, Shaker,Wrist Action,Burell Corporation.Model 75,PA.,U.S.A., Magnatic stirrer Gallinkamp-England, Calomel Reference Electrode, Gallinkamp(USA)., Sensitive balance, W.Germany, sartoris, pH Electrode, Orion Research (USA)., Silver-Silver chloride Electrode.

****Reagents:-**

Most reagents used were of analytical reagent grade (Merck):

Dibenzo-18-crown-6 (DB18C6),

Tetrahydrofuran (THF), others were used of analytical reagent grade (Aldrich):Znic chloride ($ZnCl_2$), Di-n-octyl phenyl phosphonate (DOPP) . Poly (vinyl chloride) (PVC) from (Fluka), others were used of analytical reagent grade(Britsh Drug Housees) Hydrochloric acid, Sodium chloride.

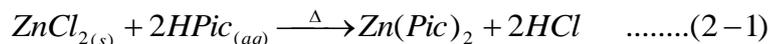
2-2 Proceder//

Stock solution of (0.1M) of the cat ions were prepared, other standard solution were prepared by subsequent dilution of the stock solution.

A- Preparation of complex:

The picrate salt of Zn^{2+} was prepared by stirring mixture of aqueous solution containing the metal oxide and picric acid at 75°C.The excess picric acid was

removed by extraction several times with benzene. The solid salts were obtained by evaporating the aqueous solution ⁽¹⁷⁾.



Then the solution of the metal picrate was mixed with the solution of the crown ether at 60°C for 15 minutes. the complex obtained by cooling the mixture to 0°C ⁽¹⁸⁻¹⁹⁾. The equation of this reaction as below:- ⁽²⁰⁾



which is : L= ligand , A= crown ether

B- Preparation of membrane:

In a 50 ml beaker with a diameter of 4.2 cm ,100-200 mg PVC dissolved in 5 ml THF (tetrahydrofuran),200-300 mg of complex dissolved in 5 ml THF, and 0.2-0.3 ml of DOPP (Di-n-octyle phenyl phosphonate) are mixed and stirred⁽²¹⁾. This beaker resting on a glass plate .and a pad of filter paper with a heavy weight on a top of the glass ring was placed .

The solvent is then allowed to evaporate at room temperature for (24) hours⁽²²⁾. The membrane formed as a film in the bottom is taken out carefully using a teflon forceps as in Fig (1).

. This film membrane is cemented to the flat end of a PVC tube (1 cm diameter) with an a adhesive of PVC dissolved in THF. One day after ,the excess membrane is cut and the tube is filled with (0.1 M) ZnCl₂ .Ag/AgCl electrode is immersed as the inner reference. The electrode is immersed in to a (0.2 M) ZnCl₂ in order to condition the electrode⁽²³⁾ as in Fig (2).

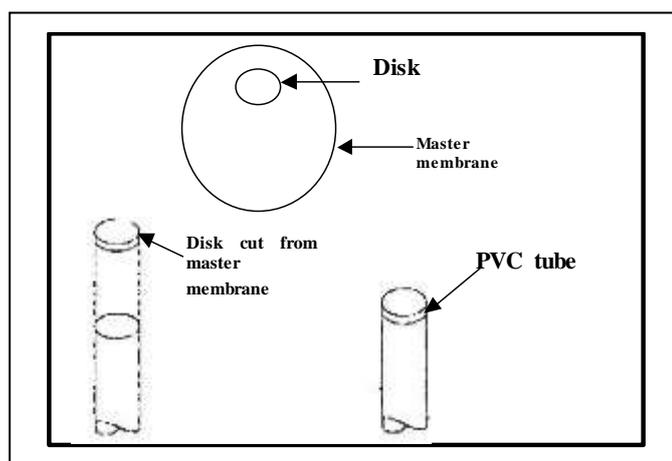


Fig (1) Cutting and mounting a PVC membrane

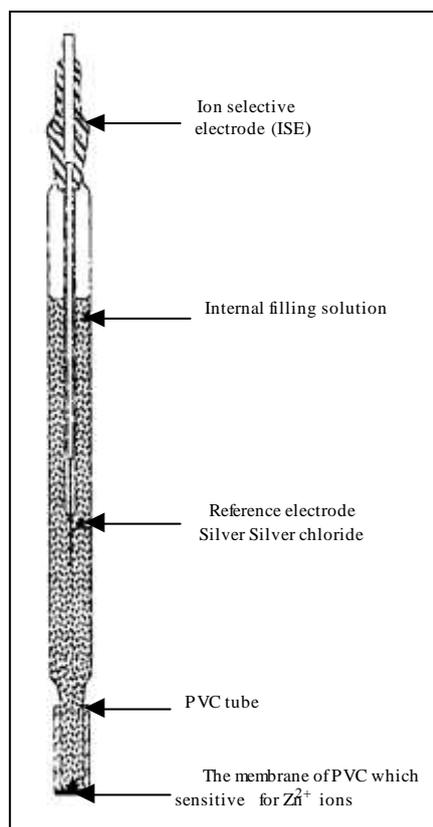
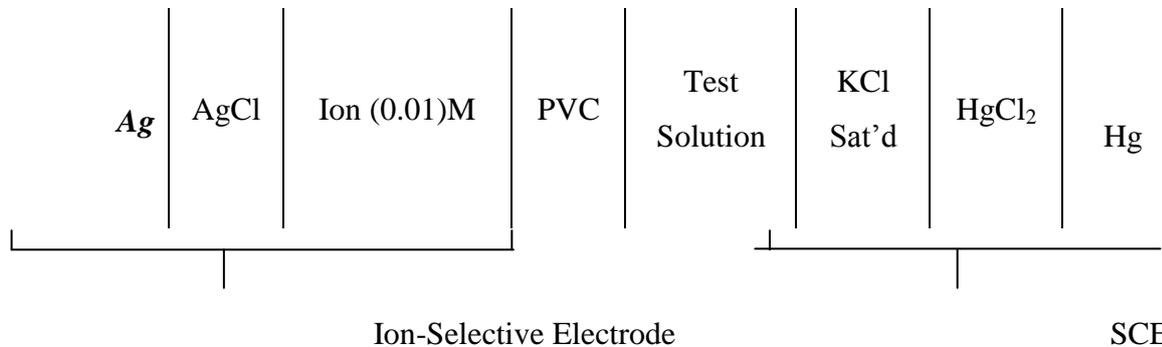


Fig (2) Assembly of the PVC matrix membrane ion-selective electrode .

Then the electrochemical cell used for measurements is at follows:-



(3) The result and discusstion

(3-1) Determination of calibration curve

All potentiometric measurements were made at room temperatures. Calibration curve for this electrode was obtained by transferring 25 ml of the ZnCl₂ standard solution (10⁻¹-10⁻⁵)M to 50 ml beakers. Immerse the Zinc electrode in conjunction with the reference electrode in the solution.

A calibratation curve was then prepared by plot on seven cycle semi log paper ,the activity coefficient (f) of Zn ions was calculated from Deby Hukel equation (1-1)⁽²⁴⁻²⁵⁾.

$$-\log f = z^2 \left[\frac{A\sqrt{\mu}}{1+1.5\sqrt{\mu}} - 0.2\mu \right] \dots\dots\dots(3)$$

where μ = is the ionic strength of the solution ($\mu = 0.5 \sum CZ^2$)

A = is the constant = 0.5091 for water at 25^o C .

the emf responses for the DOPP based membranes using DB18C6 ether, was linear at Zn^{2+} activity ranged from $1.7 \times 10^{-2} - 3.1 \times 10^{-4}$,as shown in fig (4).while the Nernstain slope of the calibration line was $27.00 \frac{mV}{decade}$,and the detection limit of this electrode was 3.9×10^{-4} activity unit.

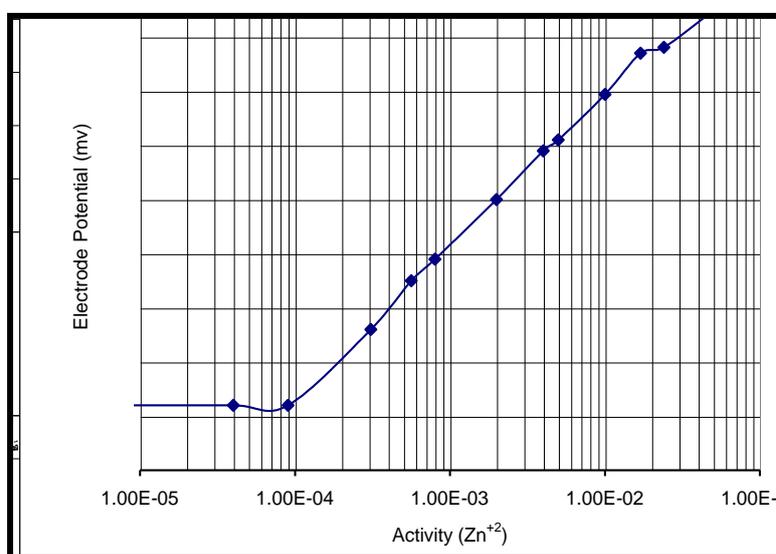


Fig (4)_Calibration curve of Zinc selective electrode based on DB18C6 and DOPP as solvent mediator.

(3-2) The effect of internal filling solution:-

The concentration of the internal filling solution (IFS) of this electrode was also investigated .Therefore; the concentrations were varied between ($10^{-4} -10^{-5}$)M $ZnCl_2$ and the electrode response was measured through out the entire linear range .The best response was obtained at (IFS) concentration of 10^{-2} M for this electrode.

(3-3) Effect of pH

Effect of pH on the potential readings at various $ZnCl_2$ solutions are prepared and the pH is adjusted to certain values by the addition of HCl or NaOH using a pH meter . For each $ZnCl_2$ concentration measured potentials at each pH values are plotted against pH .

The potential readings remained un changed within the pH range about (3.5-7.7) at various concentrations of $ZnCl_2$.

There is a slight effect at higher and lower pH values. At $\text{pH} > 7.7$ the potential was changed slightly presumably because of hydroxide ion interfered. The effect being very pronounced for low concentration of ZnCl_2 (10^{-5})M. Interference was also observed at low pH ,therefore; the working pH range for the electrode changed from(3.5-7.5).As in fig (5).

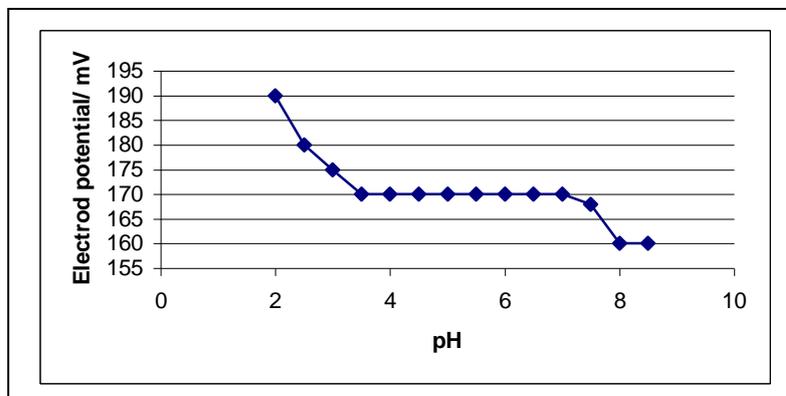


Fig (5) The effect of pH of the electrode.

(3-4) The response time of the electrodes

The response time of the electrode is measured for different ZnCl_2 concentrations. When the ZnCl_2 concentration was increased from 10^{-4} to 10^{-2} it was about 2 min. When it changed from 10^{-4} to 10^{-3} it was 3 min ,for a change from 10^{-5} to 10^{-4} it was 4 min 30 sec. The larger the change in concentration the larger is the response time, e.g. for a change from 10^{-5} - 10^{-2} it is 5 min. also the response time of the electrode depend on two important factors, the stirring rate and temperature and the response time will be shorter, when these factors are increased.

(3-5) Effect of membrane composition and thickness

When membrane mixtures in different weight quantities were used in the same size beakers the thickness of membranes were also different.. Therefore; the membrane was composition(0.1) g sensor, (0.5) g solvent mediator, (0.2) g PVC soluble in THF has the lowest slope and high thickness, while the membrane which composition was (0.04) g sensor,(0.36) g solvent mediator,(0.17) g PVC soluble in THF has the highest slope and low thickness^() which is the better than other one.

It was found that the electrode with total mass of (0.5) g has the highest slope, the membrane thickness affects the response time of the electrode and thin membranes have shorter response times. It is not possible to obtain very thin membranes with every kind of matrix material(26).

(3-6) The life time of the electrode

The membrane surface loses its sensitivity because of the effect of ruining effect, such as mechanical rubbing⁽²⁷⁻²⁸⁾ and the life time of the electrode decreases due to the shorter viscosity for the plastic substance and this cause in the decreases of ion exchange site abone the surface of membrane . The membrane surface are cleaned by washing with distilled water or by waiting in (10^{-2}) M ZnCl_2 solutions for about (24

h).The life time of the electrode is found to be about (2 months) when it is immersed in to a (10^{-2}) M $ZnCl_2$ solution for a bout (30 min) after each measurement. The sensitivity of the electrode decreases after (2 month).

The References

- 1- E.Pungor and E.Hallo-Rokosinyi,Acta Chim.Hung.,**27**,63 (1961).
- 2- Ion.Slective Electrodes (ed.E.Pungor),symposium held at Matrafured,Hugary,1972,Akademiakiido,Budapest,1973.
- 3- R.F.Overman.Anal.Chem.**43**,616 (1971).
- 4- G.Somer,Anal.Chem.**53**,2144 (1981).
- 5- G.A.Rechnitz,Anal.Chem.**41**,21 (1969).
- 6- F.Pal,K.Toth,E.Pungor,M.Farkas-Jhanke,H.Ebel,M.F.Ebel,Anal.Chim.Acta **180**,313 (1986).
- 7- E.G.Harsanyi, K.Toth,E.Pungor, M.F.Ebel, Mikro chim Acta **194**,163 (1987).
- 8- M.Faraks-Jahuke,F.Pals,K.Toth,E.Pungor, in:E.Pungor,etal(Eds.),Ion-Selective Electrodes,V.**4**,Akademiai Kiado,Budapest,373,1985.
- 9- H.Sugihara,T.Okada and K.Hiratani,Chem.Lett.,2391,(1987).
- 10- H.Sugihara,T.Okada and K.Hiratani,Anal.Sci.,**9**,593,1993.
- 11- Federation of American Societies for Experimental Biology,Life Sciences Research Office,V.1-2 ,U.S.Government printing Office,Washington D.C.1995.
- 12- Nutrition and your health:Dietary Guidelines for Americans,4th ed.Home and Garden Bulletin No.232.U.S. Government printing Office,Washington D.C.1995.
- 13- C.G.Pederson,J.Am.Chem Soc.,**89**,7017 (1967).
- 14- R.M.Azatt,K.Pawlak,J.S.Bradshaw,R.I.Bruening,Chem.Rev.,**91**,1721(1991).
- 15- H.C.Visser,D.N.Reinhoudt,F.Dejong,Chem.Soc.Rev.,**75**(1974).
- 16- J.S.,Shih,J.Chin.Chem.Soc.,**39**,551(1992).
- 17- B.E.Al-Abdilli,PH.D.Thesis,Baghdad University (1997).
- 18- O.A.Al-Araji-Iraqi Journal of Chemistry,**62**,(2000).
- 19- A.Graggs,G.J.Moody and J.D.R. Thomas,J.Chem.Educ.,**5**,541 (1974).
- 20- Y. A. Zolotov, Macrocylic Compounds in Analytical chemistry, V. 143, John Wiley and Sons. INC. New York (1997). pp. 285, 299, 180.
- 21- H. Sugihara, T. Okada, and R. Hiratani, Anal. Sci., **9**, 593(1993).
- 22- L. Sun ,T. Okada, J.P. Collin, and H. Sugihara, Anal. Chim. Acta, **329**, 64(1996).
- 23- A. Graggs, G. J. Moody and J.D.R. Thomas, J. Chem. Educ., **5**, 541(1974).
- 24- G. H. Griffiths, G.J. Moody, and J.D.R. Thomas, Analyst, **97**, 419 (1972).
- 25 -M. Matshi, and H. Frieser, Anal. Lett., **3**, 161(1970).
- 26- G. Ekmekci and G. Somer, Talanta, **49**, 83 (1999).
- 27- G. Ekmekci and G. Somer, Talanta, **49**, 91 (1999).
- 28- Z.M.Kadhun, Msc Thesis, Babylon University(2002).