

## The role of Plasticizers on the characteristics of poly (vinyl chloride )-membrane Zinc –selective electrodes based on Di benzo-18-crown-6

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### **Abstract :-**

Ion selective of pvc-membrane Zinc-selective electrodes based on DB18C6(dibenzo-18-crown-6) were tested for two plasticizers which were used as solvent mediator DOPP(Di-n-octylphenyle phosphonate) and TBP (Tri-n-butyl phosphate).The electrode gave a linear response with a Nernstian slope of  $26.50 \pm 2 \text{ mV/decade}^{-1}$  within the concentration range  $1.9 \times 10^{-2} - 4.0 \times 10^{-4}$  of Zinc ions when we used Dibenzo -18-crown-6 as a carrier and Di-n- octyl phenyl phosphonate as solvent mediator .The method is very selective and has applied for the determination of Zinc ions in samples and could be used in pH range of (2.5-6.5).In the other hand the non nernstian response for the membrane which used tri-n- butyl phosphate as solvent mediator .It has been shown that plasticizers can effect the Ion selectivities of PVC –membrane ion-selective electrodes.Zinc ion-selective electrodes based on neutral carriers of current research interest because of their potential use in clinical applications<sup>(1)</sup>.Therefore, use of ion-selective electrodes for chemical and medical analysis continues to be an area of focus <sup>(2-5)</sup>.Potentiometric ion sensors based on polymeric membranes are used in many laboratories<sup>(6)</sup>.In recent years,the supported liquid membrane systems have received attention as an alternative separation technique for metal ions from dilute solutions <sup>(7-10)</sup>.At recent years,the design and preparation of bulk liquid membrane, for the selective of some transition and heavy metal ions using different crown ether derivatives as ion carriers<sup>(11-13)</sup>.Crown ethers have demonstrated high complexing ability with various metal ions because of this of suitable neutral carriers of ion-selective electrodes<sup>(14-16)</sup>.Therefore various macrocyclic crown ethers are synthesized as ionophores for discernment of alkali metal and alkaline earth metal cations<sup>(17)</sup>.During 1986-1992, compounds such as dibenzo-18-crown-6 and diazadibenzo-18-crown-6,and 3,17-diazadibenzo-18-crown-6, and monobenzo-15-crown-5,were used as ionophores in ISE<sup>(18-19)</sup>.

ISE offer an attractive potentiometric method for the surfactant analysis<sup>(20-21)</sup>. Than the other methods such as spectrophotometry<sup>(22)</sup>, ion-pairing<sup>(23)</sup>, thin-layer chromatography<sup>(24)</sup>, gas chromatography, HPLC<sup>(25)</sup>, capillary electrophoresis<sup>(26)</sup>. Many studies of  $Zn^{+2}$  -ISE have been studied for different carrier,  $Zn^{+2}$  -ISE based on cryptand C2B22 as a carrier<sup>(27)</sup>,  $Zn^{+2}$  -ISE based on 5,6,14,15-Dibenzo-1,4-dioxo-8,12-diazacyclopenta decane-5,14-diene<sup>(28)</sup>,  $Zn^{+2}$  -ISE based on Bis(2-nitro phenyl)disulfide<sup>(29)</sup>,  $Zn^{+2}$  -ISE based on other carriers<sup>(30-33)</sup>. In this study  $Zn^{+2}$  -ISE based on Di Benzo-18-crown-6- as a carrier.

## **Experimental part**

### **Chemicals**

The sources of the reagents were as follows:

Zinc oxide (ZnO) and Di-n-octyl phenyl phosphonate DOPP C<sub>22</sub>H<sub>27</sub>O<sub>4</sub>P from Aldrich. Sodium hydroxide (NaOH), Sodium Chloride (NaCl) and Hydrochloric acid (HCl) from British Drug Houses. Tri-n-butyl phosphate (TBP) C<sub>12</sub>H<sub>27</sub>O<sub>4</sub>P, Potassium Chloride KCl and Poly (vinyl chloride) PVC from Fluka AG. Tetrahydrofuran (THF) C<sub>4</sub>H<sub>8</sub>O and Dibenzo-18-crown-6 from Merck.

All the other chemicals used were of analytical reagent grade. Deionized water was used.

### **Apparatus**

- 1- Microprocessor-based Bench pH/mV/C° Meters-HANNA instruments
- 2-Shaker, Wrist Action, Burrell Corporation, Model 75, USA.
- 3- Magnetic stirrer Gallenkamp-England.
- 4- Calomel Reference Electrode, Gallenkamp (USA).
- 5- Sensitive balance, W. Germany. Sartoris.
- 6- Silver-Silver Chloride Electrode.
- 7- pH Electrode, (HANNA instruments).

### **Membrane preparation**

In a 50 ml beaker with a diameter of 4.2 cm, 100-200 mg PVC dissolved in 5 ml THF, 200-300 mg of complex dissolved in 5 ml THF, and 0.2-0.3 ml of plasticizer are mixed and stirred<sup>(33)</sup>. This beaker resting on a glass plate, and a pad of filter paper with a heavy weight was placed on a top of the glass ring was placed.

The solvent is then allowed to evaporate at room temperature for two days<sup>(34)</sup>. The membrane formed as a film in the bottom is taken out carefully using a teflon forceps.

The resulting membrane was excised and attached to a PVC tube, with tetrahydrofuran as the adhesive. PVC membranes containing other solvent mediators were prepared in the same manner. Each PVC tube was filled with an internal solution of 0.1 M ZnO in 0.1 M NaCl and the sensor membrane was conditioned overnight<sup>(35)</sup> as in Fig (1).

### **Electrode system and EMF measurements**

The electrochemical cell arrangement was:  
Ag, AgCl/ internal solution/sensor membrane/sample solution/SCE

Then the electrode was soaked in distilled water for about (20-30 s), rinsed several times with distilled water and wiped.

The electrode was stored in 0.1 M ZnO and 0.1 M NaCl when not in use.

All experiments were performed at 25 °C.

### **The result and discussion :-**

#### **Optimization**

In figure (2), the Ion-selective electrode exhibited a linear response activity  $\text{Zn}^{2+}$  ions within the concentration range of  $1.9 \times 10^{-2} - 4.0 \times 10^{-4}$  with slope of  $26.50 \pm 2 \text{ mV/decade}^{-1}$  that which is based on Di-n-octyl phenyl phosphonate as a solvent plasticizer and Di Benzo -18- crown -6 as a carrier which devoted for Ion -selective electrode based on hydrogen-bonding interaction between host and guest molecules<sup>(35-36)</sup>.

#### **The effect of internal filling solutions**

The performance of the membrane electrode in relation to the variation in concentration of internal solution (ZnO+NaCl) was explored ( $1.0 \times 10^{-3} - 5.0 \times 10^{-2}$ ) M

and the potential response of the  $\text{Zn}^{+2}$  Ion-selective electrode was obtained. It was found that variation of the concentration of the internal solution does not cause any significant difference in the potential response except for an expected change in the concentration of internal solution between ( $5.0 \times 10^{-3} - 1.0 \times 10^{-5}$ ) M

The optimum equilibration time for the membrane sensor in the presence of ( $1.0 \times 10^{-2}$ ) M  $\text{Zn}^{+2}$  was 24 h, after which it would generate a stable potential in contact with Zinc ions different samples.

### pH dependence of the electrode

pH dependence was examined to determine the effective pH range for the electrode using DB18C6.

The pH of the solution was adjusted by adding an appropriate amount of dilute hydrochloric acid or sodium hydroxide solution.

The electrode response was independent of pH over a pH range of (2.5 - 6.5). The decrease in potential above pH (6.5) was attributable to an increase in the concentration of un protonated. The decrease in potential below (2.5) may be due to protonation of the crown ether in the membrane phase, resulting in a loss of the ability to complex with Zinc ions.

Therefore, crown ethers losing the ability for binding with Zinc ions<sup>(36)</sup>.

### The effect of solvent mediators

In figure (3), the effect of solvent mediators on response of membrane based of crown ether was examined. We tested DOPP (Di-n-octyl phenyl phosphonate) & TBP (Tri-n-butyl phosphate) as the solvent mediator.

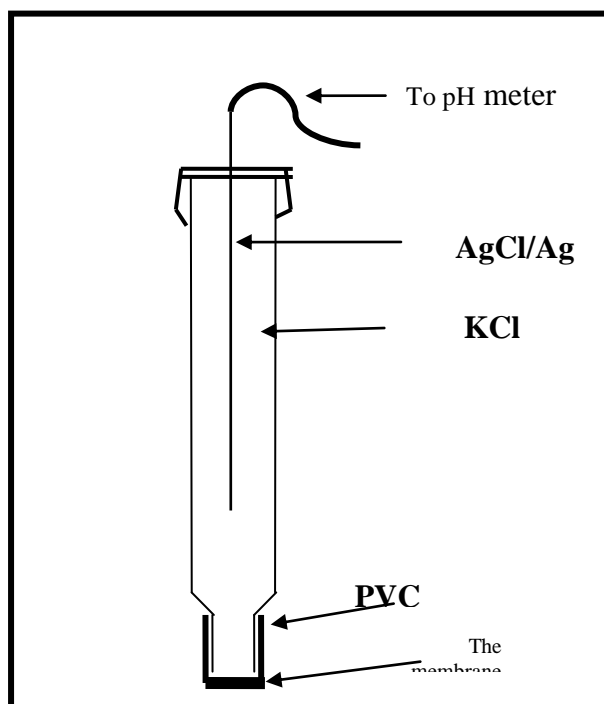
Therefore the solvent mediator interacts strongly with DOPP and  $Zn^{2+}$  ions by hydrogen bonding with the negatively polarized oxygen atom of the phosphoryl ( $P=O$ ) group of the phosphate ester.

Therefore, the role of the ionophore was diminished in the presence of a large amount of this solvent mediator<sup>(37)</sup>. It has been shown that plasticizers and also organic additives can effect the Ion selectivities of PVC membrane ion-selective electrodes<sup>(38-39-40)</sup>.

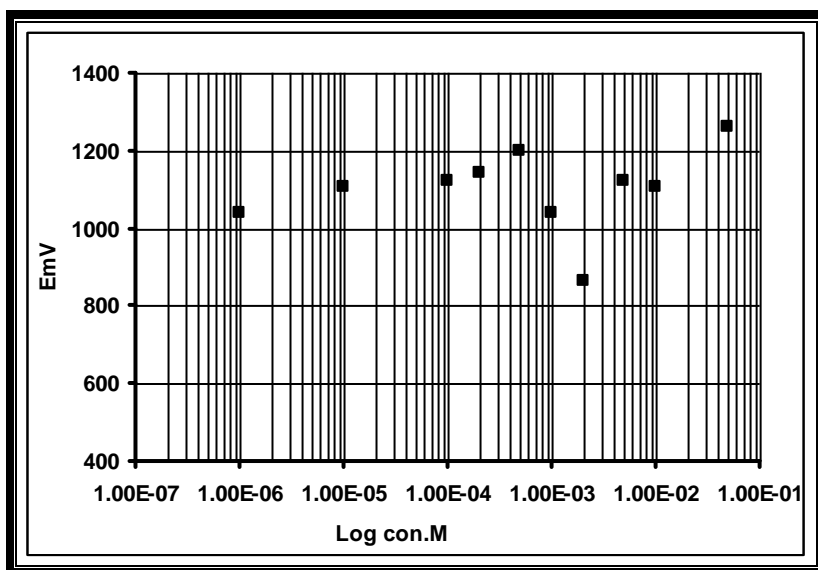
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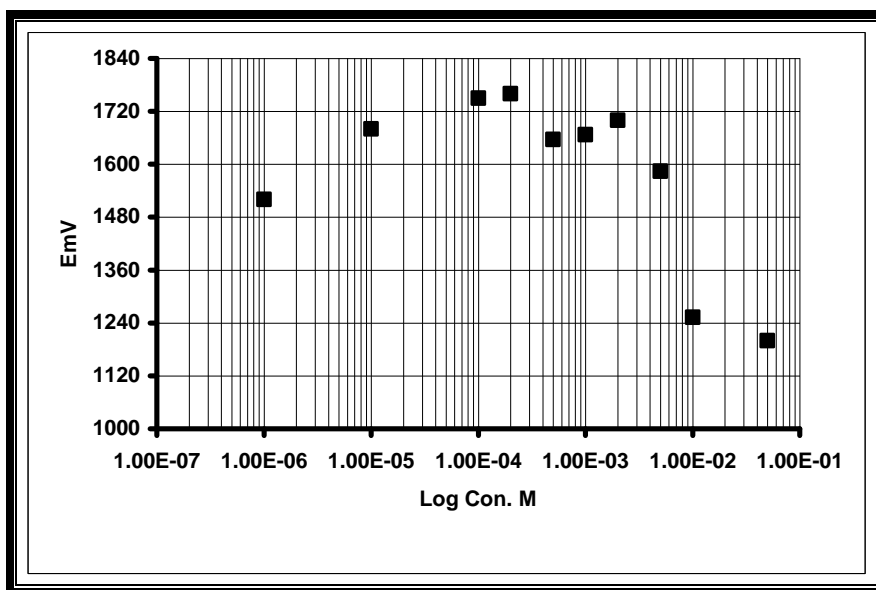
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**Fig (1)The electrode set up**



**Fig (2) Calibration curve of electrode based on DB18C6 and DOPP**



**Fig (3) Calibration curve of electrode based on DB18C6 and TBP**

## دور المدنات على خصائص غشاء قطب الزنك الانتقائي المعتمد على داي بنزو – ١٨ – كراون ٦

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### الخلاصة :-

تم اختبار أقطاب الإنتقاء الإيوني لإيونات الزنك لإغشية البولي فنيل كلورايد بإستعمال ملدنين وهما

DOPP(Di-n-octylphenyle phosphonate) and TBP (Tri-n-butyl phosphate).  
كناقل والمذيب الملدن Di Benzo18-crown-6 وأعطى القطب المعتمد على الأثير التاجي

إستجابة نيرنستية بميل DOPP(Di-n-octylphenyle phosphonate)

وطبقت  $1.9 \times 10^{-2} - 4.0 \times 10^{-4}$  وبمدى تراكيز  $26.50 \pm 2mV$  نيرنستي  
ومن جهة أخرى (2.5-6.5) يتراوح بين pH الطريقة لقياس أيونات الزنك في النماذج وبمدى  
tri-n-butyl كانت هناك إستجابة غير نيرنستية لغشاء القطب عند إستعمال المذيب الملدن  
. وتم توضيح مالمادة الملدنة من دور كبير وأثر في الانتقائية في أغشية البولي phosphate  
فنيل كلورايد لأقطاب الإنتقاء الإيوني.