1. Introduction

1-1. ***History: -***

During the period (1900-1930), four aspects of electrochemistry arose, grew, and matured. First the design of electrodes (half cell), Second, the use of these cells without electrolyte junctions to calculate thermodynamic properties captured the interest of scientist. The third topic was perturbation of cell with small current. Transport studies were formulated using dc or ac through regions of uniform electrolyte, which were well isolated from the working electrodes, and transfer numbers were determined. The fourth and most important electrochemical lesson learned was connection between the space charge, and capacitance of the phase boundary between solid conductors and electrolyte solutions [1].

Progress in ion-selective electrodes (ISE) development has occurred rapidly in the past 35 years, with promising innovations still on the horizon [2].

Ross and Frant [3] were the founding fathers of ISE's. The calcium and fluoride ISEs they developed in 1960 were the big bang that started a new era in potentiometric analysis, Kolthof and Sanderes made the first silver halide disk electrode in 1937 [4]. The idea to incorporate all membrane ingredients into **PVC** matrix came from the work of Bloch and Shatkay in 1967. The most important procedure for combining, casting, drying and mounting **PVC** sensor membrane was developed by Thomas and Moody in 1970 [5].

1-2. *Ion-selective electrode (ISE)*

Chemical sensors are miniaturized analytical devise, which can deliver real-time and on-line information on the prescience of specific compound or ions in complex samples. Usually an analyte recognition process takes place followed by the conversion of chemical information into electrical or optical signal. Ion-selective electrodes (ISE) are one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring. The principle of ion-selective electrodes operation is quite well investigated and understood [6].

An ion-selective membrane is the key component of all potentiometric ion sensors. It establishes the preference with which the sensor responds to the analyte in the presence of various interfering ions from the sample [7].

Since some selective chemistry take place at the surface of the electrode producing an internal potential. Species recognition is achieved with a potentiometric chemical sensor through a chemical equilibrium reaction at the sensor surface [8]. Thus, the surface must contain a component which will react chemically and reversibly with the analyte. This is achieved by using ion selective membranes which make up the sensor surface.

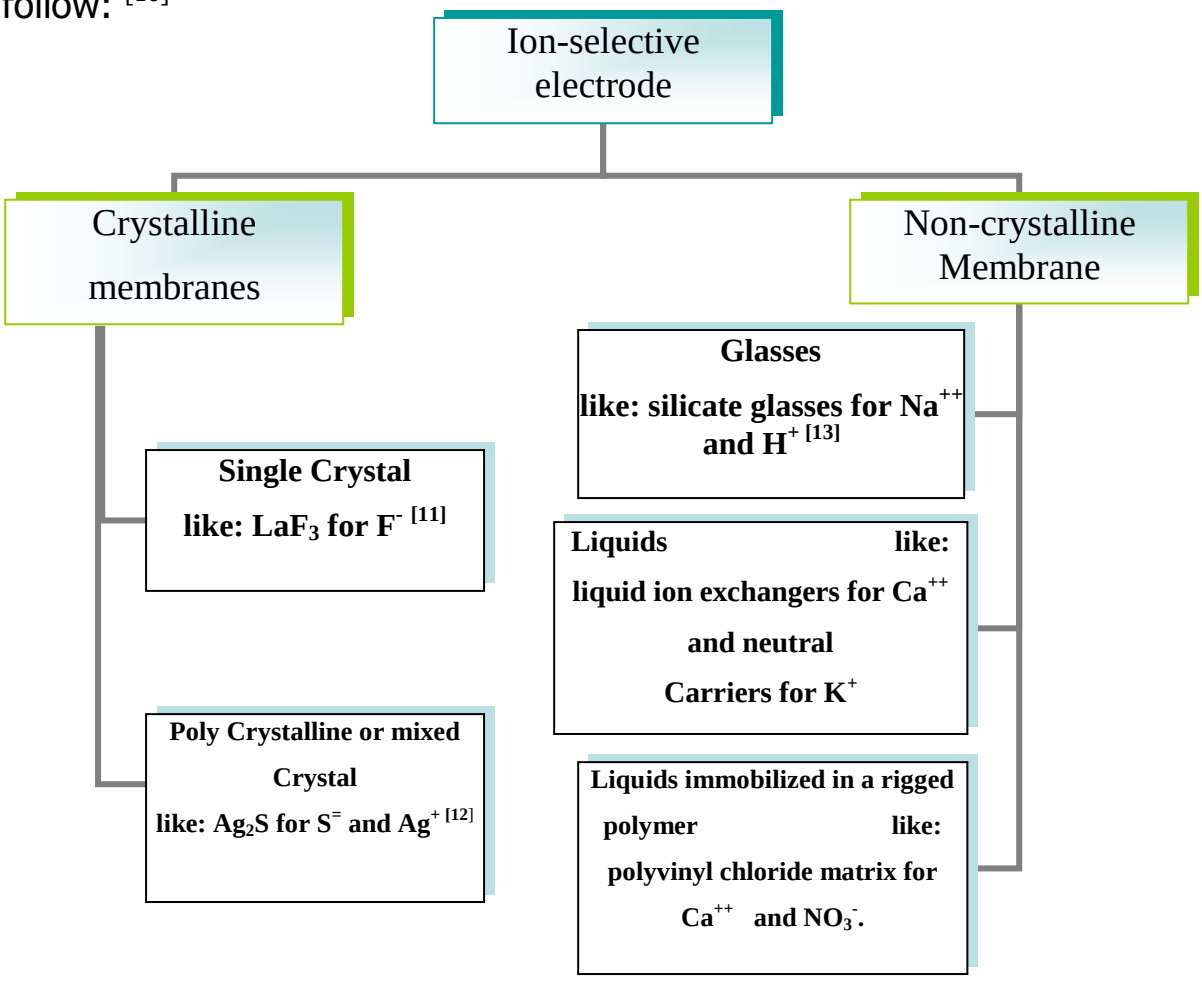
Ion selective electrodes which use such membrane were often referred to as being specific for a particular ion [9]. The term 'specific' implies that the electrode does not respond to additional ions. Since no electrode is truly specific for one ion, the term 'ion-selective' is recommended as more appropriate. 'Selective ion-

sensitive electrode' is a little-used term to describe an ion-selective electrode. 'Principal' or 'primary' ions are those which an electrode is designed to measure. It is never certain that the 'principal' ion is most sensitively measured.

1-2-1. *Classification of ion-selective electrodes:*

Ion-selective electrodes fall into two main categories; those that are consist of crystalline membrane and those that are applied to the non-crystalline membrane. The former are often called ***ion-selective*** or ***p-ion electrodes***. The term p-ion is derived from the way the data from these electrodes are usually reported, that is, as p-function such as pH, pCa, pNO_3.

Thus the ion selective electrodes could classified as follow: [10]



1-2-2.*PVC-Membrane electrode:*

The considerable interest in ion-selective electrode boosted the development of liquid ion-exchanger membrane and soon led to a new range of PVC matrix membrane electrodes [14]. The experiments shows that organic liquid of the liquid membrane ion-selective electrode could be immobilized into poly(vinyl chloride) to produce a polymer film with sensing properties as good as, if not better than, the liquid membrane itself. This is possible because the reagents and organic liquids used for preparing the liquid membrane are, in general, excellent plasticizers for PVC. Such plasticizers lower the glass transition temperature of PVC and produce homogenous and flexible films with good mechanical stability.

A general 'rule' of thumb is that PVC-based polymer membranes for potentiometric sensors should contain about 70% by weight plasticizer and 30% PVC. The amount of ionophore needed is only about 1% and is included in the amount of plasticizer [5].

PVC-based sensor-membranes contain a reagent dissolved in a suitable solvent which selectively binds with the ion of interests. Such a reagent is commonly referred to as an ionophore. In many ways polymer membranes can still be thought of as highly viscous liquid membranes and are sometimes referred to as 'gelled' liquid membrane' or 'entangled' liquid membrane. In any event, the underlying principles of the way they function are essentially the same. These polymer membranes, generally, have a fairly high electrical resistance (in order of 1MΩ) but must

conduct charge to function and, presumably, the charge carrier is the ionophore/ion complex moving within liquid channels in the membrane.

1-2-2-a. ***Membrane potential*** [15]:

The membrane potential is the electrical potential arising across a charged membrane when it separate two solutions containing the same ion, at different activities, it's magnitude depends on the difference in activities of the ions. The membrane potential includes both the diffusion potential within the membrane and the phase boundary potentials [15].

Electrode membranes have the property of rapidly establishing ion-exchange equilibrium across the membrane/solution interface. Conducting through the membrane may be ionic and/or electronic process [8].

Membrane potential may be regarded as combinations of interfacial potential terms with inter diffusional terms arising from the different mobilities of the ion in the membrane. Practically, the membrane potential is obtained from the measurement of the electromotive force of a complete electrochemical cell.

Consider a cell consisting of an ion-selective electrode, a reference electrode and a voltmeter with high input impedance to measure the e.m.f. response. The e.m.f., E, of cell is the sum of various junction potentials.

Except for the potential of the membrane (E_M), which depends on the nature of the test solution, the remaining potentials may be taken as constant, although some of the

junction potential, particularly those of the reference electrode can be troublesome.

$$E = \text{Constant} + E_M \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1\text{-}1)$$

The response of ISE, E_M, to determine certain ion (X) is represented by the ***Nernst*** equation which gives the electromotive force of the cell [15]

$$E = \text{Constant} \pm 2.303\,(RT/zF) \log a_x \quad \ldots\ldots\ldots \quad (1\text{-}2)$$

Where

- E is the potential developed by the cell.

  The Constant term depends on the junction potentials of the cell except that of membrane, the standard potential corresponding to E_M and the reference electrode system used including the liquid-liquid junction potential E_J
- 2.303 (RT/zF) is the ***Nernst*** factor with a value of 59.16 mV at 25^{o}C for monovalent ion
- a_X is the activity of the ion X in the sample solution
- z is the ion charge including sign format being positive for cation and negative for anion.

It is clear that the functional potential of any ISE depends on a number of factors including potential activity, responses selectivity in the presence of various interferants, operative pH range, response time, temperature and operative life [15]. The ideal membrane would sense one species only. All made up membranes

are not ideal showing only a higher selectivity toward one ion over the other.

1-2-2-b.*phase boundary potential:*

Since the membrane is usually interposed between the sample and an inner reference electrolyte, it is common to divide the membrane potential into three separate potentials contributions, namely the phase boundary potentials at both interfaces and diffusion potential within the ion selective membrane [16,17,18]. The potential at the membrane/inner filling solution interface can usually be assumed to be independent of the sample. The diffusion potential within the membrane becomes significant if considerable concentration gradients of ions with different mobilities arise in the membrane.

Recently, various pieces of experimental evidence have, however, been collected which show that the diffusion potential is negligible in most cases of practical relevance[19,20,21] and that the cation perm-selectivity of PVC-based membrane without additives can be explained by the presence of anionic impurities from the polymer matrix [22,23]. As it turns out, the phase boundary potential model can be used to describe the response of carrier-based ion-selective electrodes very accurately.

For ion-selective electrodes, the membrane internal diffusion potential is zero if no ion concentration gradients occur. This is often the case for membrane that shows a Nernstian response. For the sake of simplicity, diffusion potential are treated as secondary effects, in other cases are neglected, therefore it can be postulated

$$E_M = E_{Const} + E_{PB} \text{..... (1-3)}$$

Where E_{PB} is the phase boundary potential at the membrane-sample interface, which can be derived from basic thermodynamical considerations.

It is evident that the composition of the surface layer of the membrane contacting the sample must be kept constant in order to obtain an exact Nernstian response of the electrode [24]. Only within the extremely thin charge separation layer at the interfaces, were electro-neutrality dose not hold, sample-dependent changes in the concentrations of the complex and ionophore and ionic sites allowed to occur [24].Nevertheless, the exact structure of this space charge region is not really relevant to the sensor response.

While the perm-selectivity of the membrane is guaranteed by its ion-exchange properties and its hydrophobicity, which prohibits substantial co-extraction of counter ions, it is the selective complexation of the analyte ion by legand, the so-called ion carrier or ionophore, in the organic phase that ensure that the membrane response selectively to the target ion within a complicated sample matrix [25]. As shown in figure 1-1; a classification of such selective legands based on their charge type. Since the widely used uncharged carriers are neutral when uncomplexed and the complexes have the same charge as the analyte ion, the respective membrane require the additional incorporation of lipophilic ions of the opposite charge to ensure premselectivity.

Since poly (vinyl chloride) as membrane matrix already contains ionic impurities with cation-exchanger properties, neutral carrier-based cation-selective membranes are usually functional without the incorporation of anionic sites [26]. However, their selectivity and lifetime behavior is often not optimal. To a second important group of ionophores belong compounds that are electrically charged when uncomplexed and neutral when it legated to the analyte ion (figure 1-1). With charged carriers perm-selectivity can be achieved without the incorporation of additional ionic sites.

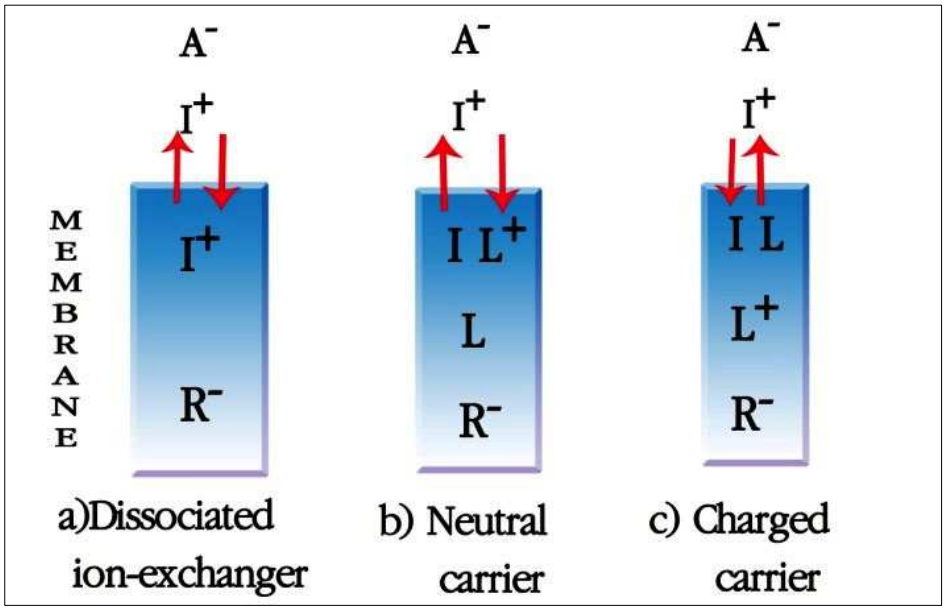


Figure (1-1): classification of ion-selective membrane (for cationic analyses)

1-2-3.*Cell design:*

The PVC membrane electrode cell is similar to the typical glass electrode or any solid state electrode cell. The potential of the electrode is registered with respect to reference electrode such as saturated calomel electrode (SCE). The cell [27] consists of:

Ag/AgCl| internal filling solution | ion-selective membrane| sample solution | KCl (sat.), Hg_2Cl_2, Hg

Cell design according to the basic rule of designing of electrolytical cells, with a condition that the current passed through the electrolytical cell equals zero, as showed in fig(1-2) [28]

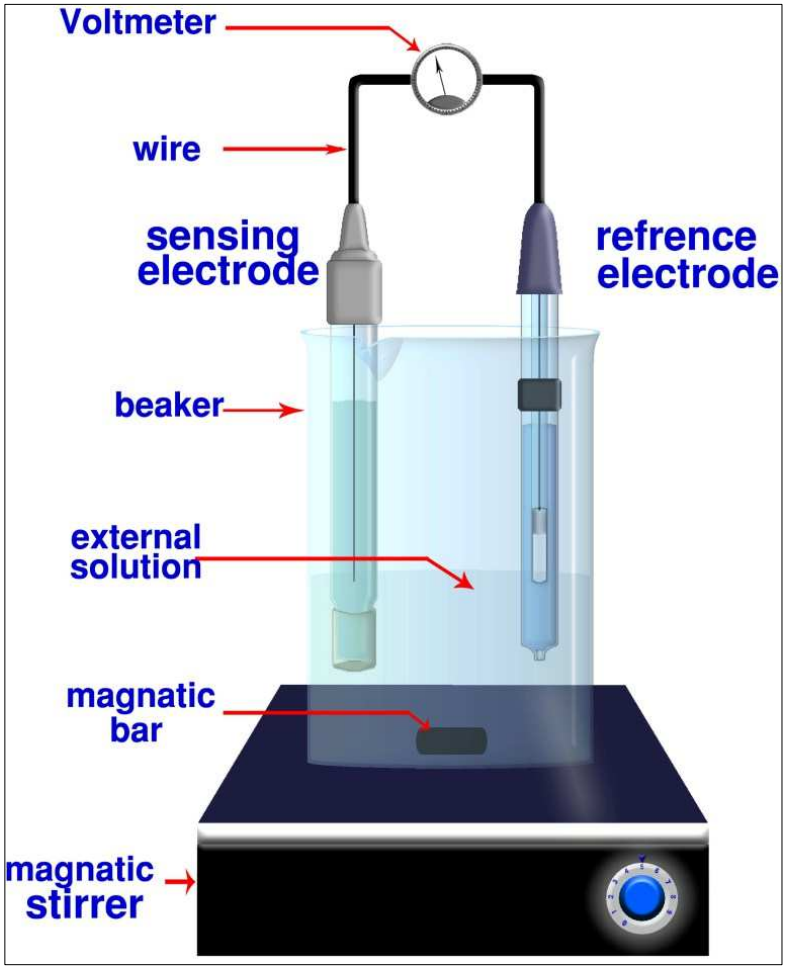
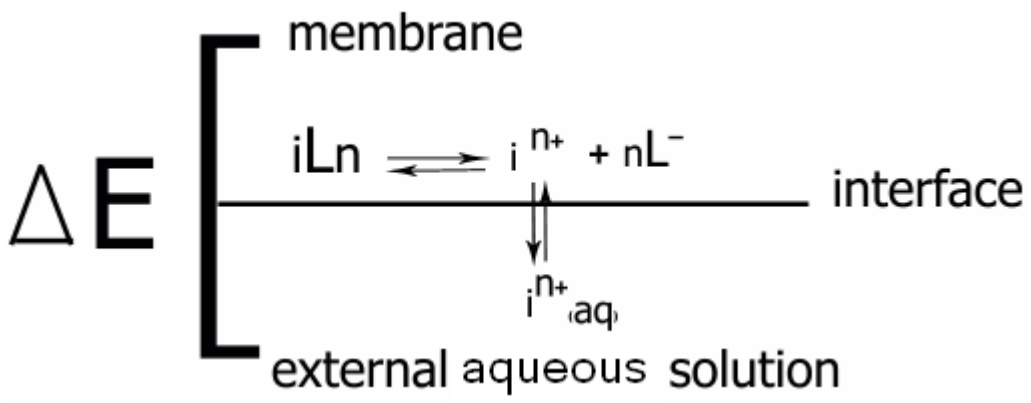


Figure (1-2): basic component of ion-selective electrode cell

The exchange that happened between the internal and external solution across the membrane depends on ionic exchange and the active ionophore which used in the membrane. The mechanism below shows the ionic exchange process to a cation through a membrane:



1-2-4.***Response:***

Long life time, good selectivity, and rapid response are important features associated with the response behavior of ISEs. The life time of ISEs are normally longer than the corresponding liquid-membrane electrode and range from 8 to 14 day for potassium electrodes [٢٩], to several months for some calcium electrodes [5], in which the slope of the calibration curve do not change significantly with time, although a decline in slope value indicates that the electrode is approaching the end of its life.

the PVC corning nitrate-exchanger electrode has been reported to give a positive drift of about 10 mV over a period of 11 weeks [30]. While the PVC uranyl electrode showed a negative drift of about 10mV after 1 month [٣١] of continuous operation.

The equilibrium static and dynamic response time may be conveniently defined as the period required attaining a fixed percentage, i.e. 50, 90, and 95% of the final steady potential response. Although the time required achieving a steady e.m.f. response within ±1mV of the equilibrium value is also recommended [٣٢]. This time was found to vary depending on critical factors such as the nature, concentration and temperature of the sample, as well as the nature and method of fabrication of the sensor material, the range and operational history of a particular electrode. The dynamic response time refers to the time required to equilibrate a conditioned electrode system after rapidly injecting a known level of an ion, or just water into the system. The static response time has to take the time for the electrodes (indicator and reference) to condition and to reach equilibrium after transferring from one solution to another. Static response times are usually longer than dynamic response times [33].

1-2-5.*Selectivity and interference:*

An interferants is any species, other than the ion being measured whose presence in the sample affects the measured potential of the cell [32].

The common effect of an interfering ion is to reduce the linear calibration range of the electrode. Ion-selective electrodes respond selectively but not specifically to ions for which they are designed, that is, no ion-selective electrode responds exclusively to ion being measured [15].

The degree of selectivity of the electrode for the primary ion, A, with respect to an interferent, B, is expressed by the potentiometric selectivity coefficient $K^{pot.}_{A,B}$, as follows [34]:

$$E = E^{o} \pm 2.303 \frac{RT}{z_A F} \log \left[a_A + \sum K^{pot.}_{A,B} \cdot a_B^{z_A/z_B} \right] \quad \ldots\ldots\ldots\ldots (1\text{-}4)$$

Where z_A and z_B are the charges of ion A and B, respectively.

E^o is the standard potential of the electrode.

This coefficient can be determined using either separate solutions or mixed solutions method, containing both the analyte A, and the interfering B ions [35].

The first method is based on two e.m.f. measurements one for solution of A ion at activity $a_A(E_1)$ and the other for solution of B ion at activity $a_B(E_2)$. The difference between two measurements is equal to [28]:

$$K^{pot.}_{A,B} = \frac{z_A F}{2.303\ RT} [\ E_2 - E_1] \quad \ldots\ldots\ldots\ldots\ldots\ldots (1\text{-}5)$$

and K^{pot} then equal to:

$$K^{pot.}_{A,B} = \frac{a_A}{a_B^{(z_A / z_B)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1\text{-}6)$$

In the mixed solution method, the e.m.f.'s are measured for solution containing a fixed concentration of interfering ion in a varied activities of analyte ion. Usually the value of $K^{pot.}_{A,B}$ is calculated by the above equation.

1-2-6.*Characterization of an ion selective electrode:*

The properties of ion selective electrode are characterized by parameters like:

- *Slope* of the linear part of the measurement calibration curve of the electrode. The theoretical value according to the Nernst equation is: 59.16 [mV/log (ax)] at 298K for a single charge ion or 59.16/2 = 29.58 [mV/decade] (25-30 [mV per decade] for double charged ion) however, in certain applications the value of the electrode slope is not critical and its value dose not exclude its usefulness.
- *Detection limit* according to the IUPAC recommendation the detection limit is defined by the cross-section of the two extrapolated linear parts of the ion-selective calibration curve [36]. In practice, detection limit on the order of 10^{-4}-10^{-6}M is reported for most of ion selective electrodes. The observed detection limit is often governed by the presence of other interfering ions or impurities. If, for example, metal buffers are used to eliminate the effects which lead to the contamination of very dilute solutions it is possible to enhance the detection limit down to 10^{-5}M [37].
- *Range of linear response*: the measuring range of ISEs is defined as the activity ratio of upper and lower detection limit and approximately corresponds to the Nernst equation. Or simply, at high and very low target ion activities there are deviation from linearity. Typically, the

electrode calibration curve exhibit linear response range between 10^{-1}M and 10^{-5}M.

- *Response time* in earlier IUPAC recommendations, it was defined as the time between instant at which the ion-selective electrode and reference electrode are dipped in the sample solution [38] ;or ,the time at which the ion concentration in a solution is changed on contact with ISE and a reference electrode. The first instant at which the potential of the cell becomes equal to its steady-state value within 1[mV] or has reached 90% of the final value (in certain cases also 63% or 95%). This definition can be extended to consider the drift of the system. In this case, is defined as the one at which EMF/time slope becomes equal to a limiting value. However, it should be pointed out that a single time constant dose not describe the form of the electrode response function. Moreover, in many investigations response time of the overall measuring system is determined, which has influence on the response time of the ISE.

1-2-7.*Potintiomitric measurements:*

Different methods can be applied to perform analyses using ISE. The method used depends upon many parameters such as the composition of the sample, the available time to perform the analyses and the required accuracy and precision for such analyses. These methods are grouped into direct reading, standard addition and potentiometric titrations [39].

1-2-7-a. *Direct potentiometric method:*

Direct measurement is the straightforward method to obtain quantitative results [40]. A calibration graph is constructed by measuring the equilibrium cell potential for several solutions of known concentrations. Then the potential of the sample is measured at the same conditions, and the concentration is read directly from the graph. This method is extremely rapid, enabling measurements to be complete in two or three minutes. This method is suitable for the analyses of all samples in which the analyte of interest is present in the free uncomplexed states.

1-2-7-b.*Standard addition method:*

In standard addition method, the electrode potential of known volume of analyte is measured, then very small volume of standard solution of the analyte added to the solution of interest, and the potential developed is measured. This technique is based on the assumption that activity coefficient of the analyte is equal before and after the addition, and the degree of complexation of

the analyte with the added standard also constant through out the measurements [41].

1-2-7-c. *Potentiometric titration method:*

Potentiometric titration methods have been also used for the evaluation of the performance of ISE [42]. The sample is titrated with a suitable titrant and the increase or decrease in titrant activity is followed with an ion-selective electrode, and Gran plot then constructed to locate the equivalence point.

Gran's plot: were devised by Gran [42] in 1952 as a way of linearizing the data obtained in potentiometric titration and thus easily and precisely locating the equivalence points of titrations. The plots are used in work with ion-selective electrode, for this original purpose and also for linearizing data from multiple standard addition procedures. The technique may be applied to both complexometric and precipitation titrations.

The theory associated with this plot is straightforward. The response of an ion-selective electrode to monovalent cation, X, in solutions free from interferents, may be represented by the Nernst equation:

$$E = E^{o} + S \log a_x \quad \text{.....} \quad (1\text{-}7)$$

Where S is the slope of the electrode response, rearrangement of eq. (1-7) gives

$$\text{Antilog } (E/S) = \text{constant} \cdot a_x \quad \text{.....} \quad (1\text{-}8)$$

Where the constant is antilog (E^{o}/S). Thus, antilog (E/S) is proportional to a_x and may be plotted, as a measure of a_x against the volume of titrant added to give a linear plot. A

particularly valuable feature of the plot is that it allows the line obtained from the titration data to be extrapolated back to an intercept on the volume of titrant axis at $a_x = 0$: thus, the equivalence point of potentiometric titrations may be obtained.

1-2-8.*Sources of Error:*

- ***Diffusion*** **–**It has been pointed out that difference in the rates of diffusion of ions based on size can lead to some error [43]. In the example of sodium iodide, sodium diffuses across the junction at a given rate. Iodide moves much slower due to its larger size. This difference creates an additional potential resulting in error. To compensate for this type of error it is important that a positive flow of filling solution move through the junction and that the junction not become clogged or fouled.
- ***Sample Ionic Strength*** **–** Covington [44] pointed out that the total ionic strength of a sample affects the activity coefficient and that it is important that this factor stay constant. In order to accomplish this; the addition of an ionic strength adjuster may be used. The ionic strength of the adjuster must be large, compared to that of the sample, such that variation between samples becomes small and the potential error is reduced [45].
- ***Temperature*** **-** It is important that temperature be controlled as the variation in this parameter can lead to significant measurement errors. A single degree (C) change in sample temperature can lead to measurement errors greater than 4% [46].

- ***pH*** **-** Some samples may require conversion of the analyte to one form by adjusting the pH of the solution (e.g. ammonia). Failure to adjust the pH in these instances can lead to significant measurement errors.
- ***Interferences*** **-** The background matrix can affect the accuracy of measurements taken using ISEs .Covington [44] has also pointed out that some interference may be eliminated by reacting the interfering ions prior to analysis.

1-3-1. ***Atenolol:***

Atenolol, (RS)-4-(2-hydroxy-3-isopropylaminopropoxy) phenylacetamide, $C_{14}H_{22}N_2O_3$ (Figure1-3), is a white powder with molecular weight of 266.3, it melts within (152-155 ^oC). It is sparingly soluble in water; soluble in absolute ethanol and methanol and practically insoluble in ether [47-51].

Atenolol is used commonly in the treatment of arterial hypertension, angina pectoris and cardiac arrhythmias [52]. Tenordin, an Atenolol tablet, is manufactured locally by the state company for Drug Industries and medical Appliance (Samara-IRAQ-SDI).

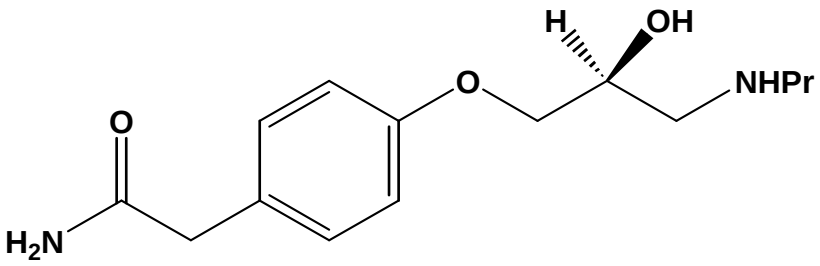


Figure (3-1): structure formula of atenolol

1-3-2.*Methods of atenolol determination:*

One of the most important ways used in Atenolol determination was Liquid chromatography (LC), which has been used for the determination of atenolol in plasma. The limit of detection was 0.015µg/mL [53]. The simultaneous determination of atenolol, metoprolol and oxperenolol, the diuretics amiloride, bendroflumethiazide, and the vasodilator hydralazine in pharmaceutical was also reported using LC method [54].

High performance liquid chromatography (HPLC) using fluorescence detector for analysis of atenolol in plasma and whole blood was described by Yee [55], at concentration levels as low as 20ng/mL. HPLC determination of atenolol in human serum has also been reported by Simons and Stewart [56], minimum delectability of the drug was estimated to be 0.02µg/mL. An assay of the orally administrated hypertension drugs (atenolol, amilodipine, nifidipine, nitrendipine, nimodipine and felodipine) has been described using HPLC [57].

Atenolol was determined also by gas chromatography GC in different biological samples using electron-capture detector. Concentrations as low as 0.01µg/mL in body fluid, 0.04 µg/mL in tissue [58], and 0.005 µg/mL in urine [59] were analyzed. GC determination of atenolol in plasma and urine was reported by Malbica and Monson [60] at Concentration of 0.02µg/mL. A rapid, specific GLC method has been used for the analysis of atenolol and

other agents such as propanolol and metoprolol. This method was sensitive to 0.01µg/mL of atenolol [61].

A fluorimetric determination of atenolol in plasma and urine by direct evaluation of thin-layer chromatography (TLC) was reported at concentration levels of 0.05 µg/mL [62]. A new simple, precise, accurate and rapid high performance thin layer chromatography (HPTLC) method have been developed for simultaneous determination of atenolol in pharmaceutical dosage forms. The percentage recoveries were 101.1% [63].

An indirect atomic absorption spectrometric method was undertaken to estimate atenolol in pharmaceutical preparation, based on its reaction with Cu^{+2} in alkaline medium [64].

Derivative spectrophotometry has been applied in the analysis of many pharmaceutical formulations [65,66]. It has proved particularly useful in eliminating matrix interferences [67]. A rapid, simple and accurate second derivative spectrophotometric method for the simultaneous determination of atenolol and nifedipine in dosage forms was developed by Umapathi et al.[68]. Fourth derivative spectrophotometric method for simultaneous determination of atenolol and chlorthalidone in a combination tablet form is described by Vetuschi and Rango [69]. This method was linear in the 5-60 and 5-30 $\mu g.mL^{-1}$ for atenolol and chlorthalidone respectively.

1-4. *Aim of the work:*

This project was aimed to construct and characterize several ion-selective electrodes for the potentiometric determination of atenolol. These electrodes utilize the solvent mediators or plasticizers, Di-octylphthalate (DOP), Di-butylphosphate (DBP), Tri-butyl phosphate (TBP) and o-nitrophenyloctylether (ONPOE). The constructed electrodes characteristic parameters that include linear range, slope, detection limit, lifetime and working pH range will be investigated.

The best combination of atenolol (ionophore), solvent mediator, and PVC matrix will be chosen. Potentiometric measurements including direct method, standard addition method and titration method will be studied.

3-1.Optimization of membrane composition:

In previous experimental investigations [72-74], it were found that kind of plasticizers selected can influence the response performance (such as slope, linear concentration range, detection limit, response time, etc.) of a PVC membrane ion-selective electrode, if other properties of the electrode, e.g. selectivity or the pH response are omitted. In this study, four plasticizers, DOP, DBP, TBP and ONPOE were used to examine the optimization of the membranes. The electro-active compound (A-PT) content of 1% of the composition was used, the conversion of atenolol into (A-PT) complex was confirmed using FTIR spectrum as shown in figure (3-1a and b):

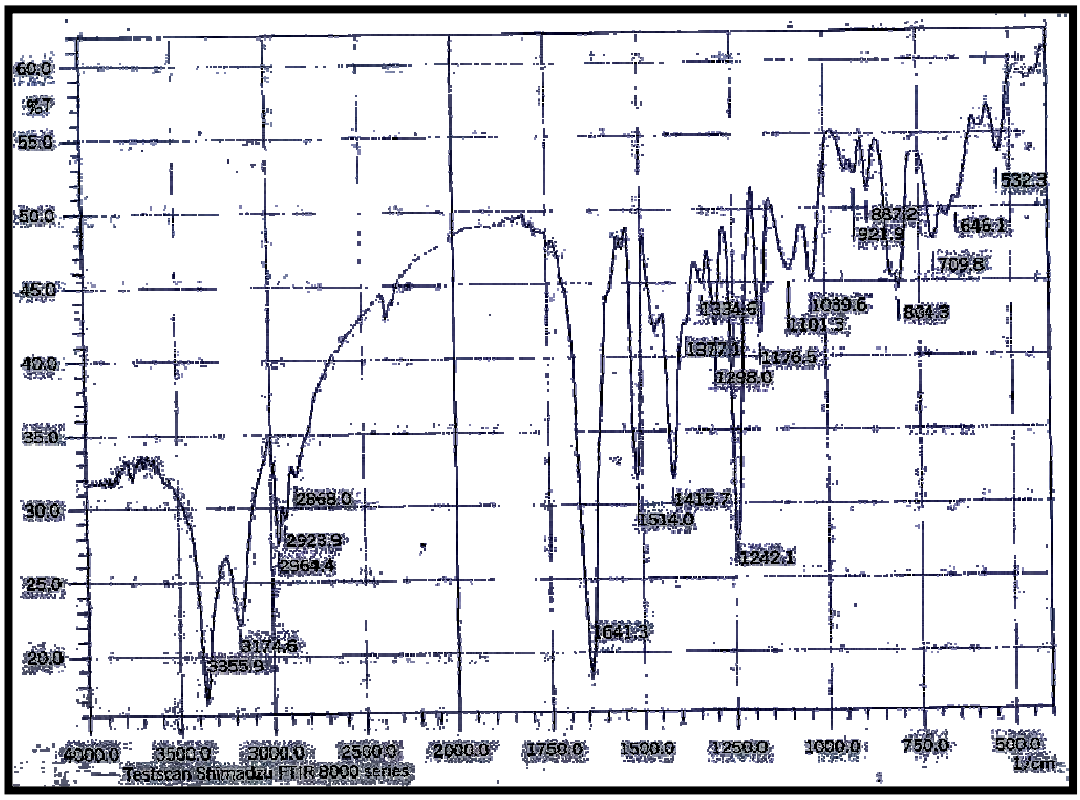


Figure (3-1a): FTIR spectrum of standard atenolol

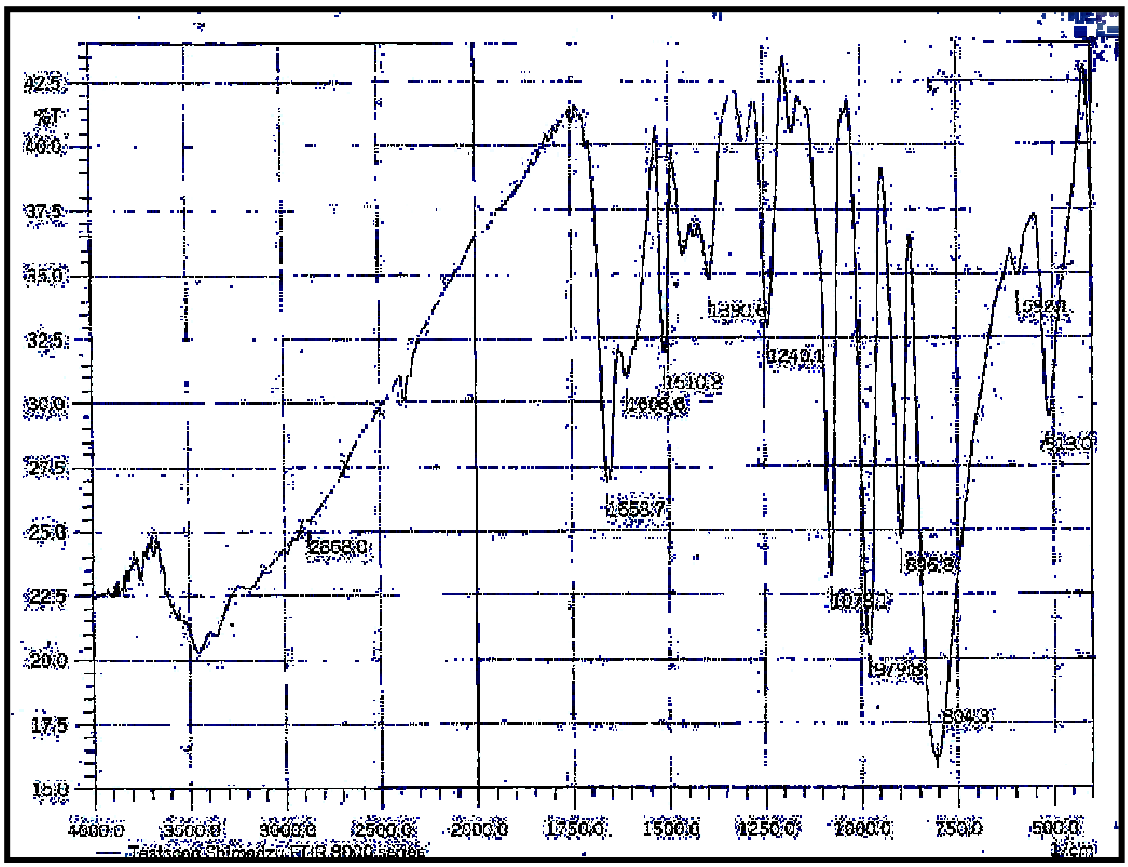


Figure (3-1b): FTIR spectrum of (A-PT) electro-active substance

The results obtained showed that the response performance of the electrodes prepared were rather different depending on the use of plasticizer and the electro-active compound. The e.m.f. values of these electrodes were plotted versus the calculated activity of atenolol ion on Orion 7-cycle semi-log graph paper. All membranes was soaked in $1x10^{-1}$M atenolol solution for 24hours in order to conditioning the membrane and calibrated every three days to determine the change in electrode parameters such as slope, detection limit and life time.

A. **Membrane I:**

First membrane was based on Di-butylphosphate (DBP) as a plasticizer; its calibration curve is shown in figure (3-2):

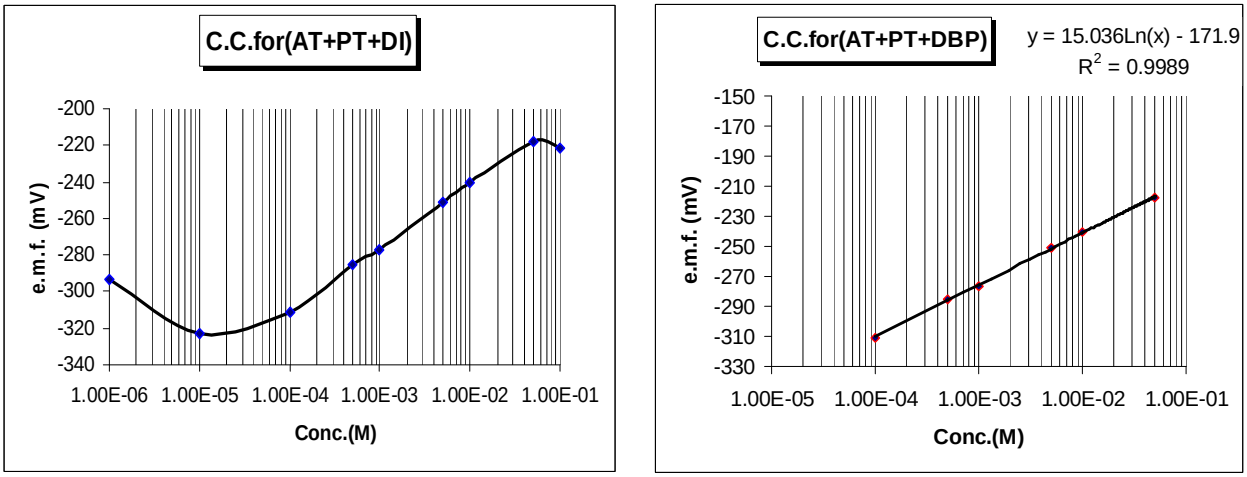


Figure (3-2): calibration curve of atenolol selective electrode containing (A-PT) ionophore and (DBP) as plasticizer

The potential response of the proposed electrode (I) at varying concentration of atenolol displayed wide linear range from $1x10^{-4}$M to $5x10^{-1}$M with slope of 34.63 mV per decade. The limit of detection was $1.1x10^{-5}$M and the lifetime was about 35 day.

B. **Membrane II:**

The second membrane was based on Tri-butylphosphate (TBP) as a plasticizer; the calibration curve for this electrode is shown in figure (3-3):

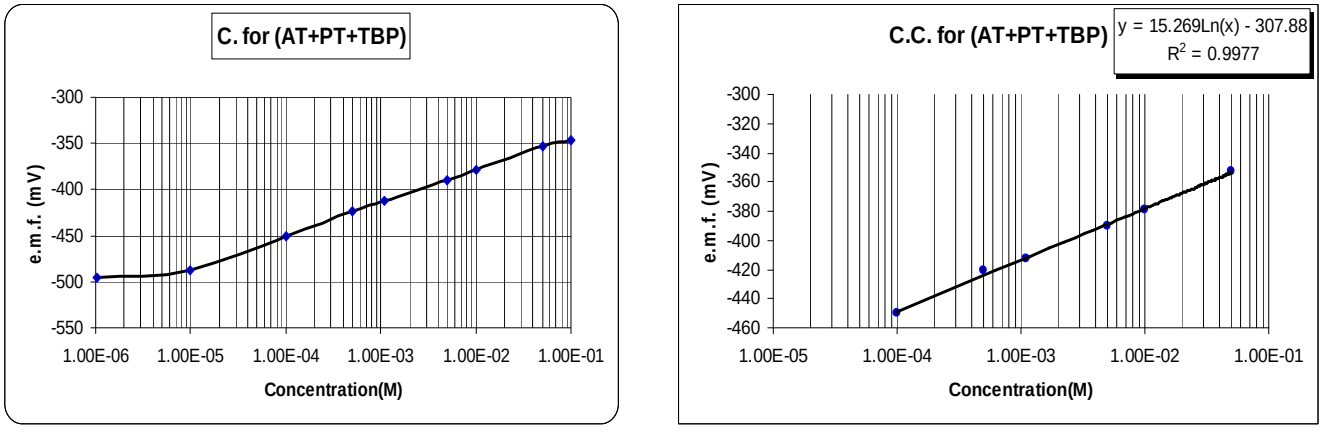


Figure (3-3): calibration curve of atenolol selective electrode containing (A-PT) ionophore and (TBP) as plasticizer

The potential response of the proposed electrode (II) at varying concentration of atenolol was displayed linear range from $1x10^{-4}$M to $5x10^{-2}$M with slope of 35.16 mV per decade. The limit of detection was $1.8x10^{-6}$M and the life time was about 45 day.

In both electrode I and II, the low slope value obtained may be attributed to the plasticizers used (TBP, DBP) which contained long alkyl group connected to phosphate groups, this may decreased the ion-exchange process between the electro-active compound (A-PT) and the external solution of atenolol, or may be attributed to the setric factor of the plasticizers (TBP, DBP) which decreased the bond strength with the electro-active compound.

C. **Membrane III:**

The Third membrane was based on O-nitrophenyloctylether (ONPOE) as a plasticizer, with calibration curve shown in figure (3-4):

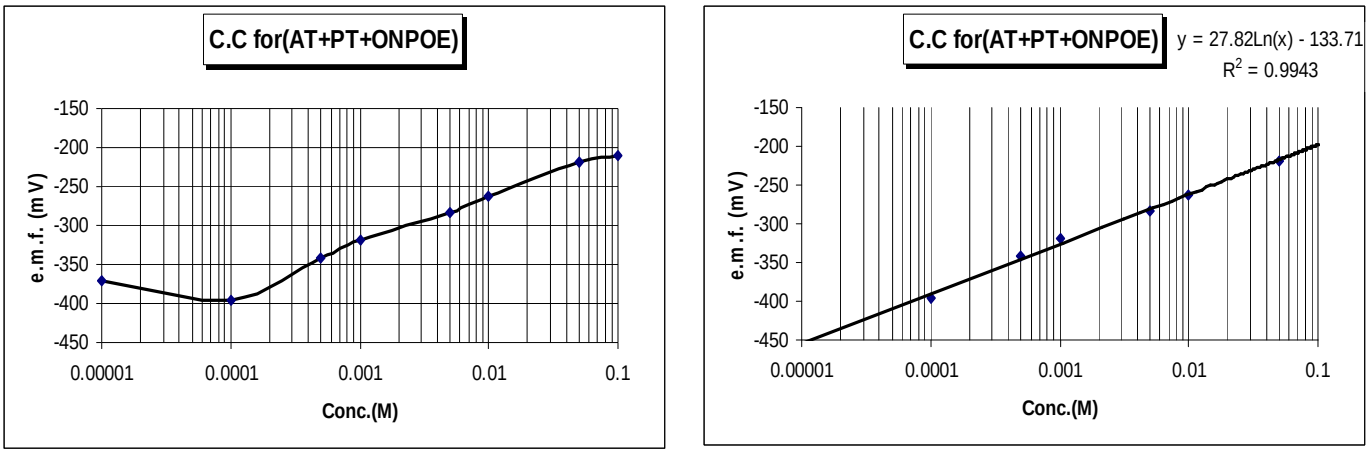


Figure (3-4): calibration curve of atenolol selective electrode containing (A-PT) ionophore and (ONPOE) as plasticizer

The potential response of the proposed electrode (III) at varying concentration of atenolol displayed linear range from $1x10^{-4}$M to $1x10^{-2}$M with a slope of 64.07 mV per decade. The limit of detection was $1.1x10^{-4}$M and the life time was about 48 hour. The electrode showed a relatively good response, however, the life time was too short, may be because of low viscosity (~11.44 cSt) of the plasticizer that allowed the plasticizer to leak out the membrane as a oily drops on the surface in a short time, and the electrode was no longer active.

D. **Membrane IV:**

The Fourth membrane was based on Di-octylphthalate (DOP) as a plasticizer; its calibration curve is shown in figure (3-5):

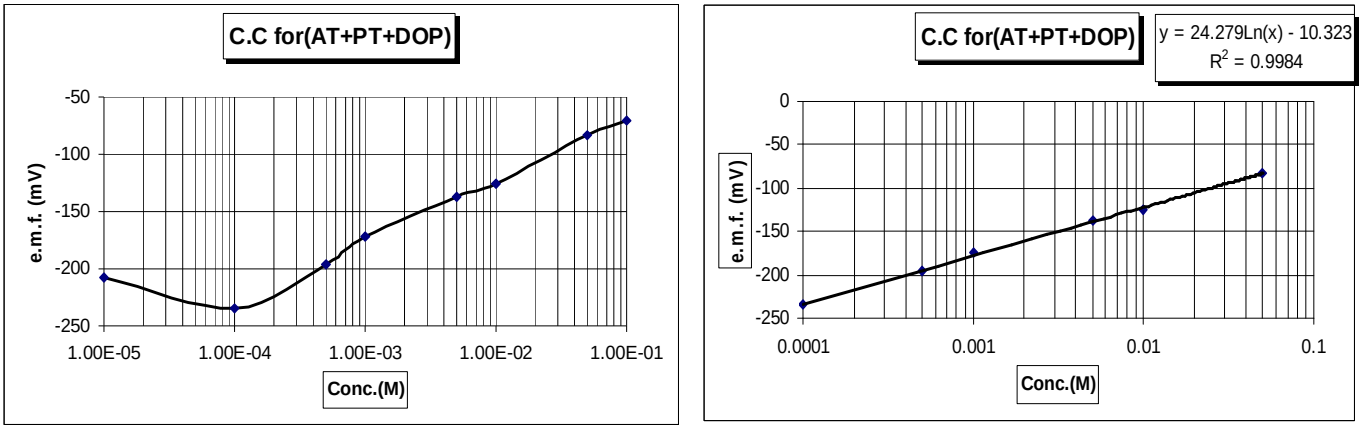


Figure (3-5): calibration curve of atenolol selective electrode containing (A-PT) ionophore and (DOP) as plasticizer

The potential response of the proposed electrode (IV) at varying concentration of atenolol displayed linear range from $1x10^{-4}$M to $5x10^{-2}$M with a Nernstian slope of 55.91 mV per decade and

correlation coefficient 0.9994. The limit of detection was $5x10^{-5}$M and the life time was about 90 day. This electrode showed a very good response in comparison with the other four electrodes, as shown in Table (3-1) that may be attributed to the compatibility of the plasticizer used to the electro-active compound from both structure and composition.

The stability of the four electrodes was monitored continuously at $1x10^{-3}$M of atenolol solution and evaluated for a period of 1 day; the standard deviation of potential drift obtained for 6 replicated measurements were ≤ (2,3,8 and 0.5) mV/day for membrane no.(I,II,III and IV) respectively (as listed in Table 3-1). This means that the repeatability of the potential response of the electrode IV (based on DOP) was relatively good. The response properties of the proposed electrode did not changed obviously after the use of electrode IV for about 90 days.

Table (3-1): standard deviation of potential drift of the electrodes

Membrane no.	Std. deviation of slope drift mV/decade
I	2
II	3
III	8
IV	0.5

Deviation from linearity at high concentrations ($5x10^{-2}$ M) was obtained, which may be due to liquid-junction potential. At

concentrations below ($1x10^{-4}$M), the curves start to deviate and non-linear response was obtained, this may be attributed to the dissociation of complex in the external solution. This phenomenon has also been reported in the literature for similar membrane electrodes [75].

The response characteristics of the electrode no. (I,II,III and IV) are summarized in Table (3-2), the concentration range of atenolol tested was $1.0x10^{-6}$M to $1.0x10^{-1}$M.

Table (3-2): response characteristic of the electrodes

Parameter	**Electrode number**			
	I	**II**	**III**	**IV**
plasticizer	DBP	TBP	ONPOE	DOP
Slope (mV/dec.)	34.63	35.16	64.07	55.91
Correlation coefficient	0.9994	0.9988	0.9971	0.9994
Linearity range (M)	$5x10^{-1}$-$1x10^{-4}$	$5x10^{-2}$-$1x10^{-4}$	$1X10^{-2}$-$1X10^{-4}$	$5x10^{-2}$-$1x10^{-4}$
Detection limit (M)	$1.1x10^{-5}$	$1.8x10^{-6}$	$1.1x10^{-4}$	$5x10^{-5}$
Potential drift (mV/day)	**2**	**3**	**8**	**0.5**
Life time	~35 day	~45 day	~2 days	~90 day

3-2.Effect of pH:

The effect of pH on the response of the electrodes was examined by measuring the potential variation in the *e.m.f.* over pH range of 1.0-11.5 for three different atenolol concentrations (10^{-4}, 10^{-3} and 10^{-1}) and the results are listed below:

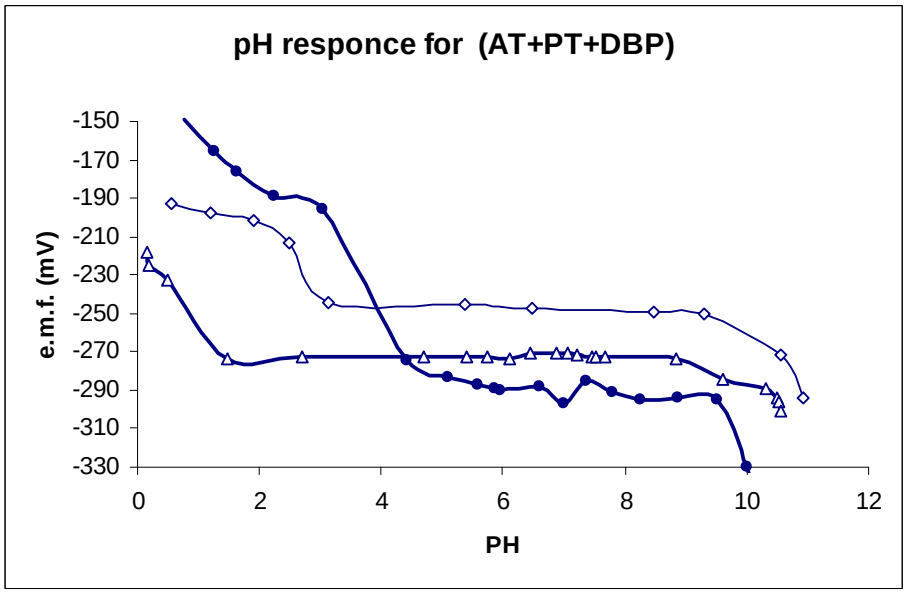


Figure (3-6): effect of pH on the potential of the 1st electrode (I). (◊=10^{-2}, Δ=10^{-3} and ●=10^{-4})M atenolol

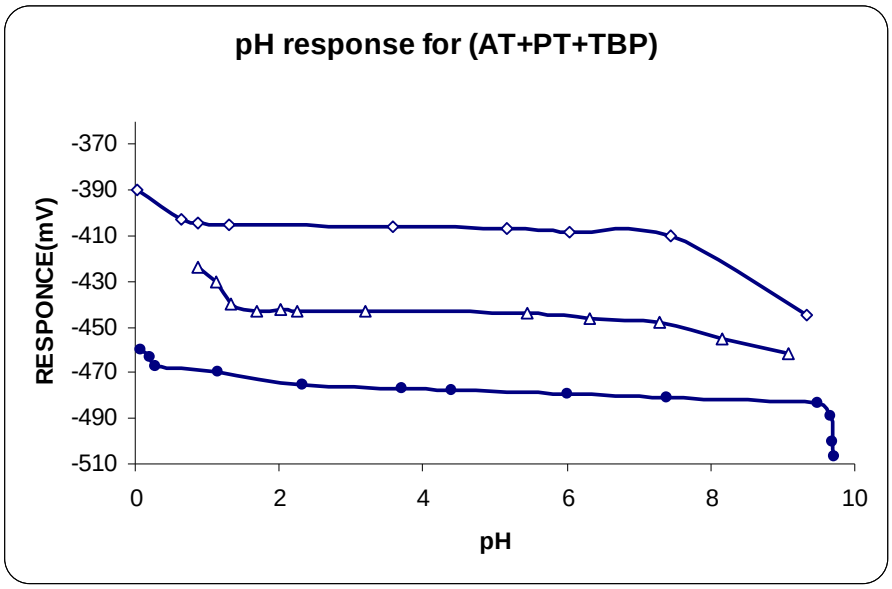


Figure (3-7): effect of pH on the potential of the2nd electrode (II). (◊=10^{-2}, Δ=10^{-3} and ●=10^{-4})M atenolol

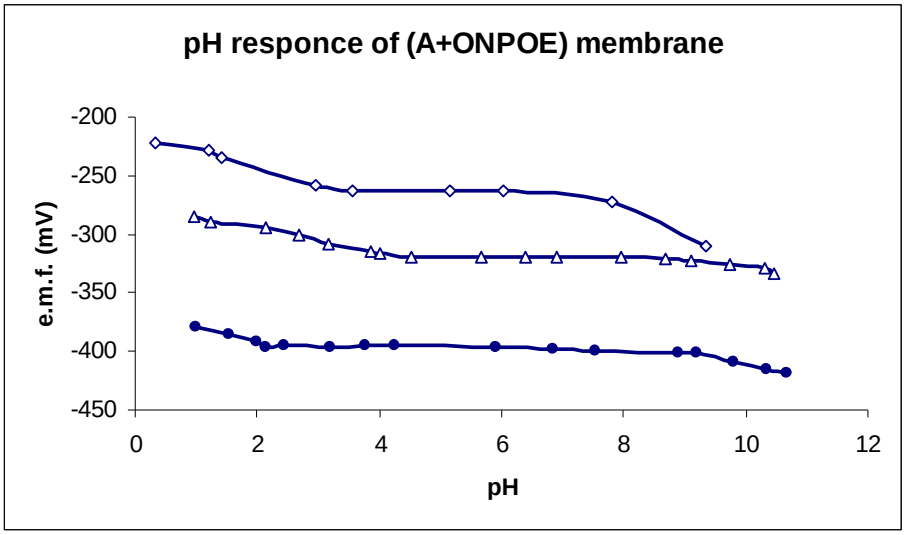


Figure (3-9): effect of pH on the potential of the 3rd electrode (III). (◊=10^{-2}, Δ=10^{-3} and ●=10^{-4})M atenolol

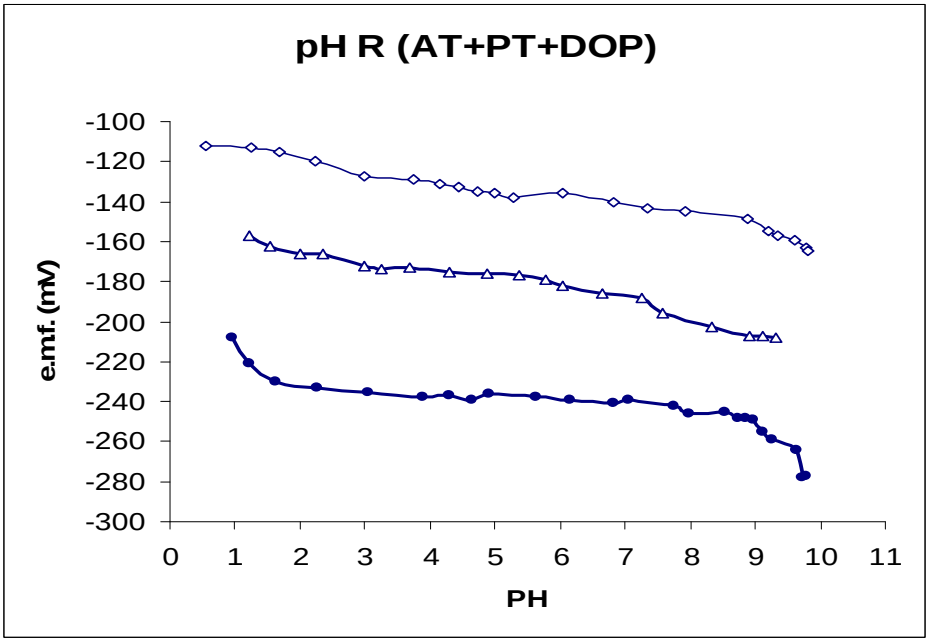


Figure (3-8): effect of pH on the potential of the 4th electrode (IV). (◊=10^{-2}, Δ=10^{-3} and ●=10^{-4})M atenolol

The pH was adjusted by introducing few drops of ammonia and hydrochloric acid solutions. As it can be seen; the potential remained nearly constant over a wide pH range. This implies that

the proposed electrodes can be used to measure a wide range of atenolol samples without pH adjustment. However, outside this range, the electrodes responses change drastically. That is, at pH values lower than 1.0, the electrodes responses has been increased rather irregularly. This may be due to that the electrodes responses to H^+ activities as well as analyte ions. The observed drifts at higher pH values could be due to some tungsten oxide or ammonium phosphates solutions formation. The working pH ranges for the electrodes are listed in Table (3-3) below:

Table (3-3): working pH ranges for electrodes (I,II ,III and IV)

Membrane No.	plasticizer	pH range		
		$1X10^{-2}$	$1X10^{-3}$	$1X10^{-4}$
I	DBP	3-9	2-9	4-9
II	TBP	1-7	2-7.5	1-9
III	ONPOE	3-6	3-6	2-8
IV	DOP	3-8	4-9	2-9

From the optimization and working pH results, it is very clear that the electrodes (III) and (IV) based on ONPOE and DOP plasticizers respectively, gives the best results, so, it has been chosen as the best combination of plasticizer and electro-active compound.

3-2.Response time

The response time for electrodes III and IV were prepared to reach potential within ±1mV of the final equilibrium value. The

response time for the electrode based on DOP as plasticizer was obtained and ranged from (5-9) s.

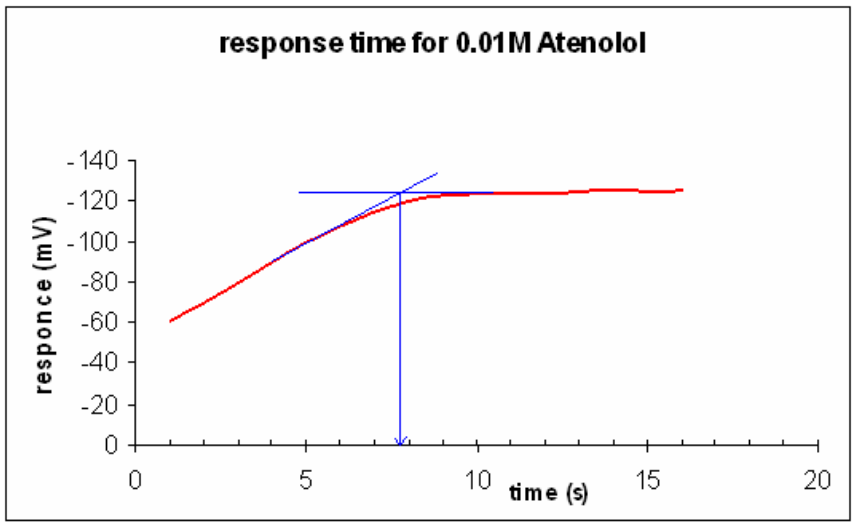


Figure (3-10): response time of electrode (IV) based on DOP, for 0.01M atenolol.

It has been noticed that the response time value for higher concentrations is higher than that of low concentration. That is, the measured response time for 0.01M and 0.0001M atenolol was 7.8 s ($t_{95\%}$=7.3) and 6 s ($t_{95\%}$=5.7)* respectively. As shown in Figures (3-10) and (3-11).

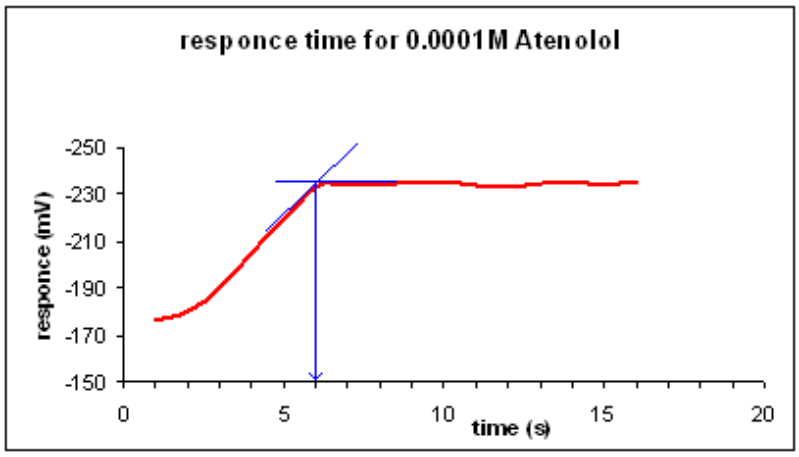


Figure (3-11): response time of electrode (IV) based on DOP, for 0.0001M atenolol.

*** Statistical factor represent the actual response time**

The same behavior was obtained when using the electrode III (based on ONPOE), that is, the measured response time for 0.01M and 0.0001M atenolol was 8 s ($t_{95\%}$=7.6) and 6 s ($t_{95\%}$=5.7) respectively. as shown in figures (3-12) and (3-13).

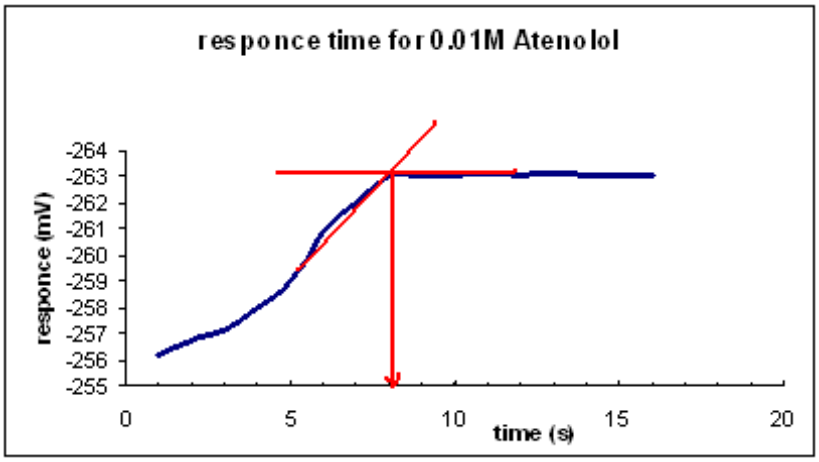


Figure (3-12): response time of electrode (III) based on ONPOE, for 0.01M atenolol.

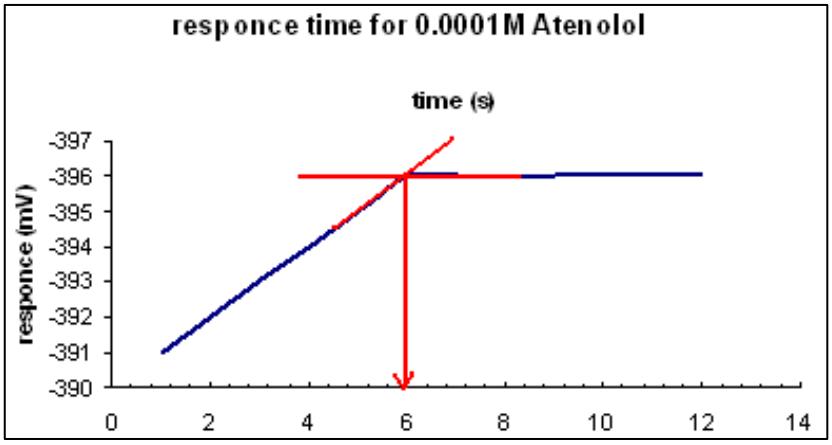


Figure (3-13): response time of electrode (III) based on ONPOE, for 0.0001M atenolol.

3-3.Selectivity:

The selectivity is obviously one of the important characteristic of ion-selective electrodes, determining whether reliable measurement in target sample is possible. It was investigated by separate solution method ($a_A=a_B=10^{-2}$M) and

potentiometric selective coefficient, which was calculated by the similar equation as described previously (equation 1-5), summarized in Tables (3-4) and (3-5) for ONPOE and DOP based electrodes respectively:

Table (3-4): values of selectivity coefficient for the electrode III based on ONPOE plasticizer

Interfering Ion	E_1 *Solution (mV)*	E_2 *Interfere ion (mV)*	*Log K*	*K*
Na^+	-125	-65	1.007	10.156
K^+	-124	-63	1.023	10.556
Li^+	-125	-70	0.923	8.372
Ba^{++}	-125	-35	1.510	32.364
Mn^{++}	-125	-39	1.443	27.730
Cd^{++}	-126	-30	1.611	40.807

Table (3-5): values of selectivity coefficient for the electrode IV based on DOP plasticizer

Interfering Ion	E_1 *Solution (mV)*	E_2 *Interfere ion (mV)*	*Log K*	*K*
Na^+	-125	-46	1.326	21.159
K^+	-124	-47	1.290	19.489
Li^+	-125	-46	1.326	21.159
Ba^{++}	-124	-18	1.779	60.051
Mn^{++}	-126	-18	1.812	64.875
Cd^{++}	-125	-12	1.896	78.700

The data given in tables (3-3) and (3-4) revealed that the selectivity coefficient obtained by the proposed electrodes for all cations tested were on order of (1-2), which indicated good selectivity for atenolol against alkali, alkaline earth and common transition metal ions.

The results in tables (3-3) and (3-4) showed also that the selectivity coefficient with monovalent interfering ions is lower than of divalent. This may be due to difference in ionic size, mobility and permeability. The values of log $K^{pot.}$ were found to range from 0.9-1.3 for monovalent and 1.4-1.8 for divalent interferes ions.

The results in the above tables showed also that the selectivity also influenced by the plasticizer used. In general the atenolol selectivities were better for electrode based on DOP plasticizer than electrode based on ONPOE plasticizer.

3-4. ***sample analysis:***

The concentrations of atenolol in prepared standard solutions were determined using ISE based on (A-PT) ionophore and DOP solvent mediator. Four potentiometric techniques were used for the determination of atenolol ion including, direct, standard addition (SA), multiple standard additions (MSA), and titration method. Standard solutions of atenolol with concentration of $1x10^{-1}$M were used in the standard addition method, and

$1x10^{-2}$M phosphotungistic acid standard solution was used in the titration method.

Gran's plots were constructed using Gran's plot paper with 10% volume correction to calculate the equivalence point precisely with MSA and titration methods.

Three samples were prepared for atenolol ion with comparable concentrations and the average for these values were used to calculate the relative error (RE) and relative standard deviation (RSD) for the results obtained by each method. The above data are listed in table (3-6).

Table (3-6): atenolol sample analyses using atenolol selective electrode based on DOP indicator.

compound	concentration				
	calculated	Measured Using potentiometric methods*			
		Direct	SA	MSA	titration
Stand. 1	$1.028x10^{-3}$	$1.017x10^{-3}$	$1.03x10^{-3}$	$1.034x10^{-3}$	$1.100\ x10^{-3}$
Stand. 2	$1.101x10^{-3}$	$1.092x10^{-3}$	$1.05x10^{-3}$	$1.055x10^{-3}$	$1.046\ x10^{-3}$
Stand. 3	$1.072x10^{-3}$	$1.037x10^{-3}$	$0.999x10^{-3}$	$1.019x10^{-3}$	$1.002x10^{-3}$
RSD %		1.01	2.52	1.74	3.64
RE %		0.98	2.46	3.61	4.93

Where: SA= standard addition
MSA= multiple standard addition
RSD = relative standard deviation
RE= relative error
***Each measurement was repeated three times.**

The calculated RSD% using titration method is relatively large 3.64% in comparison with the other methods used; this may be attributed to the precipitation of (A-Pt) complex on the surface of the membrane and poisoning the membrane. Figure (3-14) shows titration curve of atenolol sample with phosphotungistic acid standard solution.

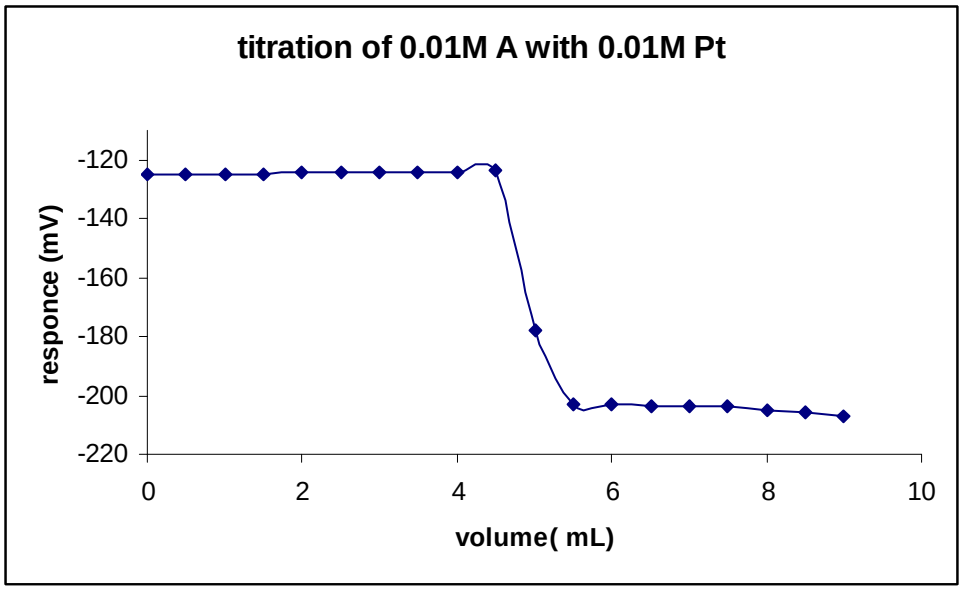


Figure (3-14): titration curve for sample solution containing 0.01M Atenolol with 5mL of 0.01M PT standard solution.

From the resulting precipitation titration curve (figure 3-14), it is seen that the amount of atenolol can be accurately determined with the electrode.

However, the relative error obtained with SA and MSA methods were 2.52 and 1.47 respectively. That's in fact related to experimental evidents which reveled that the effect of interferents can be eliminated when we are using standard addition method.

Figure 3-15, shows the multiple standard addition method for the determination of 0.01M atenolol sample.

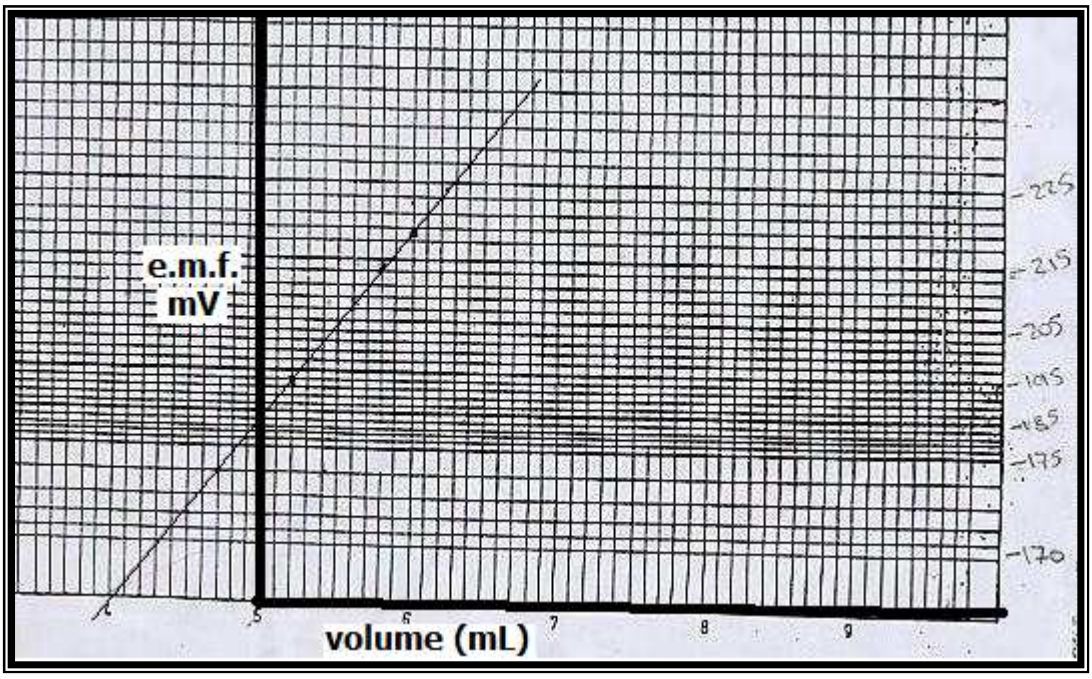


Figure (3-15): Gran plot of response (mV) versus volume (mL) of the added stander for the determination of atenolol by multiple standard addition method.

3-5.Analytical application of the selected electrode:

With the electrode IV, accuracy of the proposed electrode for determination of atenolol was assessed by determining 0.001M atenolol solutions using the direct potential method and the data obtained showed in table (3-7) which indicates the average recovery and standard deviation to be 98.46% and 0.1%, respectively. The direct potential method was applied to the determination of atenolol in pharmaceutical tablets (*Tenordin, Ateno and Novaten)*.

Tenordin gives the best recovery (recovery= 98.54%), while *Ateno* gives (98.34%) and *Novaten* gives (98.50%). As listed in Table (3-7).

Table (3-7): sample analyses of tablet using atenolol selective electrode based on DOP indicator.

pharmaceutical	*Tenordin*	*Ateno*	*Novaten*
Concentration	$1x10^{-3}$	$1x10^{-3}$	$1x10^{-3}$
founded	$0.9854x10^{-3}$	$0.9834x10^{-3}$	$0.9850x10^{-3}$
Recovery %	98.54	98.34	98.50
Error %	1.46	1.66	1.50

Future work

Based on the above study, future work can be applied on other ISE's which can be fabricated using:

1. Different types of drugs or amines, with different properties and chemical structure, to obtain wide selectivities over multiple drugs.
2. Different plasticizers to get better idea on their influence on the electrode performance.
3. Other types of matrixes as alternative to PVC matrix.
4. Other amount and percent of components proportions in membrane, through fixing one of the components and changing the other.

In addition further study is needed to the:

1. Application of these membranes in analyses of other drug samples with similar active groups.
2. Study the selectivity behavior using other methods and also by using more interfering ions.

2. Experimental part

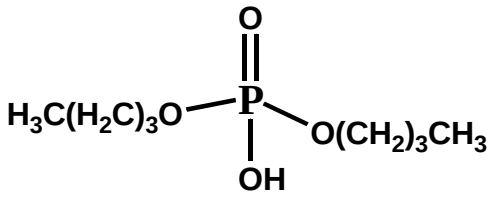
2-1.Instruments and equipments:

Expandable ion analyzer, ORION, model EA 940 with a calomel reference electrode. Ultra pure water manufacturing devise, TORAYPURE, model LV-08 (Mihama, Japan). FTIR-8300 fourier transform infrared spectrophotometer SHIMADZU. Clear PVC tubing (6mm o.d.).

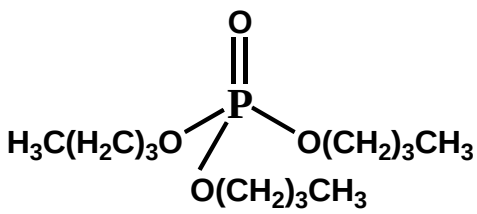
2-2.Chemicals:

Atenolol and TENORDIEN tablets (50mg atenolol) were a gift from the State Company of Drug Industries and Medical Appliances (Samara- IRAQ-SDI), NOVATIN tablets (100 mg atenolol) (Ajanta pharmaceutical limited company, India) and ATENO Tablets (100 mg atenolol)(Egyptian International pharmaceutical industries company [EIPICO],Egypt) were purchased from local market. The following plasticizers:

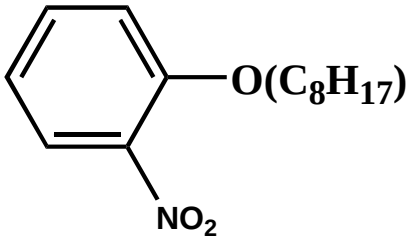
- Di-butylphosphate (DBP)



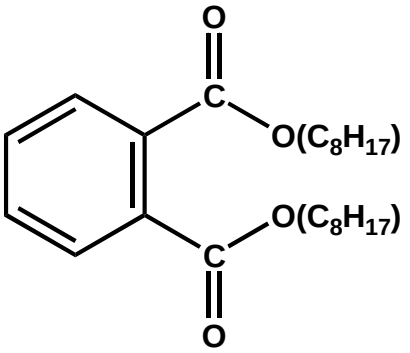
- Tri-butylphosphate (TBP)



- O-nitrophenyloctylether (ONPOE)



- Di-octylphthalate (DOP)



Were obtained from Fluka AG, (Switzerland). Other chemicals and reagents of analytical grade reagent were obtained from Fluka, BDH and Aldrich companies.

2-3.Preparation of standard solution:

All solutions were prepared in doubly distilled deionized water (resistivity ~18 MΩ). Stock solutions of 0.01M of $NaNO_3$, KCl, LiBr, $BaCl_2$, $MnSO_4$ and $CdSO_4$ were prepared. More diluted solutions were prepared by subsequently dilution of the stock solutions.

A standard solution of 0.1M atenolol was prepared by dissolving 1.3315g of standard atenolol and completes the solution up to 50ml. The other atenolol standard solutions were prepared by subsequent dilution of the above solution.

2-4. Preparation of Ion-pair Compound:

The atenolol ion-selective electrode is developed [70] based on the use of ion-pair compound of atenolol-phsphotungatate (A-PT) as the electro-active substance.

The preparation of ion-pair of (A-PT) was performed by mixing 20ml of 0.01M solution of atenolol with 25ml of 0.01 phsphotungatate (PT) with stirring. The resulting precipitate was filtered off, washed with water, dried at ~60°C. The composition of the ion-pair compound, (A-PT), was confirmed using FTIR.

2-5. Casting the membrane:

The method of immobilizing the atenolol matrix into the PVC matrix membrane was made as described by Moody et al. [29]. A 0.040g of (A-PT) matrix was mixed with 0.360g of plasticizer and 0.17g of PVC powder, after that 7.0ml of THF was added with stirring until the formation of viscous solution. The above solution poured into a glass casting ring about 30mm length and 35mm in diameter. It consists of two pieces; one of them is the glass cylinder and the other is glass plate. The two pieces was pasted together by using (PVC-THF) viscous mixture (to make sure no loss in the membrane mixture) figure (2-1). The top side of the cylinder was covered with a pad of filter paper on which a heavy weight (~200g) was placed. The assembly was left for 2-3 days to allow graduate evaporation of the solvent.

2-6. Assembling the ion-selective electrode:

The glass ring with adhering membrane was carefully removed from the glass plates as shown in figure (2-1) (3rd step). The membrane was then detached away from the edge of the ring. A disc of the membrane was cut equal to the external diameter of a PVC tube, step 4, on of sides of PVC tubing was flatted and smoothed by placing it on glass plate moistured with THF-PVC solution with aid of vertical rotation.

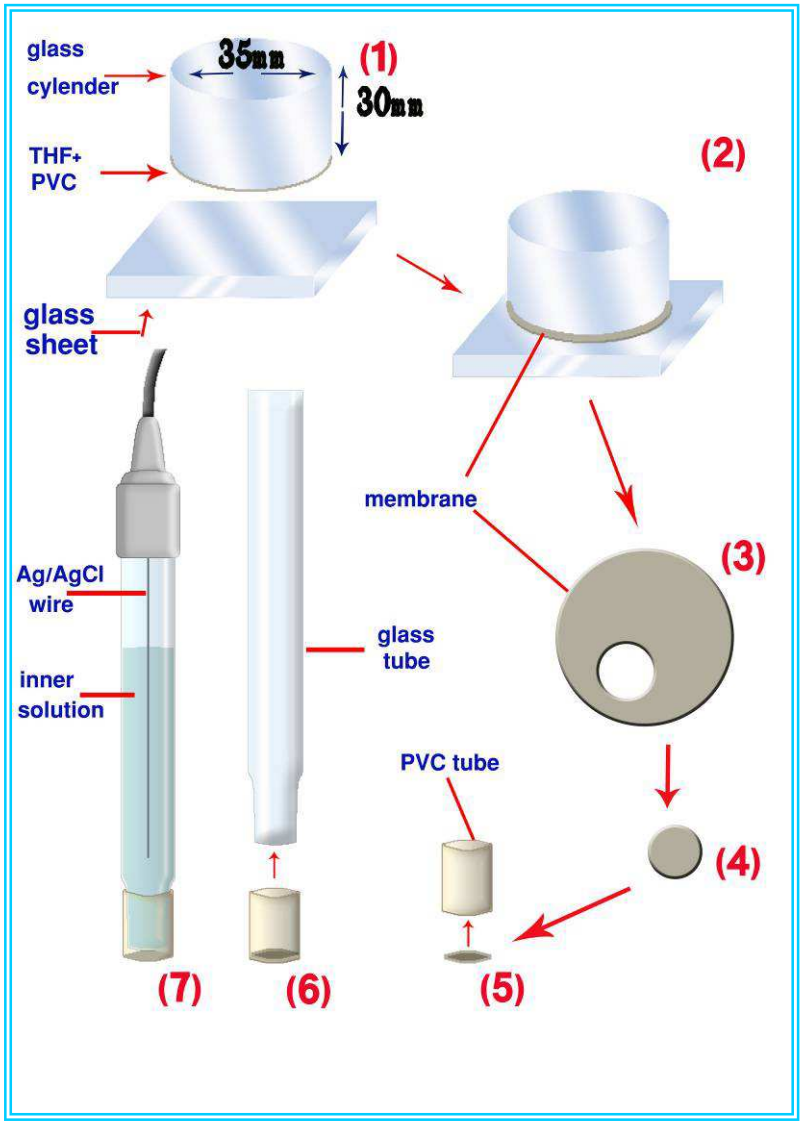


Figure (2-1) Assembling the Ion-selective Electrode:

The disc then mounted with a forceps on the polished end, the outer edge of the disc membrane was carefully sealed to the end of the PVC tube, step (5).

Next step is connection into a glass tube, step (6). The other side of the glass tube was assembled with plastic cover in which Ag/AgCl wire was inserted through it, the tube was filled 3/4 with 0.1M atenolol solution before fixing the cover, step (7). The electrode was then conditioned by placing it in 0.1M solution containing the ion to be measured (at least 3 hour's) before using.

2-7.Potential measurement

An atenolol selective electrode and saturated calomel electrode (SCE) were used as indicating electrode and the reference electrode, respectively. The e.m.f. measurements were carried out at room temperature using the following cell:

SCE. / test solution / ISE

A calibration curve was constructed for each ISE using several standard solutions ranged from 10^{-6}-10^{-1} M atenolol. The test solutions were constantly stirred with magnetic stirrer. The activity coefficients of the above standards were calculated using Deby-Hükle equation [15] (2-1):

$$\text{Log } f = Az^2 \sqrt{\mu} / (1+0.329\ R \sqrt{\mu}) \quad \ldots\ldots\ldots\ldots (2\text{-}1)$$

Where f is the activity coefficient, z is the charge of the analyte ion, μ is the ionic strength of the solution, A is constant which depend on temperature and solvent (A= 0.511 for water at 25°C) and R is the effective ionic radius of actual ion (R was taken

as 6A°) [15]. Calibration curves were then prepared by plotting the potential versus the activity on Orion semi-log graph paper.

From the calibration curve all statistical facts including slop; correlation coefficient, concentration range and detection limit, which characterize the manufactured electrodes.

The effect of pH on the response of membrane was examined by measuring the potential of the standard solutions with concentrations ($10^{-4,}$ 10^{-3}, 10^{-2}) M at different pH ranged from 1-12; where the pH values were adjusted with ammonia and HCL solutions.

The life time of each membrane was calculated; that is the decrease in Nernstian response with the time after first measurement.

2-8. Selectivity measurements

The selectivity of the electrode has been measured by the separated solution method [71]. According to this method a 20mL of 0.01M solution of the prepared atenolol, and 20mL of 0.01M from each other interfering ion were mixed. The potential of each solution is then measured one-by-one. The potential response to interfering ions was then measured according to equation (1-5).

2-9. Sample analysis:

Three synthetic samples of atenolol in the range 10^{-3} M concentration were prepared. The concentration of these samples were calculated using direct, standard addition (SA) and titration method using Gran plot (except for direct method).

In the direct method the e.m.f. of sample is measured directly using atenolol indicator electrode (see fig 1-2). The concentration was then calculated using calibration curve of standard atenolol.

In the standard addition method the sample of 20mL with concentration of $1x10^{-3}$M is introduced followed by addition of 0.1 mL of 0.1M increments. The e.m.f. is calculated before and after each addition. The concentration of the sample is calculated [14] using equation (2-2) for a single point increment:

$$C_u = C_s \, x[V_s/(V_u + V_s)] \, /[(10^{\{(E2-E1)/m\}}) - (V_u/(V_u + V_s))] \ldots (2\text{-}2)$$

Where, C_u, and C_s are the concentration of atenolol in the unknown and the standard, respectively, V_s and V_u are the volume of standard, and sample, respectively, E1 and E2 are the electrode potential (mV) of the pure solution, and potential after the addition, and m is the electrode slope. These methods depend on the fact that the plot of electrode potential (mV) against concentration (M) is a logarithmic curve. Thus any particular ratio of the amount of increase in mV in response to a particular increase in concentration (i.e. the slope of the curve) will only fit in one unique part of the curve and thus the concentration before and after addition can be determined.

A SA Gran's plot was also prepared on semi-antilog graph paper by plotting the cell potential versus the added volume of standard. The concentration of each sample was then calculated (MSA method) by extrapolating the x-axis of the calibration line[45].

A precipitation titration was then performed on the samples under study after the addition of phosphotungistic acid solution. The titration is then followed potentiometrically using the prepared ISE. A titration curve using Gran plot was then constructed for each sample.

Conclusion

Atenolol-selective PVC membrane electrodes based on ion-pair compound of A-PT and (DBP, TBP, ONPOE and DOP) as plasticizers were synthesized. The slope and linear range of atenolol concentration for electrode constructed with the plasticizer DOP was better than the other three electrodes, that is, the slope was the nearest to Nernstian slope and linear range was wide enough to do measurements.

The linear range, slope and limit of detection of DOP electrode were $5x10^{-2}$-$1x10^{-4}$M, 55.91 mV per decade and $5x10^{-5}$M, respectively. The effect of pH on the potential response indicated that major influence of pH occurred when pH of the solution was in the range of 4-8.

The practical utility of the electrode has been demonstrated by use it as indicator electrode in potentiometric precipitation titration of Atenolol solution with phosphotungistic acid solution. Standard addition method has been also successfully applied and presenting an excellent results.

The proposed electrode was successfully applied to the determination of atenolol in pharmaceutical preparation. The analytical method proposed proved to be a simple, rapid and good accuracy.

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Summary

Atenolol ion selective electrodes have been prepared based on phosphotungistic acid using many plasticizers which were: Di-butylphosphate (DBP), Tri-butylphosphate (TBP), o-nitrophenyloctylether (ONPOE) and Di-octylphthalate (DOP).

The properties of the prepared electrodes have been studied including: slope, concentration range, detection limit, life time, and pH effect.

The electrodes no. (I,II and III) of (DBP, TBP and ONPOE) respectively, gave a linear range from ($1x10^{-4}$-$5x10^{-1}$, $1x10^{-4}$-$5x10^{-2}$ and $1x10^{-4}$-$1x10^{-2}$)M respectively, with slopes of (34.63, 35.16 and 64.07) mV/decade. The limit of detection was ($1.1x10^{-5}$, $1.8x10^{-6}$ and $1.1x10^{-4}$) M and the lifetime were about (35 day, 45 day and ~ 48 hours) respectively.

The fourth membrane was based on (DOP), displays linear range from $1x10^{-4}$M to $5x10^{-2}$M with a Nernstian slope of 55.91 mV /decade and correlation coefficient 0.9994. The limit of detection was $5x10^{-5}$M and the life time was ~90 day.

The stability of the four electrodes was monitored continuously and evaluated; the standard deviation of potential drift obtained were ≤ (2,3,8 and0.5) mV/day for membrane no. (I,II,III and IV) respectively.

From the optimization and working pH results, it is very clear that the electrodes (IV) based on DOP plasticizer give the best result; so, it has been chosen as the best combination of plasticizer and electro-active compound.

The practical utility of the electrode has been demonstrated by use it as indicator electrode in potentiometric precipitation titration of atenolol solution with phosphotungistic acid solution. Standard addition method has been also successfully applied and presenting an excellent results.

The proposed electrode was successfully applied to the determination of atenolol in pharmaceutical preparation. The analytical method proposed proved to be a simple, rapid and good accuracy.

الأسم : معتز عدنان علي
تاريخ المناقشه: ٢٣-٦-٢٠٠٥
العنوان: بغداد / الدوره/ م ٨٠٨/ ز ١١ / د ٢٣
رقم التلفون:٠٧٩٠٢١٥٨٣٥٣
E-mail: mutazadnan@yahoo.com

الخلاصه

تم تحضير عدة أقطاب ايونيه في مادة PVC حساسه للأتينولول بالاعتماد على المعقد (Atenolol-Phosphotungistic acid) كماده فعاله. هذه الماده الفعاله تكون مذابه في عدة مواد ملدنه منها

, Di-butylphosphate (DBP), Tri-butyl phosphate (TBP), O-nitrophenyloctylether (ONPOE), Di-octylphthalate (DOP),

من خلال منحنى التدرج تم دراسة خواص هذه الاقطاب والتي تشمل (منحنى الانحدار و مدى التركيز وحد التحسس و عمر القطب و تأثير ال pH) ومن خلال الدراسه وجد ان الأقطاب المتكونه من (DOP) كماده ملدنه تمتلك مواصفات جيده يمكن الأعتماد عليها في تعيين الأتينولول بصوره دقيقه، منحنى الأنحدار لهذه الأقطاب كان يساوي تقريباً (55.91 mV/decade) مدى التركيز التي تتحسسهُ هذه الأقطاب تراوحت من $1x10^{-4}M$ الى 5 $x\ 10^{-2}M$، حد التحسس لهذه الأقطاب كان بحدود $5x10^{-5}M$ فيما كان مدى التصحيح ٠,٩٩٩٤ ومدى pH تراوح من ٤ الى ٨.

أيضاً تم دراسة تداخلات بعض الأيونات الموجبه مع الأقطاب بواسطة طريقة المحاليل المنفصله وتم تعيين معامل الأنتقائية لهذه الأيونات، وتبين ان تداخلات الأيونات الأحاديه تكون أكبر من تداخلات الأيونات الثنائيه.

لدراسة الخواص العمليه في محاليل قياسيه محضره مختبرياً وكذلك في نماذج دوائيه، تم استخدام القطب كقطب كاشف في عملية التسحيح الترسيبي وأستخدمت أيضاً طريقة الأضافات القياسيه معطيةً نتائج ممتازه.

Republic of Iraq
Ministry of Higher Education and Scientific Research
Al-Nahrain University
College of Science
Department of Chemistry

Preparation and characterization of atenolol selective electrode

A Thesis submitted to the College of Science Al-Nahrain University in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

By
Mutaz Adnan Ali
(B.Sc 2002)

Rabee Al Thany 1426 **May 2005**

Supervisor certification

We certify that this thesis was prepared under our supervision at the Department of Chemistry, College of Science, Al-Nahrain University as partial requirements for the Degree of Master of Science in Chemistry.

Assistant Professor
Dr. Shahbaz A. Maki

Senior Researcher
Dr. Nabil S. Nassory

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

Assistant Professor
Dr. Shahbaz A. Maki
Head of the Department of Chemistry /College of Science/ Al-Nahrain University

Examining Committee's Certification

We, the Examining Committee, certify that we read this thesis and have examined the student ***Mutaz Adnan Ali,*** in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science, in Chemistry.

Examining Committee	Chairman	Member	Member	Member (Advisor)	Member (Advisor)
Signature					
Name					
Title					
Date					

Approved for the College of Graduate Studies

Assistant Professor

Dr.Laith Abd Al-Aziz

Dean of College of

Science Al-Nahrain

University

In the Name of Allah the most Merciful, the most Compassionate

"Allah will exalt those of you who believe, and those who are given knowledge, in high degrees"

[58:11]

الآهداء

الى الذين أحبوا و تمنوا لي النجاح

الى الذين صبروا و تحملوا لأجل ذلك الكثير

أعز الناس

والدتي و والدي

الى من أشد بهم أزري في الحياة أخوتي

الى رفاق الدرب الطويل أصدقائي

أهدي بحثي المتواضع ...

معتز

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Mutaz

2005

جمهورية العراق
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من قبل

معتز عدنان علي

بكالوريوس ٢٠٠٢ (جامعة النهرين)

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بسم الله الرحمن الرحيم

"يرفعُ اللهُ الذينَ آمنوا مِنكم والذينَ أوتوا العلمَ درجت"

"صدق الله العظيم"

سورة المجادلة الآية (١١) .