Electrochemical analysis of response behavior of silver selective electrode based on triazine derivatives

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Abstract: *The study concerned with the development and construction of three potentiometric sensors selective for Ag^+ depends on incorporation of some insecticides compounds derivatives of triazine; such as [Diniconazole (DC) (I), Ametryn (AM) (II), Prometryn) PM) (III)] in the membrane and forming relative complexes by conditioning these sensors in Ag^+ solution. These sensors showed very good sensitivity and selectivity toward Ag (I) with good Nernstian slopes 56.7±0.2, 48.7±0.1, 55.0±0.8 mV/decade with lower limit of detections 5.75.0X10^{-6}, 5.3.0X10^{-6}, 3.5.0X10^{-6} M in pH range 3.5-7, 4.5-8, 4-8 over the concentration range 10^{-5} -10^{-2} M respectively, all the factors which affected on the sensitivity and selectivity of these sensors were studied, such as the percentage of ionophore in the membrane, the effect of solvent mediator, the concentration of internal solution, PVC derivatives and pH media. The comparison between the three sensors are evaluated, from the results obtained, it was found that the more selective one is the sensor (I) which has the Nernstian slope 56.7 mV/decade, the lowest detection limits $5.75x10^{-6}$ M and fast response time less than 10 sec. All the proposed sensors are used for detection and determination of silver ion in its solution by direct potentiometric measurement technique with 0.1 M NaCl and gave a sharp inflection points.*

Keywords: *potentiometric sensors, silver, triazine derivatives, sensitivity of potentiometric sensors, selectivity of potentiometric sensors.*

I. INTRODUCTION

Silver is a useful element in many respects, such as electrical and electronic applications, photographic film, manufacturing of fungicides and in drugs [1].

Various methods for the determination of silver at trace quantities including spectro-photometery [2], atomic absorption spectro-scopy [3], fluorimetry [4], stripping voltammetry [5], flow injection analysis [6]. Most of these methods are very expensive but ion selective electrode have the advantages of good selectivity, cheapness and ease of operation.

Concerning preparation of ion selective electrodes, several studies had been achieved, from which; the study of Oue *et al.*(1998) [7] included preparation of silver-ion selective electrode using 3-(4'-Triethoxy-silylbutyl)-monothia-16- crown -5 immobilized on silicone-rubber membranes by covalent bonding. The neutral-carrier-type Ag^+ electrode possesses high Ag^+ selectivity's against heavy or transition metal ions compared with conventional solid-state membrane Ag^+ electrode, Marin *et al.* (1997) [8] used 1-furoyl-3-phenylthiourea as ionophore and the membrane was directly cast on conductive composite graphite-epoxy . This sensor showed a linear response at 10^{-6}-10^{-2} M with a Nernstain slope of 58 mV/decade. The response time was 20s, Chen *et al.*,(2000) [9] prepared silver ion-selective electrodes using polymeric membranes based on nitrogen containing calixarene derivatives. The electrodes gave a good Nernstian response of 49-53 mV/decade for silver in the activity range $5x10^{-6}$-$5x10^{-2}$ M. The electrode was used as indicator electrode in titrations of Ag^+ with Cl$^-$ ions, Zeng *et al.* (2003) [10] synthesized two novel tweezers-like 25, 27-dihydroxy-26, 28-bis (phenyl-thiaethoxy) calix [4] arenes. The influences of substitutes on the behavior of the ISEs were evaluated under the same conditions. ISEs based on 6-12 as neutral ionophores were prepared, and their selectivity coefficients for Ag^+ were studied against other alkali, alkali-earth metal, lead, ammonium ions and some transition metal ions using the fixed interference method (FIM). These ISEs showed excellent Ag^+ selectivity over most of the interfering cations except for Hg^{2+} and the performance of Lim *et al.* (2002) [11] was calyx, furano, pyrrole and related compounds that used as neutral carriers for Ag-selective polymeric membrane electrode. The Ag ion-selective electrode gave a good Nernstian response of 57.1 mV/ decade for Ag ion in the activity concentration range 1 x l0^{-6} to l x l0^{-2} M, especially at low pH.

The aims of the present work are concerned with the development and construction of three potentio-metric sensors selective for Ag^+ depends on incorporation of some insecticides compounds derivatives of triazine.

II. MATERIALS AND METHODS

II.1. Apparatus:

An Orion digital pH/mV-meter (model SA 720) was used for pH and mV measurement, connected with silver indicator sensor with conjunction with Orion Ag/AgCl double junction reference electrode (Model 90-02) filled with 10% w/v KNO_3 in the outer compartment. An Orion combination pH electrode (model 91-02) was used for pH adjustment.

II.2. Chemicals and solutions:

The ionophores including three triazine derivatives; diniconazole (I) ((E)- (RS)-l-(2, 4-dichlorophenyl) 4,4-dimethyl-2-(1H, l,2,4- triazol. = l-yl) pent-l-en-3-01) (Fig. 1), ametryn (II)-N^2-ethyl-N^4-isopropyl-6-(methylthio)-l, 3, 5-triazine-2.4 diamine (Fig. 2) and prometryn (III) N^2, N^4,-di-isopropyl-6-methylthio 1, 3, 5-triazine-2, 4 diamine (Fig. 3).These ionophores were obtained from National Organization for Agriculture Research. High molecular weights; Poly (vinyl chloride) (PVC) and carboxylated poly (vinyl chloride) (PVC-COOH), nitrophenyloctyl ether (NPOE), dibutyl sebacate (DBS), di-octylphthalate (DOP) and THF were obtained from Fluka. Different metal salts (chloride, sulfate, and nitrate) were obtained from Aldrich chemical Company.

II.3. Preparation of membrane sensors:

Three PVC-silver membranes were prepared using diniconazole (I), plasticizer and PVC-COOH. PVC-silver membrane incorporating of a1netryn(Il), PVC and dioctyl phthalate (DOP)was prepared as described above. Three PVC silver membrane based on prometryn (III) as an ionophore was prepared as described including ionophore, plasticizer (dibutyl sebacate, DBS), dioctylphthalate (DOP) or o-nitrophenyloctylether (NPOE) and PVC-COOH. The effect of membrane composition was studied by incorporating varying amounts of ionophore (Ill) "PVC and DBS with THF", plotted as a function of silver ion concentrations. Two PVC derivatives (PVC and PVC-COOH) were used in the preparation of two different membranes with ionophore (III) and (DBS) as plasticizer. A semi - transparent flexible membranes were obtained. The sensor body contain lO^{-2} $AgNO_3$ as an internal reference solution. All potentiometric measurements were made at 25°C. The sensor in conjunction with a double junction Ag/AgCl reference electrode was immersed in 10^{-1} M $AgNO_3$ and 10^{-3} KNO_3 of pH5. The potential change for each concentration was recorded. Calibration curves were constructed by plotting the potential change against the logarithm of Ag-ions concentrations at pH5.

II.4. EMF measurements:

All measurements carried out at 25°C with cells of the following type:
Ag/AgCl/KCI (0.1 M) /0.1 M KNO_3/sample solution//sensor membrane//internal filling solution/ AgCl/Ag.
Sensors calibrations were carried out at 25°C by measuring the potential of lO^{-6}-lO^{-2} M $AgNO_3$ solutions. The potentials were plotted as a function of silver (I) ion concentrations. The lower detection limits was taken at the point of intersection of the extrapolated linear segments of the silver (I) calibration curve. Sensor life span was examined by repeated monitoring of the slope of silver calibration curve.

II.5. Effect of pH and dynamic response time:

The effect of pH on the silver selective electrode sensors (I), (II) and (III) were tested by measuring the potential at pH 10 values pH of over the range 2-12 in solutions containing Ag(I) ions .The pH of the solutions of 10^{-4} and10^{-3} M were varied by adding small aliquots of concentrated NaOH or HNO_3 solutions. The corresponding mV readings were recorded after each addition. The pH dependences of the three ionophores used in silver sensors were examined by plotting the change of potential against pH values. Dynamic response times of the electrodes were measured in constantly stirred solution of varying Ag (I) concentrations. The stability of the potential was

measured for different Ag^+ concentrations during 180 sec period for each concentration, and examined by plotting potentials as a function of time.

A standard stock of 10^{-1} M $AgNO_3$ solution was prepared. A series of diluents concentrations are prepared with buffer acetate of pH 5 and other series of diluents concentrations prepared by 10^{-3} KNO_3 pH 5 .The potentials were plotted against concentration for two different buffer solutions for the Ag^+ sensor based on ionophore (III),to clarify the effect of type of buffer on the sensor.

II.6. Effect of internal solution:

The concentrations of the internal filling solution of the proposed sensors I, II, III were varied 10^{-2}, 10^{-3}, 10^{-4} M silver nitrate solution and the calibration curve of Ag (I) was measured at different concentrations to choose the concentration of the internal solution which gives the best response for Ag (I) ions .

II.7. Selectivity of membrane sensor:

Selectivity coefficients $K^{POT}_{Ag,M}$ of $AgNO_3$ sensor were measured using the separate solutions method (Robert *et al.,* 2000), where selectivity coefficients were calculated using equation.

$$-\log K^{POT}_{Ag,M} = [E_M - E_{Ag}/S]$$

Where E_{Ag} and E_M are the response potentials of the sensor for silver nitrate ion and interference M, respectively at 10^{-3} M and S is the sensor slope (mV/decade) potentials are recorded for concentration from low to high analytical application

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II.8. Analytical Application:

II.8.1. Direct Potentiometric determination of silver:

The working silver sensors based on ionophone I, II, and III in conjunction with a double junction Ag/AgCl reference electrode were immersed in 8 x 10^{-3}, 1.5 x10^{-2} and 1.8 x 10^{-2} of $AgNO_3$ were titrated against 0.1 M of NaCl, the potential change for each addition was recorded.

The titrations data were plotted for the three sensors based on ionophore (I), (II), (III) and the equivalent volumes were determined and recovery can be calculated.

III. RESULTS AND DISCUSSION

III.1. Sensor characteristics:

Ag^+ ISEs have been intensively studied and extensively used for the formation of coordination networks based on the binding of silver. There has been increasing number of reports on Ag(I) selective electrodes based on carriers, such as crowns, macrocyclic tetrathioethers, pyridophanes and so on. [12].

In preliminary experiments, the new triazine derivatives (diniconazole), (ametryn) and (prometryn) dissolved in various plasticizer are used to prepare PVC niembrane selective for Ag (l). The results showed that at 25^oC, sensor based on ionophore (I) displays a linear response for Ag^+ over the wide concentration range of $1x10^{-2}$ - $1x10^{-5}$ M with a detection limit $5.75x10^{-6}$ M and a calibration slope of 56.7 ± 0.2 mV/decade, the slope of sensor is near to the theoretical Nernstian value, oxygen atoms have affinity to be hard donors [13]. The best results were obtained membranes containing N and O atoms in the ionophore (I) [11].

In the case of ionophore (ametryn), the sensor has sensitivity to silver ions. In the light of the soft heavy metal ions displaying great affinity for soft coordination centers like nitrogen, sulfur, we try to explain the properties of the electrodes in terms of coordinating ability of the S or N atoms in ionophores. The coordination interaction between electron donors and acceptors cause the electrode to respond to metal ions. The presence of alkyl groups increases electron cloud density on S atoms. Therefore the coordinate covalent bond of Ag-S is strengthened, functionalization of their upper and lower provides ametryn (II) with variable inclusion capability and variable

complexation characteristics. Membrane sensor exhibit calibration slope 48.7±0.1 mV/decade with a detection limit 5.3x10^{-6} M in the linear range 10^{-2}-10^{-5} M.

The soft heavy metal ions, Ag^+ display great affinity for soft coordination centers like sulfur atoms. By using ionophore (III) with functional groups containing nitrogen and sulfur atoms as the neutral carriers in ion selective electrodes. It will be expected to be sensitive to soft heavy metal ions. The behavior of ionophore (Ill) as sensing molecule in silver ion selective PVC membrane electrodes gave a near Nemstian slope 55.5±0.3 in the concentration range 10^{-5}-10^{-2} M with limit of detection 3.5x10^{-6} M is shown in Fig.(14) and Table (6). (Bates *et al.,* 1995). The performance characteristics were evaluated under many different variables such as plasticizer, pH variation, effect of internal solution concentrations.

III.2. Effect of pH and response time:

The pH dependence of ionophore (I), (II) & (III) silver sensors were examined using 10^{-3} and 10^{-4} M $AgNO_3$ solutions over the pH range 2-l0. The electrode responds were hardly affected by change in the range 3.5-7, 4.5-8, 4-8 respectively. After pH 8 precipitation occurs due to formation of AgOH. (Chen *et al*., 2001) [14] Figs.(4-6) respectively. Adjustment of pH was performed using dilute nitric acid and sodium hydroxide. The sensors I, II and III have response time less than 10-l0-20 sec. respectively. Effect of types of buffer was investigated on ionophore (Ill) sensors by using two different types of buffer 5. KNO_3 pH5 as ionic strength and buffer acetate pH5 to ensure the electrodes were functioning (Bates, *et al.,* 1995) (Table 1). The effect of the two buffer is not critical. No great difference is obtained in the two cases as shown in Fig.(7).

III.3. Effect of internal solution:

The proposed sensor has also been observed at different concentrations of inner reference solution. On the basis of the observed working range with various solutions Fig.(8) and Table (2) for ionophore (I) and Fig.(9) and Table (3) for ionophore (Ill) 0.01M concentration of the reference solution is suitable one. A decrease in the detection limit of the sensor is observed at lower concentrations of the inner filling solution. Potentials generated at the membrane interface as well as the diffusion potential depend on the concentration of inner filling solution and that of the sample solution. A compatible correspondence between the two is necessary for optimal functioning of the membrane sensor. The decrease in detection limit of the membrane electrode at smaller concentrations of inner reference solution may be an outcome of large variations in both the interfacial and diffusion potentials.

III.4. Effect of solvent mediators:

Potentiometric response of sensor based neutral ionophore is greatly influenced by the polarity of the membrane medium, which is in turn defined by the dielectric constants of the major membrane components. Silver PVC-COOH matrix membrane incorporating (I) with two different plasticizers having different dielectric constants 7-24 namely (DOP) and (NPOE) were tested Fig. (10).

The results are shown in Table (4). Performance characteristics of membrane plasticized with (NPOE) showed high sensitivity, wide linear response range and near Nernstian slope. With (DOP) smaller slope was obtained but equal lower limit of detection to (NPOE). Fig. (11) show the effect of solvent mediator on sensor(III) and the results are tabulated in Table (5).

III.5. Effect of PVC derivatives:

The membranes of the sensor based on ionophore (III) were fabricated from PVC and PVC-COOH, As shown in Fig.(12). In the case of PVC-COOH, the characteristics of the membrane showed more sensitive and give near Nernstian slope but in the case of (PVC) gave a lower slope than expecting from Nernstian. The difference between them is illustrated in Table (7).

III.6. Effect of membrane composition:

From the response slope and linear range given in Table (8), it is immediately obvious that the amount of ionophore influences the performance characteristics of the PVC membrane electrode as shown in Fig (13). The l0 mg is the suitable weight which used in the preparation.

III.7. Selectivity of (l), (II) and (Ill) electrodes:

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of other cations. This is measured in terms of the potentiometric selectivity coefficients (Robert *et al.,* 2000) [15] with 10^{-3}M concentration level of alkali, alkaline earth and transition metal ions. The results obtained are given and shown in Table (9), Figs.(15-17) for the ionophore (I), (ll), and (Ill) respectively.

Potentiometric selectivity coefficients of Ag-sensor (II) membrane based sensor for some common cations were evaluated using the separate solutions method (SSM), (Ma & Hassan, 1982) [16]. It can be seen from Table (9) that (I), (II) and (III) sensors exhibit high selectivity towards Ag^+ ions over many of the ions under investigation. The selectivity was measured for 10^{-3} M concentration of the analyte and the interferents.

III.8. Analytical applications:

Potentiometric titration of $AgNO_3$ with NaCl, Sensor based on (I), (II) and (III) ionophores were used for monitoring direct titration of Ag^+ ion. With 0.1 NaCl with $1.8x10^{-2}$, $1.5x10^{-2}$, $8x10^{-3}$ M of $AgNO_3$ using sensor (I) Fig.(18) and 10^{-2} ,10^{-3},$0.7x10^{-3}$ M $AgNO_3$ with standard 0.1 NaCl using sensor (II) Fig. (19) and $1.5x10^{-2}$, $0.8x10^{-3}$, $1.9x10^{-2}$ M $AgNO_3$ with standard 0.1 NaCl using sensor (III) Fig.(20). Typical titration curve is shown, and a sharp inflection break at the equivalence point is obtained.
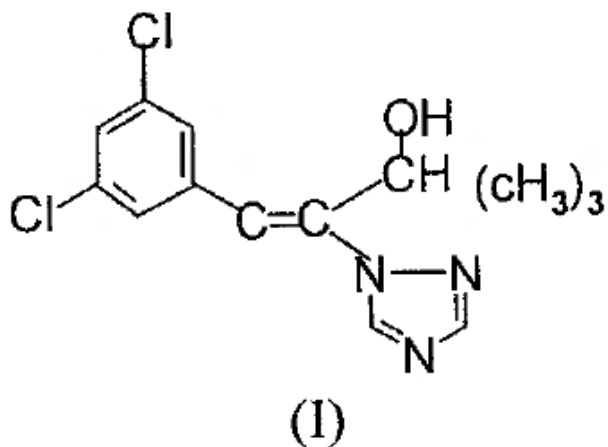
Fig. 1. Diniconazole (I) ((E) - (RS) —l- (2, 4 — di-chloro-phenyl) 4,4- dimethyl -2- (1H, l,2,4- tiiazol. = l-yl) pent-l-en-3-01)
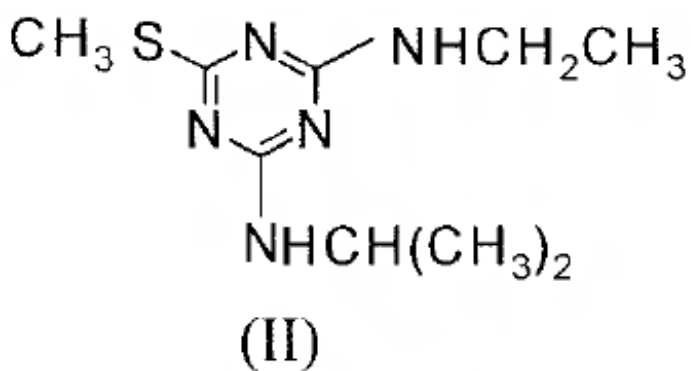

Fig. 2. Ametryn (II)- N^2 — ethyl — N^4 —isopropyl~6— (methylthio) —l , 3, 5-triazine — 2.4 diamine
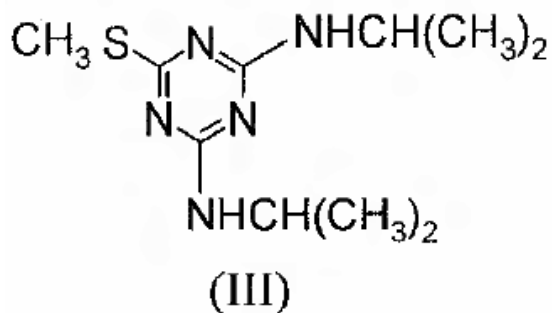

Fig. 3. Prometryn (III) N^2, N^4, -di-isopropyl-6-methylthio 1, 3, 5-triazine-2, 4 diamine
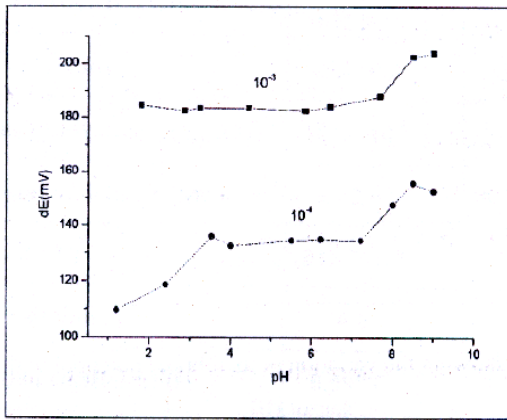
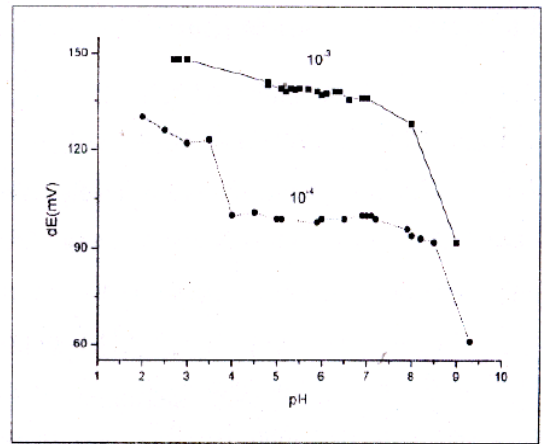**Fig. 4.** Plot showing the variation of membrane potential with pH for sensor (I) .

Fig. 5 · plot showing the variation of membrane potential with pH for sensor (II)
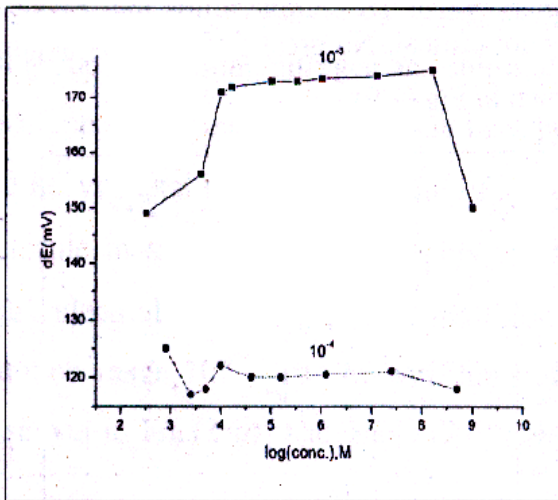
Fig. 6. plot showing the variation of membrane potential with pH for sensor (III)
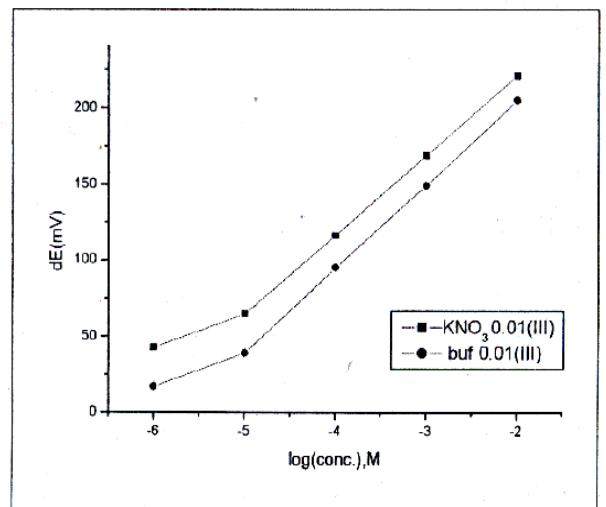

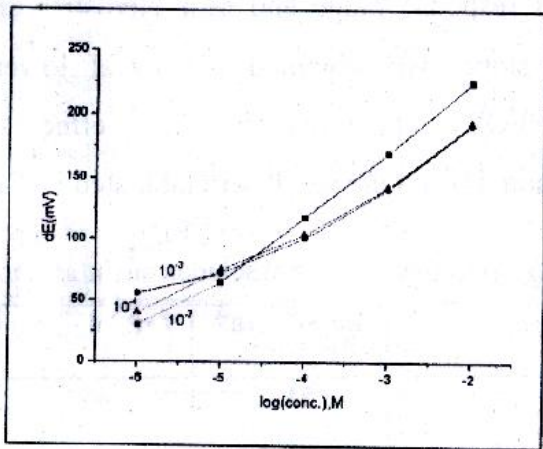**Fig.7.** Calibration curves using (KNO_3 &buffer acetate) back ground

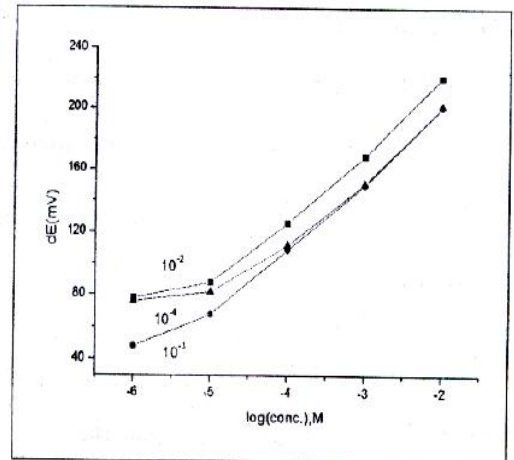**Fig. 8.** plots of mV vs. log(Ag$^+$) at various concentrations of internal solution of sensor (I)

Fig. 9. plots of mV vs. log(Ag$^+$) at various concentrations of internal solution of sensor (III)
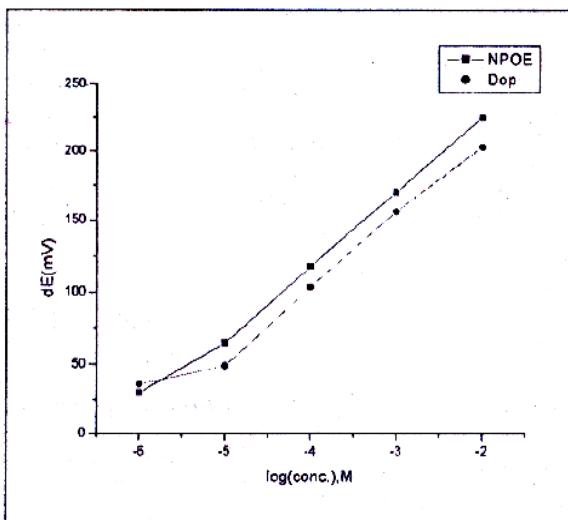

Fig. 10. Effect of plasticizer on the response of Ag+ sensor based on ionophore (I).
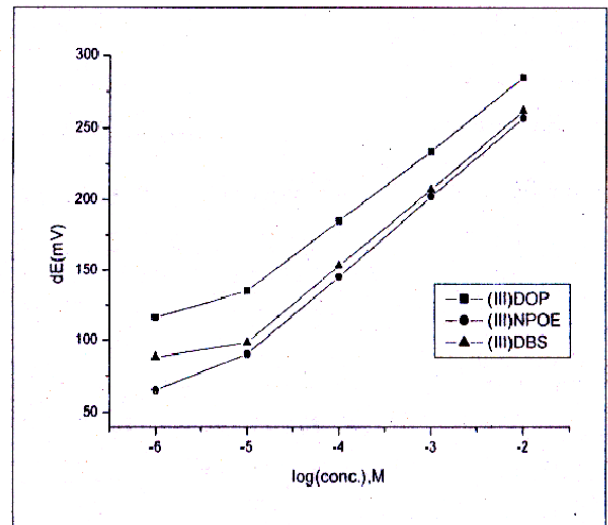

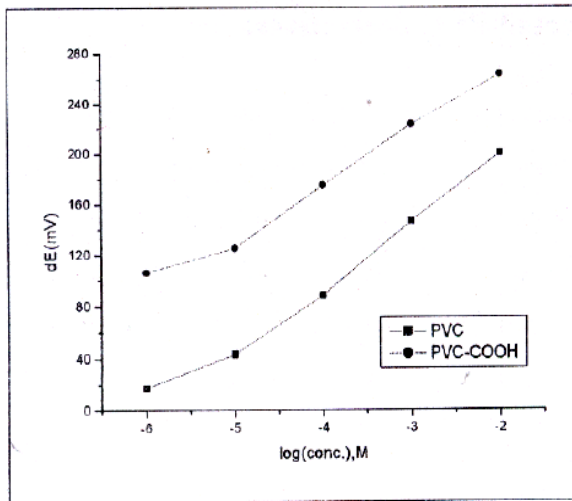**Fig. 11.** Effect of plasticizer on the response of sensor (III)

Fig.12. Effect of the PVC derivatives on the characteristics of the Ag sensor (III)
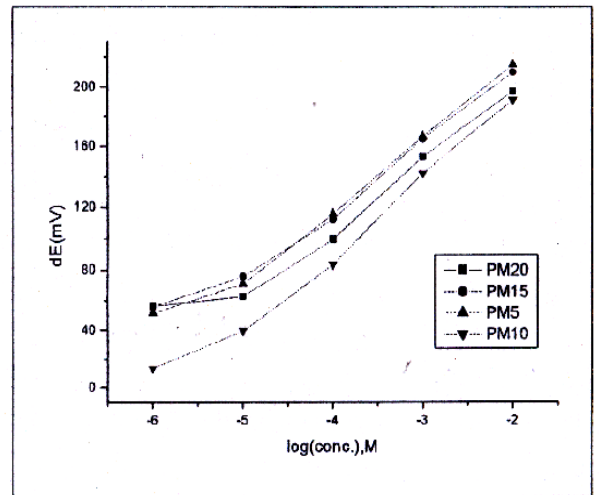
Fig.13. Effect of composition of ionophore (PM) on sensor (III)
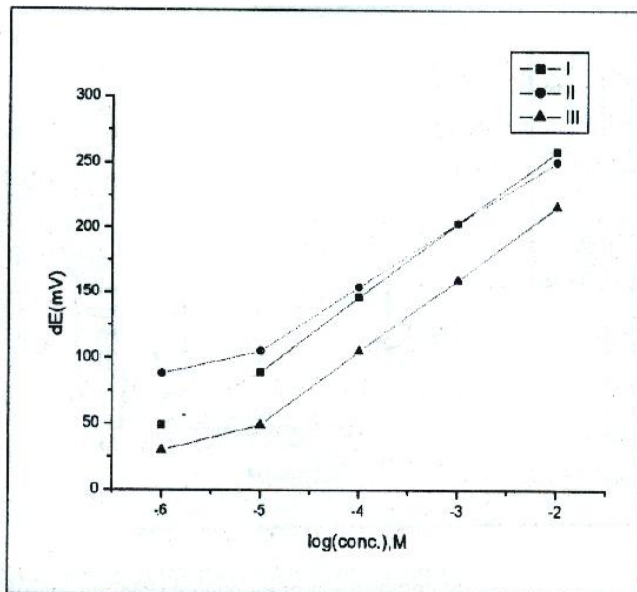
Fig. 14. Calibration curves for silver sensor based on (I),(II),(III) ionophores
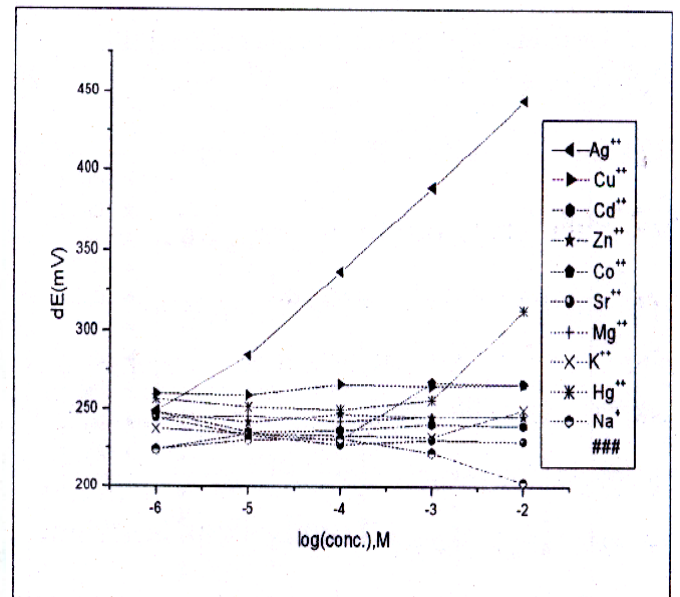
Fig. 15. Selectivity characteristics of sensor (I)
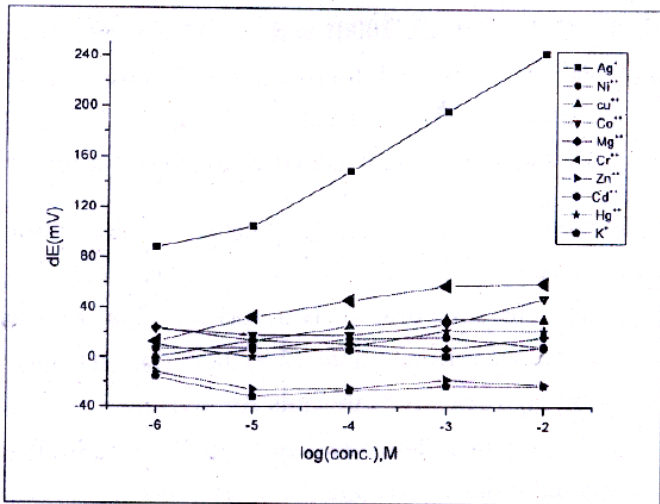
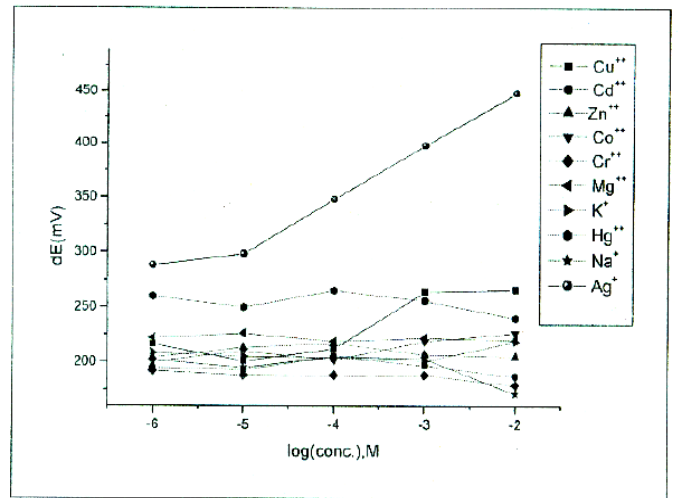**Fig. 16.** Selectivity characteristics of sensor (II).

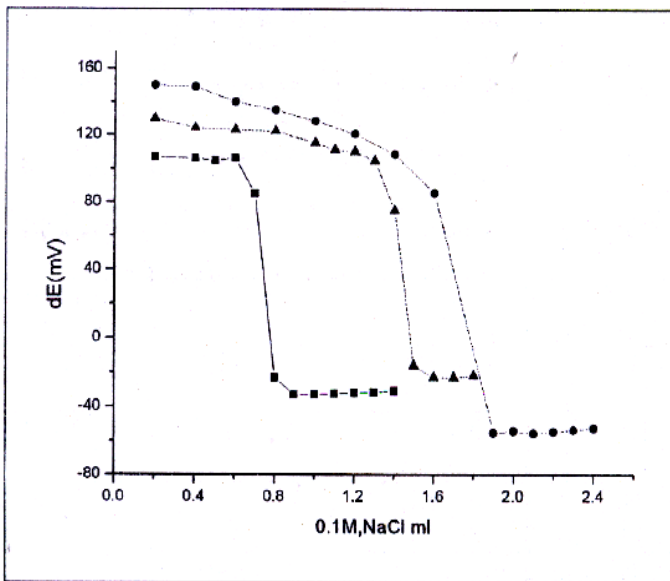**Fig. 17.** Selectivity characteristics of sensor (III).

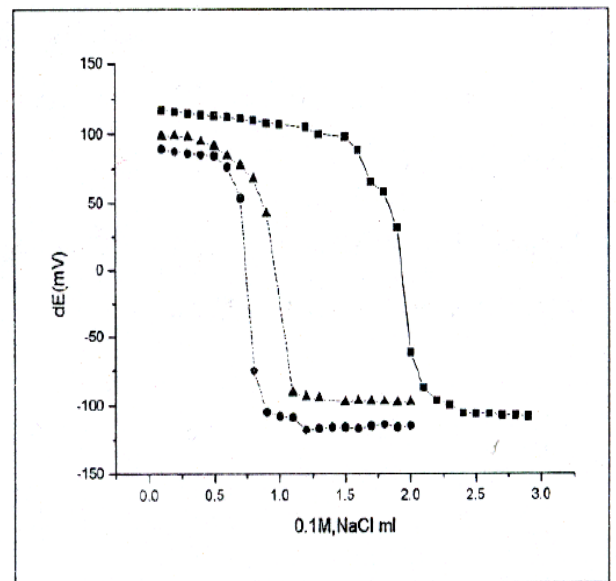**Fig. 18.** Typical potentiometric titration curves of AgNO₃. Based on sensor (I) with NaCl

Fig. 19. Potentiometric titration of Ag NO₃ using PVC membrane sensor based on sensor (II) with NaCl

Table .1. Characteristics of sensor based on ionophore (III) in KNO_3 and acetate buffer back grounds

PARAMETER	KNO3 pH = 5	Buffer Acetate pH = 5
Slope,(mV/decade)	55.2±0.2	52.1±0.2
Linear concentration range,(M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Lower limit of detection,(M)	3.8×10^{-6}	4.3×10^{-6}
Intercept,(mV)	315.2±1.0	325.26
Standard deviation	0.6	0.5
Correlation coefficient,(r)	0.99997	0.99998
Working pH,(pH)	5	5

Table .2. The effect of internal solution on the sensor (I)

PARAMETER	Int.Soln.10^{-2}	Int.Soln.10^{-3}	Int.Soln.10^{-4}
Slope,(mV/decade)	53.2	40	39.22
Linear concentration range,(M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Lower limit of detection,(M)	1×10^{-6}	4.2×10^{-6}	2.1×10^{-6}
Intercept,(mV)	330.7	266.5	265.82
Correlation coefficient,(r)	0.99994	0.99252	0.99233
Standard deviation	0.94	7.77	7.72

Table .3. The effect of concentration of internal solution on sensor (III)

PARAMETER	Int.soln. 10^{-2}	Int.soln.10^{-3}	Int. soln.10^{-4}
Slope,(mV/decade)	49.5± 0.1	44	39.5
Linear concentration range,(M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Intercept,(mV)	307	286	275
Lower limit of detection,(M)	4.9×10^{-6}	3.37×10^{-6}	2.2×10^{-6}
Correlation coefficient,(r)	0.99711	0.99845	0.99367
Standard deviation	5.36	3.87	7.07

Table .4. Effect of solvent mediators on the response of Ag$^+$ using sensor (I)

PARAMETER	Di octyl phthalate (DOP) $\varepsilon = 7$	2-nitrophenyl-octylether (NPOE) $\varepsilon = 24$
Slope, (mV/decade)	49.6	53.2
Linear concentration range, (M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Lower limit of detection, (M)	1×10^{-6}	1×10^{-6}
Intercept, (mV)	300	330.7
Standard deviation	5.10	0.94
Correlation coefficient, (r)	0.99798	0.99994

ε : dielectric constant

Table .5. The effect of plasticizers on sensor (III)

PARAMETER	DOP	NPOE	DBS
Slope, (mV/decade)	49±0.2	55.8±0.2	54.6±0.1
Linear concentration range, (M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Lower limit of detection, (M)	5.4×10^{-6}	5.5×10^{-6}	5.2×10^{-6}
Intercept, (mV)	384.4±0.9	368.8	371.1±0.5
Standard deviation	0.59	0.6	0.3
Correlation coefficient, (r)	0.99997	0.99997	0.99999

Table .6. Potentiometric response characteristics of sensors (I), (II) and (III)

PARAMETER	Ionophore (I)	Ionophore (II)	Ionophore (III)
Slope, (mV/decade)	56.7± 0.2	48.7± 0.1	55.5 ± 0.3
Linear concentration range, (M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Intercept, (mV)	372.7±0.6	348.7 ± 0.6	326.4±1.4
Lower limit of detection, (M)	5.75×10^{-6}	5.3×10^{-6}	3.5×10^{-6}
Working pH, (pH)	3.5 – 7	4.5 – 8	4 – 8
Response time, (s)	<10	<10	<20
Standard deviation	0.38	0.4	0. 86
Correlation coefficient, (r)	0.99999	0.99999	0.99995
Life span, (week)	6 weeks	4 weeks	4 weeks

Table .7. Potentiometric response characteristics of the sensor (III) with two different PVC derivatives

PARAMETER	(PM)-PVC-COOH	(PM)-PVC
Slope, (mV/decade)	52.7	46
Linear concentration range, (M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Lower limit of detection, (M)	4.3×10^{-6}	2.7×10^{-6}
Intercept, (mV)	304	358
Correlation coefficient, (r)	0.99864	0.99875
Standard deviation	4.35	3.66

Table .8. Effect of percentage of ionophore (III) on the composition of membrane

PARAMETER / Comp. %	2%	1.5%	1%	0.5%
Slope, (mV/decade)	45.53	45.43	51.3	48.16
Linear concentration range, (M)	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Intercept, (mV)	287	299.93	293.8	310
Lower limit of detection, (M)	7.2×10^{-6}	3.3×10^{-6}	3.2×10^{-6}	4×10^{-6}
Standard deviation	4.63	4.66	4.04	1.82
Correlation coefficient, (r)	0.99794	0.9979	0.99876	0.99971

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