

Synthesis of Calcium-Zincon Complex and Exploitation it in the Assembly of Calcium Ion-Selective Electrode.

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ARTICLE INFO

Received: 16 / 5 /2008
Accepted: 22 / 12 /2008
Available online: 19/7/2022
DOI: 10.37652/juaps.2009.15513

Keywords:

Calcium Ion-Selective Electrode (Ca-ISE), Zincon ,
Poly (vinyl chloride) (pvc) , Liquid ion exchanger ,
Neutral carriers, Tetra hydro furan (THF).

ABSTRACT

A new calcium ion-selective electrode was assembled from complex synthesized by calcium ion and zincon which doped in pvc with suitable mediator and solvent . The prepared complex was identified by UV- Visible and IR spectrophotometry. The new electrode was characterized by its high slope (29.55 ± 0.02 mV/decade) compared with calcium phosphate electrode (26.67 ± 0.022 mV/decade) and long lifetime (10 months) . The linear range of the electrode was 10⁻⁵-10⁻¹M and the detection limit was 10⁻⁵M . Response time was in the range of 20-60 seconds depending on the concentration of the solution and the lifetime of the electrode. The electrode was linearly working at a pH of (5-10).

Most of anions were severely interfered and these were exploited to determine calcium and the anions in precipitation titrations . Cations were slightly interfered especially at high interferent concentrations .

The new electrode was applied for the determination of calcium in tap water which offered excellent results compared with flame emission photometric method.

Introduction:

Most calcium ion-selective electrodes were based on liquid ion- exchanger(1) and neutral carrier systems(2). The best development of calcium ion-selective electrode was poly vinyl chloride (pvc) matrix incorporated with either liquid ion exchanger or neutral carrier ionophore(3). These essentially liquid based membranes were easily prepared by simple dissolving pvc in a solution of liquid ion exchanger or neutral carrier ionophore system in tetrahydrofuran and slowly evaporating at room temperature(4). These pvc matrices membrane ISEs possess similar response behaviour to their liquid membrane counterparts but much simpler design, the considerable economy in sensor materials and sometimes longer lifetimes are additional desirable features which have led to their more general use(5).

The plasticizing solvent mediators should be of high viscous for longer functional lifetime of electrodes and the nature of the solvent mediator itself can have significant influence on the selectivity of electroactive component(6). Most of these electrodes were applied in clinical analysis(7-9). The present work aims to prepare new electroactive material for calcium ion- selective electrode based on calcium complex rather than ion exchangers or neutral carriers . Zincon (1-(2-hydroxy-5-sulphophenyl)-3-phenyl-5-(2-carboxy phenyl)Formazan was known as Photometric reagent which forms stable complexes with rare earth and transition metals(10,11).

This ligand (zincon) is a tetra dentate chelating agent rich of electrons(12) which coordinate to metal ions (involving calcium) to form stable , conductive and sensitive complexes(13,14).

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Calcium-zincon complex has been prepared in this research and exploited to assemble a new membrane sensitive and selective to calcium ions.

Experimental:

All chemicals were A.R. grade. Double distilled water was used for the preparation of solutions. All measurements were carried out at room temperature .

Preparation of calcium – Zincon complex: The method of Gaber et al(15) was followed in the preparation of calcium – zincon complex with some modifications.

Therefore, equivalent amounts of calcium nitrate tetra hydrate (M.W=236.1) and zincon (M.W=480.43) in ethanol with drops of water were mixed in a soxhlet and refluxed for more than three hours. The modification was found out necessary to get sufficient amount of complex to prepare the membrane.

The solid complex was filtered , washed and dried in a desiccator containing silica gel.

IR identification of the zincon and Ca-zincon complex: IR spectra of zincon and the complex were measured in KBr discs using Philips PU 9706 IR Spectrophotometer in the range of 4000- 600 cm^{-1} on the same chart. (Table 1)

UV-visible analysis of zincon and complex: Small amounts of the complex and zincon were dissolved separately in ethanol and the UV- visible spectra were taken using 6405 JENWAY UV/visible spectrophotometer in the range of 200-800 nm against ethanol as a blank.

Determination the percentage of calcium in calcium-zincon complex: Accurate amount of Ca-zincon complex was boiled in water for half hour, the solution was cooled, and completed to the certain volume. A

series of calcium standard solutions were prepared in the range of (5-100) ppm and the atomic emission readings were taken by flame emission photometer from Barlowoird Scientific Ltd, for sample and standard solutions.

Preparation of the main membrane for Ca-ISE: The technique of Craggs et al.(16) was followed to prepare the main membrane of Ca-ISE by dissolving 0.04 g of Ca-zincon complex in 0.36 g of the plasticizer; O-Nitro phenyl phenyl ether. Another solution of 0.17 g of pvc (Breon 111 EP, BPchemicals International Ltd.) in 6.5 ml of tetra hydrofuran was prepared and both solutions were mixed together and transferred into a cylindrical glass casting resting on a smooth glass plate. The glass cylinder was covered with filter paper pad and held by suitable weights and left for 3 days for slow evaporation of the solvent at room temperature. The glass cylinder with adhering membrane was then carefully removed from the glass plate and inverted to allow any solvent remaining on the under surface to evaporate . The membrane was prised away from the inside edge of the ring ,wrapped in tissue paper and stored in a plastic container and kept in a refrigerator at 4o C .

Calcium ion-selective electrode assembly: A disc of 8mm diameter and 0.4mm thickness was cut by suitable porer and held to polyethane tube by adhesive of pvc in THF . The polyethane tube was filled with a mixture of 0.1M CaCl_2 and 0.1M KCl saturated with AgCl to form the internal reference solution. An Ag/AgCl electrode was inserted inside the internal solution and connected to a suitable cable to the ion-meter as shown in Fig(1).

Following the same procedure, another calcium-ISE was prepared using the electroactive material: calcium bis di(1,1,3,3-tetra methyl butyl phenyl

phosphate) in the same mediator (o-Nitro phenyl phenyl ether) for comparison and evaluation of the new electrode.

Calibration of the new electrode and calcium di phosphate electrode: A series of standard solutions containing different activities ranged from 10^{-6} – 10^{-1} M were prepared from calcium chloride di hydrated salt.

Another series of solutions containing different concentrations of calcium ions in 0.1M KNO₃ were prepared from the same salt. The calibrations were performed for the new electrode and di phosphate electrode to find out the performance of the electrodes. Calibrations were also done at different periods to know the lifetimes of the electrodes.

pH effect on the response of the new Ca-ISE: Tris(Hydroxy methylamino methane (Tris-Buffer) was used to prepare buffer solutions with pHs in the range of (1.5 – 12.5) applying hydrochloric acid and ammonia solutions for each calcium ion concentration ranged from 10^{-5} - 10^{-1} M. The potentials of the prepared buffer solutions were measured by new Ca- ISE relative to calomel reference electrode and plotted versus pH values.

Interference studies of anions and cations on calcium ion determination by the new Ca-ISE: Most of anions are severely interfered, since they form precipitate with calcium ions such as oxalate , carbonate, sulphate, phosphate and fluoride. However, the interference of these anions were exploited in determination of calcium and the corresponding anions by potentiometric precipitation titrations. Chloride and nitrate ions do not interfere, thus, calcium chloride and calcium nitrate solutions were used as standards for calibration of Ca-ISEs.

Mixed solutions method(17) was used to study the effect of a number of cations on the response and selectivity of the new Ca-ISE. The method involved constant activity of the interferent ion while variation the calcium ion activity in the range of (10^{-5} – 10^{-1})M. The following ions (Na⁺, K⁺, Mg⁺², Ba²⁺ , ,Fe³⁺ Al³⁺ , Hg²⁺ and Ni²⁺) were examined as interferents in the determination of calcium ions and selectivity coefficient

$$K_{Ca,M}^{pot} \text{ (Table 2)}$$

The potentiometric selectivity coefficients were calculated from the following relation: $a_{Ca^{2+}} = K_{Ca,M}^{pot} * (a_M)^{Z_M/Z_{Ca}}$ where $a_{Ca^{2+}}$ = the activity of calcium ions which was practically determined from the calibration curve (Fig.2) , a_M = activity of the interferent cation and Z_{Ca} and Z_M are charges of Ca⁺² and interferent cation respectively.

Applications of the new Ca-ISE:

1-Determination of calcium in drinking water: The calibration curve method was applied to determine calcium in drinking water of university quarter . The calibration curve was set up by plotting the recorded potentials against the log of calcium standard activities at pH 6 and conformable ionic strength of 0.1 for the sample and standard solutions. The concentrations of calcium in drinking water were picked up directly from the calibration curve.

2-Potentiometric titrations of some anions: The calcium ions were titrated with some anions including oxalate, carbonate, phosphate, sulphate and fluoride using different concentrations. A promising results were obtained where a clear, suitable and practical potential shifts were observed at equivalence points.

3-Potentiometric titrations: Potentiometric titrations in (2) were exploited to determine calcium in drinking

water. The determination was confined on the titration of calcium ions with oxalate ions and EDTA in basic medium ($\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ buffer is used to adjust the pH in the range of 8-10). The results are comparable to those obtained by flame emission photometry and calibration curve methods.

4-Gran's plot : Gran's plot was subduced also to determine calcium in drinking water(18). The method was a modification of potentiometric titrations and multiple standard addition methods. The technique involved plotting of antilog (E/S) instead of $E(S=\text{slope of the electrode response which}=2.303RT/2F)$ against multiple added volumes of standard calcium solutions to 50ml of drinking water after pH adjustment at 8. The results obtained have clarified also the little effect of cations interferences in drinking water on monitoring of calcium and confirmed the high selectivity of the new Ca-ISE. (Fig.10) ,(table 3).

Results and Discussion:

UV-Visible spectral analysis of zincon and its Ca-complex:

Three absorption maxima were observed in the zincon and Ca-zincon complex.⁽¹⁹⁾ The first absorption is due to $n \rightarrow \sigma^*$ electronic transition at 210 nm on oxygen $-\ddot{\text{O}}-$ and nitrogen $-\text{N}-$: where O-H and N-H in zincon become Ca-O and Ca-N in the complex and no change in absorption maximum. The second absorption is attributed to $\pi \rightarrow \pi^*$ electronic transition which requires lower energy in zincon at (300 nm) which shifts to shorter wavelength (280 nm) in complex as a result of localized penta and hexa rings formation in the complex. The third absorption is obtained at 540 nm in zincon as a result of $n \rightarrow \pi^*$ electronic transition which is shifted into 555 nm in the complex because of the ease

of excitation of n-electrons in the complex in the absence of the acidic hydrogen atoms (Fig.3).

2- IR spectra identification of zincon and Ca-zincon complex: Table (1) shows the sites of absorption spectral bands of positions groups in zincon and Ca-zincon complex.

It is clear from Table (1) that the stretching vibration absorptions of the functional groups are shifted to lower wave numbers which confirm the coordination of these groups in complex formation with calcium ions through these rich electron sites. The absence of δ OH for phenol group at 1320 cm^{-1} and carboxyl group at 1350 cm^{-1} indicates also that these two groups are participated in complex formation after replacement of hydrogen ions in phenol and carboxyl groups. The appearance of broad band at 3500 cm^{-1} represents the water absorption band in ligand and the complex (Figs 4 and 5).

3- Determination of calcium in the Ca-zincon complex:

The percentage of Ca in Ca-zincon complex was found to be 7.2% which is approximately equal the theoretical value. This percentage confirmed that the complex has comprised two water molecules in its structure which was confirmed also by IR broad band at 3500 cm^{-1} rendering the complex in the octahedral form (Figures: 4 and 5)

4- Calibration of the new Ca-ISE and compare it with the calcium diphosphate complex -electrode.

A calibration curves were set up for both electrodes and a linear range of $(10^{-5} - 10^{-1}) \text{ M}$ was obtained (Figs. 6 and 7).

The nernstian response for the new Ca-ISE was $29.55 \pm 0.02 \text{ mV/decade}$ and $26.27 \pm 0.022 \text{ mV/decade}$ for the di phosphate electrode. The slopes were gradually decreased and became $28.75 \pm 0.032 \text{ mV/decade}$ and $21.03 \pm 0.04 \text{ mV/decade}$ respectively after 10 months. Therefore, the lifetime of the new electrode is

approximately 10 months through them the electrode is functioning very well and offered encouraging and optimistic results.

The response time of the new electrode was in the range of 20-60 seconds depending on the solution concentration and electrode lifetime⁽²⁰⁾.

When the serial standard calcium solutions were prepared in 0.1 M KNO₃, the electrode became more sensitive and showed more stable measurements with simultaneous lowering in response time. These states were explained in the term of conformation of solutions ionic strength which showed rapid response of the electrode in addition to the lower detection limits (10⁻⁶ M)⁽²⁰⁾.

The response mechanism of the new electrode depends on the electronic conductivity of coordination sphere which is rich of electrons in addition to the ion exchange of calcium ions in the membrane with the corresponding calcium ion in the external solution that generates a potential directly proportional to the log activity or concentration of the calcium ions⁽²¹⁾.

5- pH effect on the response of the new Ca-ISE. The best pH for the linear response of the new Ca-ISE was found in the range of (5-10) where the electrode response was suitable and steady for most of calcium ion concentrations (Fig. 8). This range was diverged with more dilutions of concentrations where the response was affected by the extreme acidic and basic media. At pH above 10, the decrease in electrode response was due to the formation of Ca(OH)⁺ and Ca(OH)₂ precipitates. At pH less than 5 the elevation in electrode response was due to response of the electrode to hydrogen ions in addition to calcium ions⁽²²⁾.

6- Interference studies of cations on the response of new Ca-ISE. It was found in this study that there is no

interference of the cation: (Na⁺, K⁺, Mg⁺², Ba²⁺, Fe³⁺, Al³⁺, Hg²⁺ and Ni²⁺) on the response of the new Ca-ISE at low concentrations of these cations (10⁻⁵ – 10⁻³ M). At higher concentrations (10⁻² – 10⁻¹ M), the electrode has recorded rather little effect of some cations (Na⁺, K⁺, Mg⁺², Hg²⁺ and Ni²⁺) Table(2). However, the selectivity of the electrode was relatively high which was proved from the very low values of selectivity coefficients in the range of (6.31 * 10⁻⁴ – 2.5 * 10⁻¹) Table(2). The lower interferences exhibited in the presence of sodium ions has enabled the electrode to be applied twofold successfully in the biological researches and studies⁽⁵⁾.

6- Applications of the new Ca-ISE: The results of determination of calcium ions in drinking water of university quarter were compiled in Table(3).

In the calibration curve method, the concentration of calcium ions was picked up from the calibration graph and found matching the values obtained by flame emission photometry. The relative error of -0.51% was due to experimental errors. The precipitation titration of calcium ions in drinking water with oxalate ions offered a value of 98.1 ppm. The rather high relative error (+0.61%) was attributed to the solubility of calcium oxalate (0.00067 g/l at 25°C).

A satisfactory values of calcium ion concentrations (96.8 ppm) were obtained in the complexometric titration with EDTA compared to flame emission photometric method. The relative error was -0.72% which might be attributed also to experimental errors. The obtained Ca-EDTA complex was in the form of octahedral⁽²³⁾ because EDTA is hexadentate by two nitrogen atoms and four oxygen atoms (Fig.9).

Gran's plot offered excellent results of calcium ion concentrations (97.6 ppm) which were in good

agreement with the values obtained by flame emission photometry and proved the accuracy of the method.

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Table (1): IR spectra of zincon and Ca-zincon complex (wave number, Cm^{-1}).

Functional group	$\gamma_{\text{N-H}}$ (nm)	$\gamma_{\text{C=O}}$ (nm)	$\gamma_{\text{C=N}}$ (nm)	$\gamma_{\text{N=N}}$ (nm)
Zincon	3120	1670	1620	1540
Ca-zincon complex	3090	1650	1605	1525

Table (2): Selectivity coefficients of the new Ca-ISE in presence of various activities of some cations

$$K_{Ca,M}^{pot} = \frac{a_{Ca^{2+}}}{a_M^{(2/2m)}}$$

Interferent of cation	activity a_m (M) of interference	$a_{Ca^{2+}}$ from the graph	Selectivity coefficient
Na ⁺	10 ⁻²	2.5 X 10 ⁻⁵	2.5 X 10 ⁻⁵
	10 ⁻¹	5.1 X 10 ⁻⁵	5.1 X 10 ⁻³
K ⁺	10 ⁻²	1.88 X 10 ⁻⁵	1.88 X 10 ⁻¹
	10 ⁻¹	4.47 X 10 ⁻⁵	4.47 X 10 ⁻³
Mg ²⁺	10 ⁻²	5.8 X 10 ⁻⁵	5.8 X 10 ⁻³
	10 ⁻¹	1 X 10 ⁻⁴	1 X 10 ⁻³
Ni ²⁺	10 ⁻³	6.3 X 10 ⁻⁵	6.3 X 10 ⁻²
	10 ⁻²	1.26 X 10 ⁻⁴	1.26 X 10 ⁻²
	10 ⁻¹	1.59 X 10 ⁻⁴	1.59 X 10 ⁻³
Hg ²⁺	10 ⁻²	5.5 X 10 ⁻⁵	5.5 X 10 ⁻³
	10 ⁻¹	6.31 X 10 ⁻⁵	6.31 X 10 ⁻⁴
Al ³⁺ , Fe ³⁺	10 ⁻⁵ -10 ⁻¹	No interference	

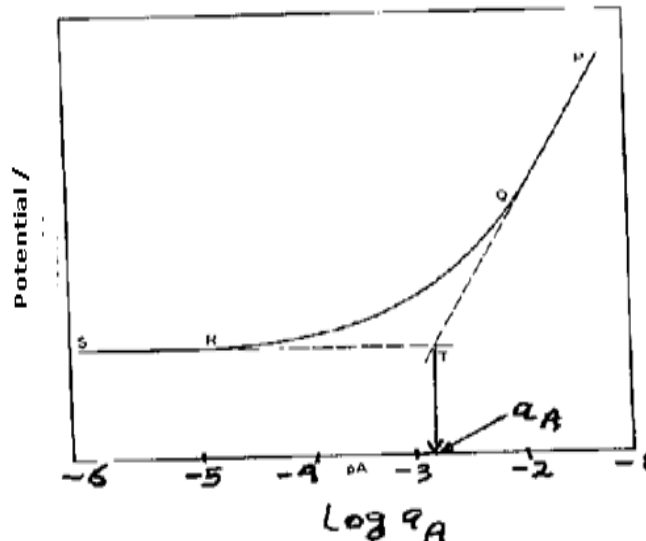


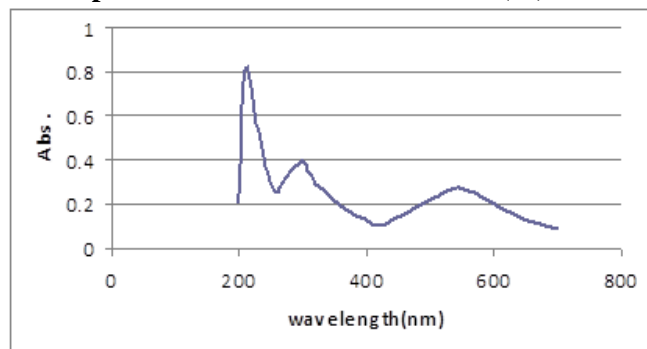
Fig (2) : Calibration curve of the new Ca- ISE in the presence of the intrferent cation (M) .

Table (3): Calcium ion concentration in drinking water of University Quarter (in ppm).

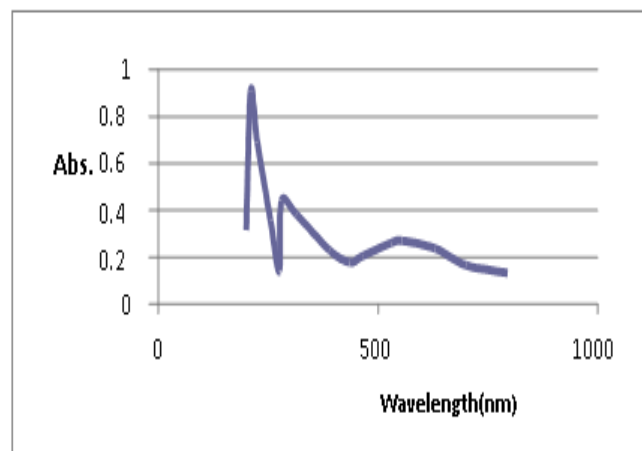
Method of analysis	Ca concentration	Relative error%
Flame emission photometry	97.5	reference value
Calibration curve	97.0	-0.51
Titration with oxalate	98.1	+0.62
Titration with EDTA	96.8	-0.72
<p>Gran's plot</p>	97.6	+0.10

Each value in the Table(3) was an average of at least three measurements of the sample. Average coefficient of variation (c.v.) in each method is within the range of 1.45-3.45%. Correlation coefficient of the linear range was 0.996.

Fig (1): Calcium ion- selective electrode assembly .



(A)



(B)

Fig (3) : Uv – Visible spectra of zincon and its complex with calcium .

(A) : spectrum of zincon in ethanol .

(B) : spectrum of Ca - zincon complex in ethanol .

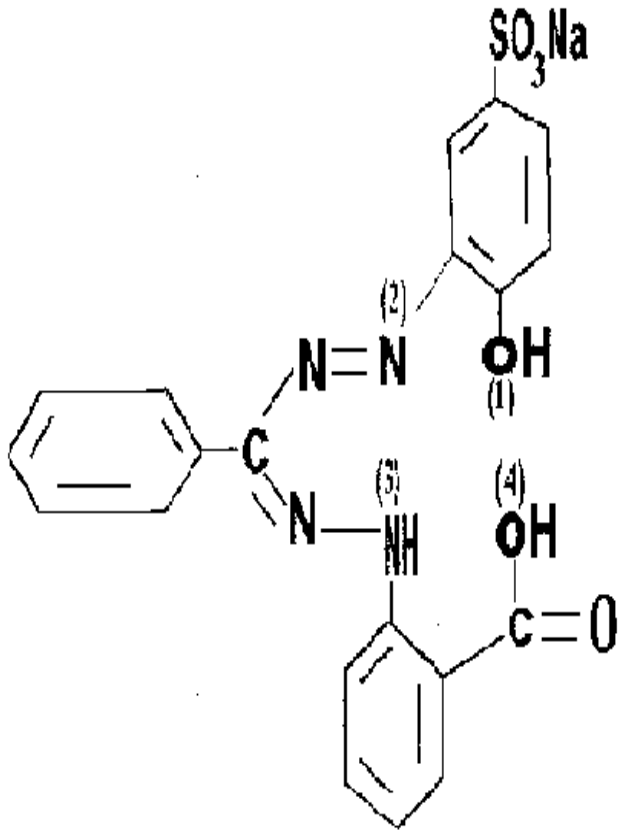


Fig (4) : Structure of formula of zincon as sodium salt.

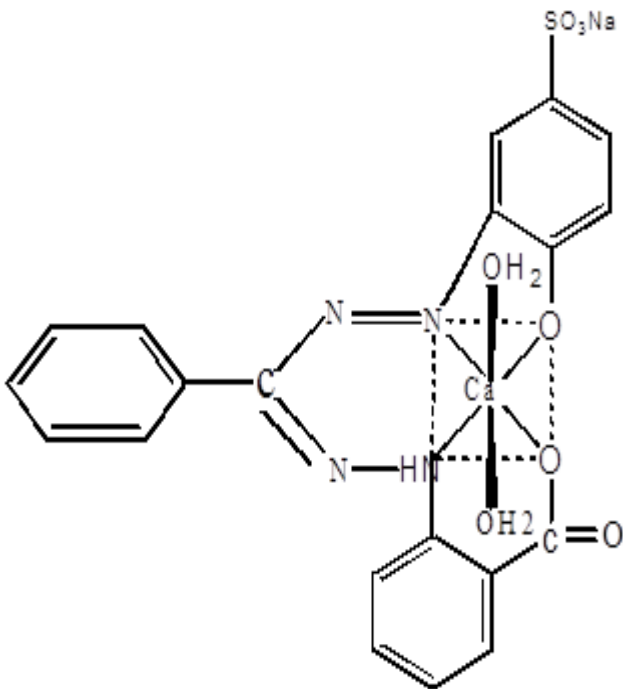


Fig (5) : Octahedral form of Ca- Zincon complex .

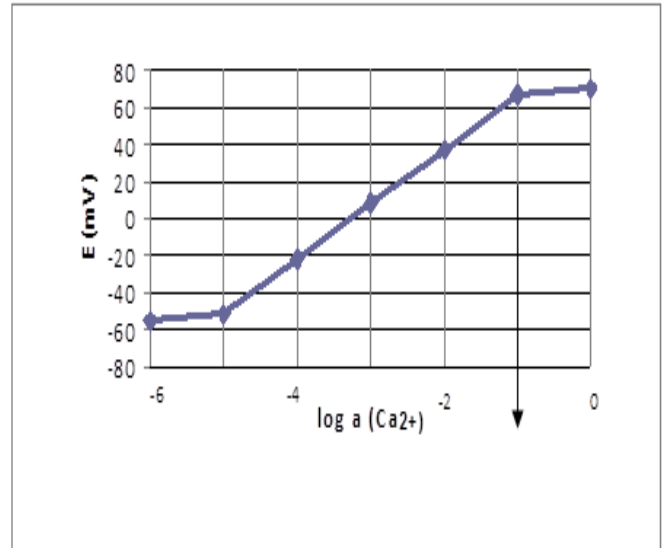


Fig (6) : Calibration curve of new Ca- ISE in the first week of its use .

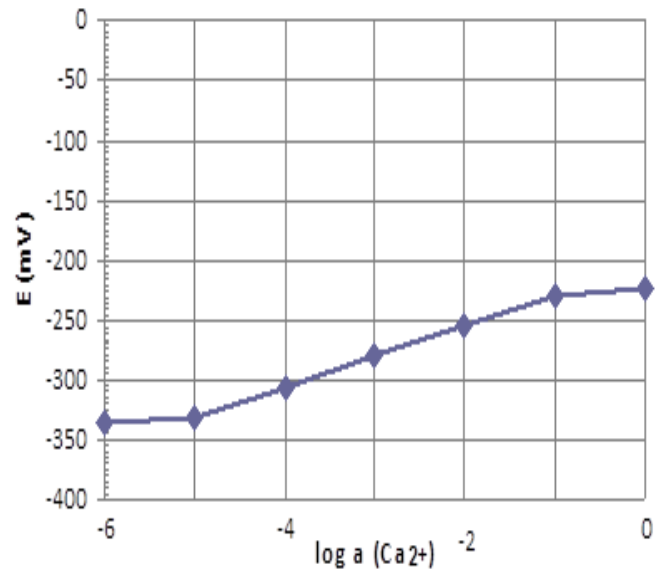


Fig (7) : Calibration curve of Calcium diphosphate- ISE in the first week of its use .

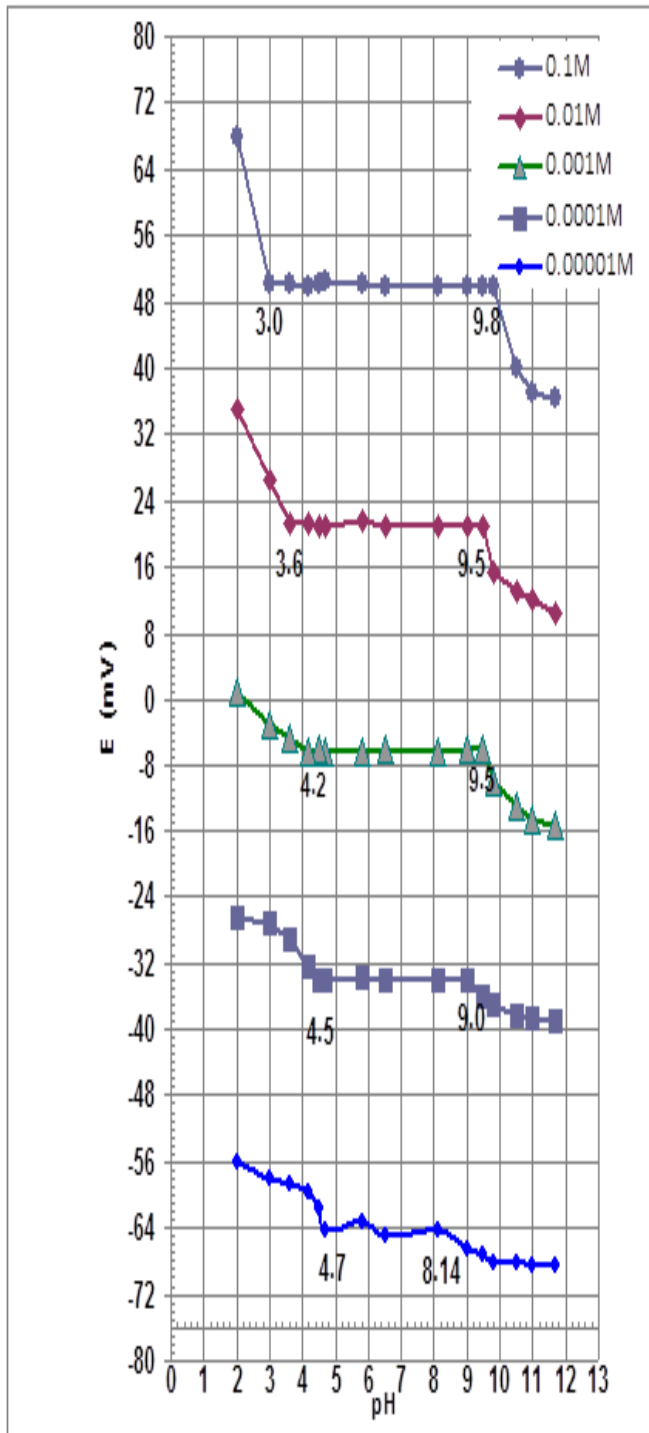


Fig (8) : Effect of of pH on the linear range of the new Ca – ISE .

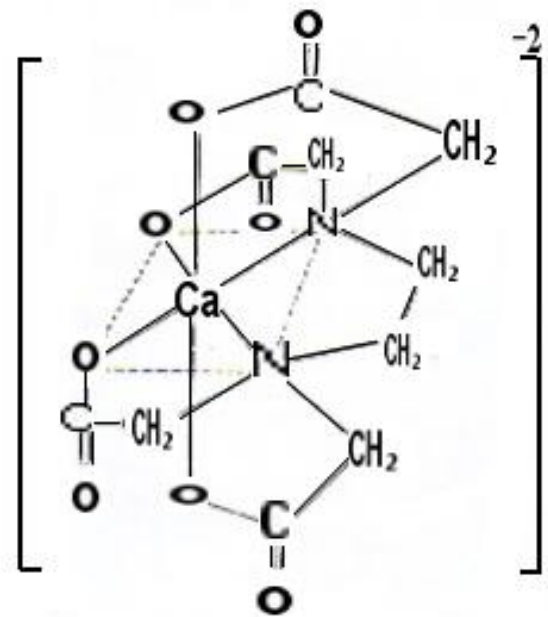


Fig (9) : Schematic diagram of Ca – EDTA complex in basic medium .

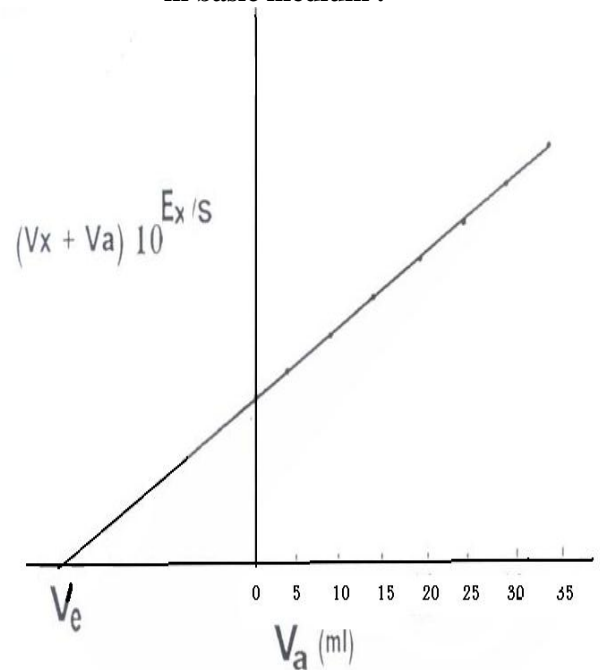


Fig (10) : Typical Gran ,s plot for calcium detrmnation in tap water .

تحضير معقد الكالسيوم زنكون واستثماره في تصنيع قطب الكالسيوم الانتقائي

خميس احمد العيساوي

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اسماعيل خليل الهيتي

صمم في هذا البحث قطب جديد نو عشاء انتقائي لايون الكالسيوم من معقد ايون الكالسيوم مع الزنكون المدمج مع مادة ملدنة ومذيب مناسب. وشخص المعقد الناتج بمطيفية الاشعة فوق البنفسجية والمرئية والاشعة تحت الحمراء. وقد تميز القطب الجديد بميله النيرنستي الكبير (29.55 ± 0.02 mV/decade) مقارنة بميل قطب الكالسيوم ثنائي الفوسفات (26.67 ± 0.022 mV /decade) فضلا عن عمره الطويل (١٠ شهر). اما الاستجابة الخطية للقطب الجديد لايون الكالسيوم فكانت ضمن المدى 10^{-5} – 10^{-1} مولاري وحد الكشف عن ايون الكالسيوم كان 10^{-5} مولاري، اما زمن استجابة القطب الجديد فتراوحت بين ٢٠ – ٦٠ ثانية اعتمادا على تركيز المحلول وعمر القطب.

اما مدى pH الذي يعمل فيه القطب بدون تداخل فهو (٥ – ١٠). تتداخل معظم الايونات السالبة وقد استثمر هذا التداخل بتقدير ايون الكالسيوم والايون السالب في تسحيحات الترسيب ، اما الايونات الموجبة فابدت تداخلات قليلة لاسيما في تراكيزها العالية . وقد استعمل قطب الكالسيوم الجديد في تقدير ايون الكالسيوم في مياه الشرب بالطرق الجهدية المختلفة حيث اعطى نتائج ممتازة مقارنة بطريقة الانبعاث الذري اللهيبي .