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CALCIUM ION SELECTIVE ELECTRODE BASED ON POLYURETHANE NANOFIBRES IONOPHORE &ITS ANALYTICAL APPLICATION.

Chemistry

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ABSTRACT

A new, efficient Calcium ion selective electrode has been prepared using Polyurethane nanofibre based ionophore.The prepared ionophore is characterized by UV, FT-IR, XRD.. The sensor exhibits a near Nernstian response for Ca(II) ion over a concentration range of 1.0 X 10-8 M to1.0 M. The proposed sensors revealed relatively good selectivity and high sensitivity for Ca(II) over a monovalent cations. It can be used with in the pH range of 5.57 to 6.24. The effect of medium and the selectivity coefficient values was evaluated using fixed interference method.. It was also successfully used in the analysis of concentration of Calcium ion in various real samples.

KEYWORDS:

Calcium (II), Polyurethane nanofibre, Potentiometry, Selectivity coefficient,

1.Introduction:-

The introduction of new ion-selective electrodes has played a fundamental role in the development of various sensory elements according to the charge and size of the target ion in clinical and environmental assays[1-8]. Potentiometric methods using ISEs for determining the metal ion have been studied extensively due to their importance in biological process[9], easy handling, nondestructive analysis and in expensive sample preparation, applicability to coloured sample and turbid solution. Calcium is the major element in the body. It plays a Vital role in the formation of bone,neuro muscular function, coagulation&membrane permeability.In plants it helps in transpiration which leads to growth of the plant.

A new calixarene based Ca-ISE that has preferential selectivity to calcium ions was developed by Mckittrick et al; in 1996.A Photocured membrane selective to calcium, based on the calcium ions bis[4-(1,1,3, 3-tetramethylbutyl) phenyl]phosphate ionophore with the lipophilic additive was developed by Di Benedetto et al; in 1997.In 2001 Lindfors and Ivaska developed Ca^{2+}selective electrode based on Polyaniline (PANI)-based membrane.

Taking into consideration of all the above facts that a new simple ionophore such as polyureth ane nanofibres have been used as an electroactive phase for the fabrication of Ca^{2+} ion selective electrodes. In the present study the electrode show good selectivity and reproducibility over Ca^{2+} ion and the results are presented in this paper.

2. Experimental Method

2.1 Chemicals used:

Polyurethane, Reagent grade tetrapropyl ammonium bromide, tetrahydrofuran, Ethyl acetate, Dimethyl Acetamide,DMF, Dioctyl phthalate (DOP), sodium tetra phenyl borate (NATBP), tetra hydro furan (THF) were obtained from E.Merck and can be used without further purification. Throughout double distilled ionized water used.

2.2 Synthesis of ionophore(Polyurethane fibres)&Fabrication of the electrode:

0.4g of Polyurethane was dissolved in 2 ml of DMF, the solution was kept overnight in stirring to obtain a homogeneous solution. Then it was subject to electrospinning process at room temperature of 25^0C.The fibres were coated on copper wire that was polished and irradiated using UV light.

Condition involving electrospinning of Polyurethane:

Conditions	Optimum condition used in this study
Polymer concentration	12 Wt%
Volume flow rate	2 ml/hr
Tip to collector distance	20 cm
Electrical Voltage	24KV
Needle Size	24 gauge

2.3 Physical measurements:

For recording UV&Visible spectrum PC based UV double beam spectrometer 2202 was used.FT-IR spctra were recorded on a FT-IR spectrometer. (model Shimadzu prestige-21 series) EIS was carried out using Solatron SI 1280B frequency response analyser.The surface morphology of the Copper wire was investigated by Scanning Electron microscopy(SEM)using FEI Quanta 3D FEG focused on ion beam/scanning electron microscope.

In UV spectrum the peak at 221nm corresponds to CN group (Pavianet al; 2001)-fig-1

In FT-IR Polyurethane are shown in fig-2

The peak at 1720 Cm^{-1} corresponds to the Carbonyl frequency&the peak at 3325Cm^{-1} attributed to the NH stretching vibration.The C-H group frequency was observed in the region of 2964 Cm^{-1} (Silverstein et al; 2005).

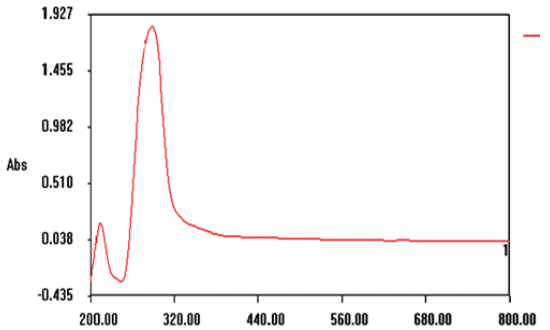

Fig-1-UV SPECTRUM OF THE IONOPHORE

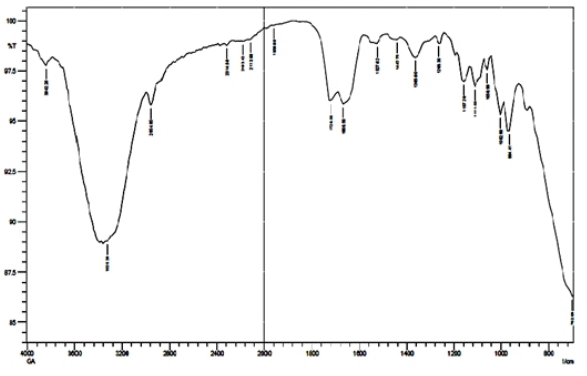

Fig-2-FT-IR SPECTRUM OF THE POLYURETHANE

2.4 potential measurements:

All the membrane electrode potential measurements were performed at constant temperature (30^0 C) using digital potentiometer (EQUIP-TRONICS EQ 602) in configuration with silver electrode as a reference electrode. The representation of electrochemical cell for the EMF measurement is as follows.

Internal Reference Electrode(immobilise dCu wire)	Internal Reference(1M $CaCl_2$ Solution)	External Reference Electrode (Ag/AgCl)

3. Results and Discussion:

3.1 working concentration range and slope of Ca^{2+} sensor:

ELECTRODE RESPONSE:

The electrode potential for a series of standard solution of Ca(II) ions was measured using potentiometer. The electrode gave a linear response to Ca(II) ion concentration range of 1M to $1x10^{-8}$M.The values are given in Table-1.Standard Electrode potential(E^0) was determined by standard methods (Gurtu and Gurtu,2011) at 25^0C,it was found to be 0.0175V.The slope value was obtained from the calibration curve fig-3 &it was found to be 22 mv/decade.

ELECTRODE RESPONSE
TABLE – 1

Concentration of $CaCl_2$ (M)	EMF(Half Cell Potential) volts
1	0.08
$1x10^{-1}$	0.039
$1x10^{-2}$	-0.025
$1x10^{-3}$	-0.048
$1x10^{-4}$	-0.064
$1x10^{-5}$	-0.076
$1x10^{-6}$	-0.095
$1x10^{-7}$	-0.097
$1x10^{-8}$	-0.102

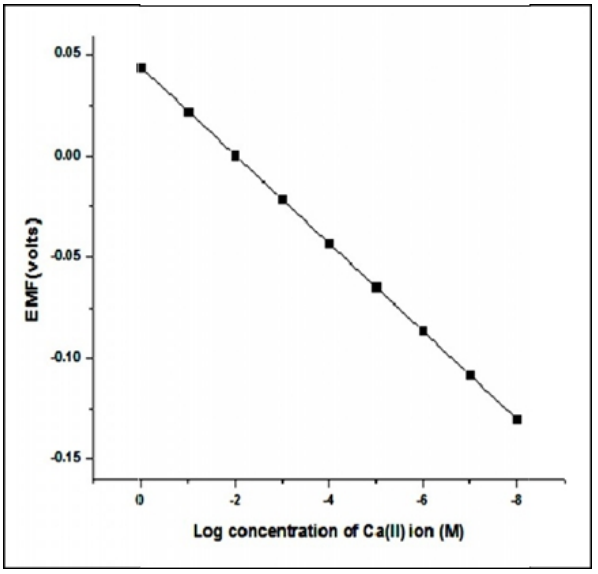

Fig-3-ELECTRODE RESPONSE

3.2 EFFECT OF pH ON ELECTRODE RESPONSE

The effect of pH on the response of electrode was studied in this work. The electrode potential of standard Ca(II) solution of varying pH had been measured. It was found that the electrode worked well over a pH range of 3.42to 4.63 Table-2

Table – 2 Effect of pH

Conc (M) of Ca^{2+} ion	E.M.F (Half cell potential) Volts	P^H 3.42	P^H 4.63	P^H 5.57	P^H 6.24
1	0.08	0.076	0.078	0.079	0.083
$1x10^{-1}$	0.039	0.029	0.031	0.034	0.037
$1x10^{-2}$	-0.025	-0.030	-0.027	-0.026	-0.024
$1x10^{-3}$	-0.048	-0.052	-0.049	-0.046	-0.043
$1x10^{-4}$	-0.064	-0.067	-0.065	-0.063	-0.061
1x10-5	-0.076	-0.079	-0.077	-0.071	-0.064
1x10-6	-0.095	-0.100	-0.097	-0.094	-0.091
1x10-7	-0.097	-0.098	-0.096	-0.085	-0.087
1x10-8	-0.102	-0.098	-0.089	-0.075	-0.089

3.3 Effect of Medium: Table-3

The influence of the electrode was also investigated in a partially non-aqueous media using 25-75% water-acetone,water- DMA, & water-ehanol. The working non-aqueous media of the electrode was found to be 25% 50%acetone medium,50%&75% DMA medium&50% of ethanol medium in the conc of 10^{-8}M Ca^{2+} ion.25% of DMF medium in the concentration range of 10^{-8}M of Ca^{2+} ion.

Table-3

Conc. Ca^{2+} Solution(M)	E.M.F (Volts)	Acetone 25%	Acetone 50%	Ethanol 50%	Ethanol 75%	DMA 50%	DMA 75%	DMF 25%
1	0.08	0.079	0.082	0.079	0.077	0.077	0.079	0.085
$1x10^{-1}$	0.039	0.031	0.042	-0.042	0.041	0.035	0.037	0.037
$1x10^{-2}$	-0.025	-0.025	-0.021	-0.027	-0.025	-0.027	-0.025	-0.024
$1x10^{-3}$	-0.048	-0.047	-0.035	-0.059	-0.057	-0.055	-0.049	-0.045
$1x10^{-4}$	-0.064	-0.065	-0.059	-0.067	-0.066	-0.071	-0.069	0.066
1x10-5	-0.076	-0.080	-0.079	-0.080	-0.086	-0.079	-0.078	-0.075
1x10-6	-0.095	-0.091	-0.085	-0.095	-0.092	-0.094	-0.097	-0.094
1x10-7	-0.097	-0.095	-0.096	-0.099	-0.098	-0.098	-0.1	-0.097
1x10-8	-0.102	-0.096	-0.099	-0.101	-0.1	-0.099	-0.101	-0.099

3.4 Selectivity: Table-4

The potential response of the prospoed electrode to common cations were investigated by fixed interference method. It was found that the potential remains unaffected in the presence of Na^+&K^+ cation.

Table-4

CATIONS	SELECTIVITY CO-EFFICIENT VALUES
Na+	$9X10^{-5}$
K+	$1x10^{-5}$

5.Analytical applications:

The new prepared electrode was successfully used in determination of calcium ion real samples like milk, Pharmaceutical analysis (Shelcal Tablet),hardeness of Water &blood sample analysis. It is also used as an indicator electrode for EDTA titration(fig-4) with Ca^{2+} ions in the laboratory.

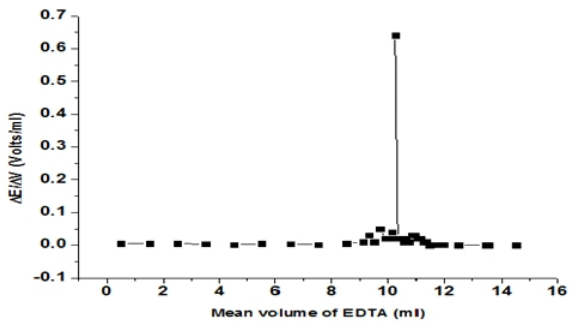

FIG-4-EDTA TITRATION WITH Ca2+ ion

6.Conclusion:

A new simple, highly specific & selective calcium ion electrode has been prepared. The life time of the prepared electrode was found to be 5 months with good reproducibility of E.M.F values.

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