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Calcium ion Selective Electrode Based on Acyclic Polyether Based Ionophore & its Analytical Application

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Abstract

A new, efficient Calcium ion selective electrode has been prepared using acyclic polyether based ionophore. The prepared ionophore is characterized by UV, FT-IR, XRD. Electrochemical impedance spectroscopy (EIS) technique is also employed to study the electrochemical & surfacereactions. The sensor exhibits a near Nernstian response for Ca(II) ion over a concentration range of 1.0 X 10^{-4}M to1.0 M. The proposed sensors revealed relatively good selectivity and high sensitivity for Ca(II) over a mono and divalent cations. It can be used with in the pH range of 3.42 to 6.24 . The effect of medium and the selectivity coefficient values was evaluated using fixed interference method found to give a better response. The influence of temperature on electrode potential was studied & it can be used in the determination of thermodynamic functions like ΔG, ΔH & ΔS. It was also successfully used in the analysis of concentration of Calcium ion in various real samples.

Key words: Calcium (II), Acyclic Polyether, Potentiometry, Selectivity coefficient, Electrochemical impedance spectroscopy.

1. Introduction

The introduction of new ion-selective membrane electrodes has played a fundamental role in the development of various sensory elements according to the charge and size of the target ionin 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[9,10], 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 & membranepermeability. In plants it helps in transpiration which leads to growth

of the plant.

Ross developed (1967) the first Calcium ion-selective electrode for clinical purposes. The development of PVC membrane techonology (Shatkay, 1967), *i.e*, immobilization of an active agent in a poly (vinyl) matrix allowed electrodes with longer life time to be manufactured & made clinical analysis. Simon *et al*. & Amman *et al.* (1972) developed the neutral carrier ionophore.

Taking into consideration of all the above facts that a new simple ionophoresuch as acyclic polyether 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

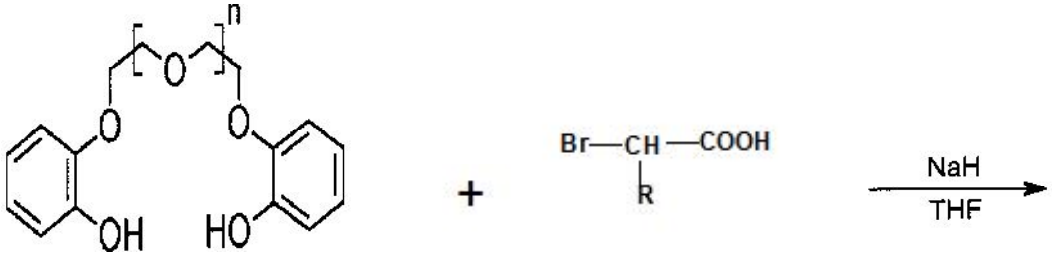
2.1 Chemicals used:

NaH, Bisphenol A, Reagent grade bromoproponicacid, tetrahydrofuran, Ethylacetate, methylene chloride, 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.

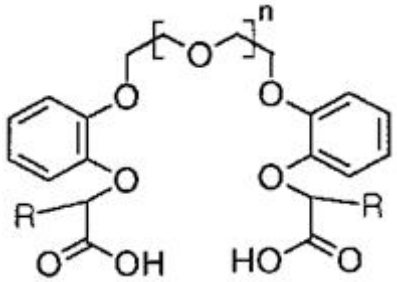
2.3 synthesis of Ionophore:

NaH (53% dispered in mineral oil) present in the mineral oil was removed by using nitrogen atmosphere. A solution of Bisphenol A was prepared by 7.861g bisphenol A is mixed with 150 ml of dry tetrahydrofuran & the solution was added to the above solution.13.2 ml of 2-bromoproponic acid was added dropwise to the reaction mixture & it was stirred for 2 hour at room temperature, after the addition of acid, the mixture was stirred for 10h at room temperature. Then 9 ml of water is added carefully to the above mixture & ice bath is maintained to destroy the unreacted excess NaH, it have a homogeneous solution. The aqueous layer was separated & yhe solution was poured into 50 ml of ethyl acetate, to remove unreacted bisphenol A & organicimpurities. The aqueous layer was washed with ethyl acetate. It was acidified with Conc. HCl to pH 1, then the crude was extracted with methylene chloride. The methylene chloride solution was dried over MgSO4&evaporated in vacuum. The colourless oil was obtained, which was recrystallized from 50 ml of diethyl ether to give white crystals.

The yield is 1g, Melting point is 1920C The synthetic route for the preparation of acyclic polyether di carboxylic acid is shown below (Kim *et al*, 1999).



Bisphenol A **R: 2-bromoproponicacid**



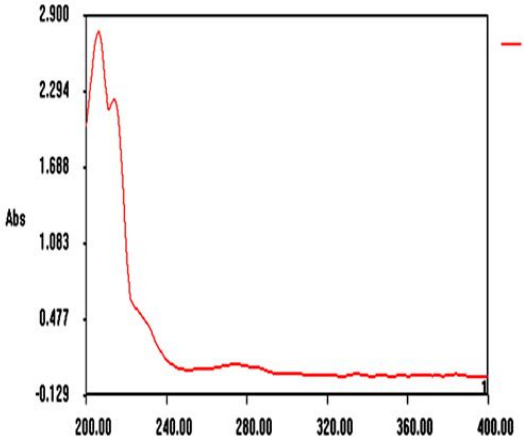
Acyclic polyether dicarboxylic acid

2.2 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)X-ray diffraction (XRD) analysis was carried out using PAN analytical x-Pert pro diffractometer from CuKα radiation(X-Ray tube PW 3050/60), EIS was carried out using Solatron SI 1280B frequency response analyser.

In UV spectrum the peak at 214nm corresponds to π-π * of C=O group (Pavian *et al.*; 2001)-fig-1 In FT-IR the peak at 1627 Cm-1 attributed to the presence of C=O. (Silverstein *et al.*; 2005) The –OH group frequency was beserved in 336 cm-1- fig-2.

From X-ray diffraction study the composition was found to be $C_4 H_{62}\cdot_4 O_{23}$-fig-3



Wave number cm-1

Fig-1-UV –Spectrum of Acylic polyether

2.3. Synthesis of ionophore:

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The yield is 1g,Melting point is 192^{0}C

2.4 Fabrication of Ion selective electrode:

A copper wire was polished with emery paper &it was washed with distilled water&THF.The copper was dipped into the concentrated solution (0.3g of ionophore+0.1g of DOP+PVC+3 ml of THF) for some minutes, so that a non-transparent coating was formed.The wire was taken out from the mixture and dried overnight. The electrode was finally conditioned to attain stable equilibrium for 10 days by dipping in 1M$CaCl_2$.

2.5 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.

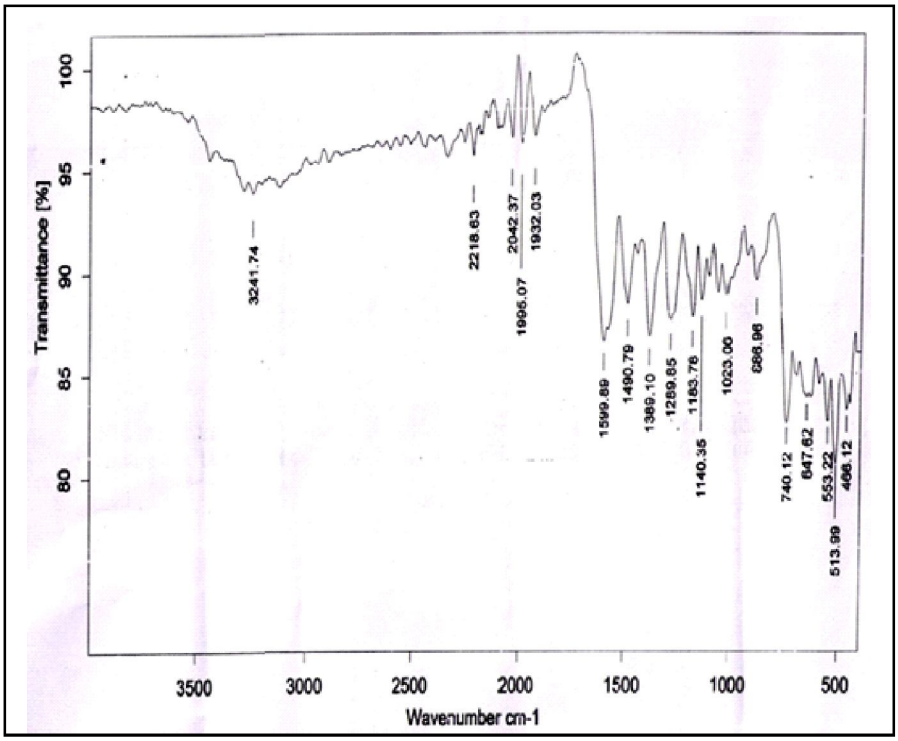

Fig-2-IR- Spectrum of the ionophore

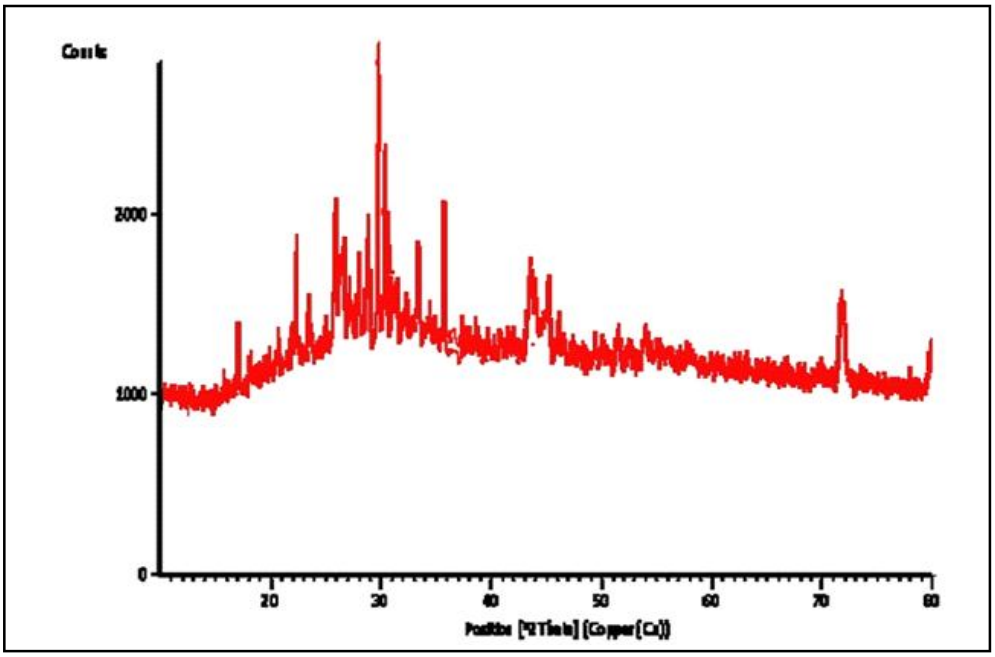

Fig-3-XRD pattern of the ionophore

Internal Reference Electrode (immobilized Cu 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:

0.3 g of ionophore & predetermined ratio of DOP was dissolved in 3 ml of THF and copper wire was dipped in different time interval. 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 $1x10^{-4}$ 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 -0.029V. The slope value was obtained from the calibration curve fig-4 & it was found to be 31 mv/decade.

Electrode Response

Table 1

Concentration of $CaCl_2$ (M)	EMF (Half Cell Potential) volts
1	-0.002
$1x10^{-1}$	-0.059
$1x10^{-2}$	-0.112
$1x10^{-3}$	-0.136
$1x10^{-4}$	-0.156
$1x10^{-5}$	-0.156

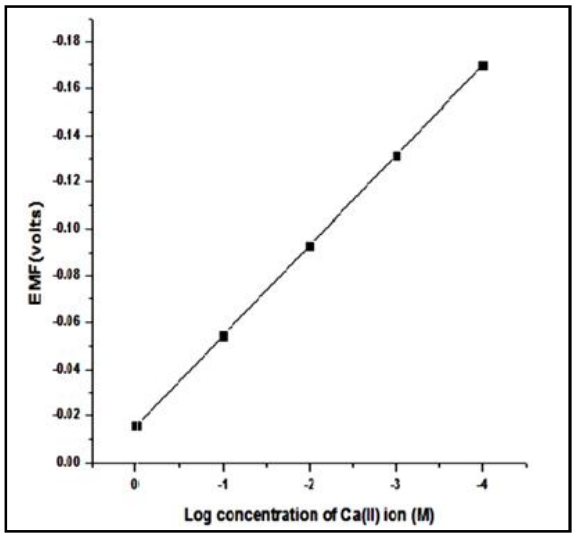

Fig-4-Electrode Response

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 workedwell over a wide pH range of 3.42 to 6.24. Table-2.

3.3 Effect of Medium: Table-3

The influence of the electrode was also-ninvestigated in a partially non-aqueous media using 25-75% water-acetone, water-DMA, & water-DMF. The working non-aqueous media of the electrode was found to be 50%&75%acetone medium in the concentration range of 10^{-2}M of Ca^{2+} ion, 25%, 50% of DMA medium in the concentration range of 10^{-2}M of Ca^{2+} ion,25%,50%,75% of DMF medium in the concentration range of 10^{-3}M of Ca^{2+} ion.

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	-0.002	-0.003	-0.005	-0.001	-0.003
$1x10^{-1}$	-0.059	-0.059	-0.061	-0.060	-0.058
$1x10^{-2}$	-0.112	-0.113	-0.114	-0.113	0.111
$1x10^{-3}$	-0.136	-0.130	-0.132	-0.135	-0.136
$1x10^{-4}$	-0.156	-0.158	-0.157	-0.155	-0.154

Table 3

Conc.Ca^{2+} Solution(M)	E.M.F (Volts)	Acetone 25%	Acetone 50%	Acetone 75%	DMF 25%	DMF 25%	DMF 75%	DMA 25%	DMA 50%	DMA 75%
1	-0.002	-0.003	-0.004	-0.002	-0.004	-0.002	-0.003	-0.005	-0.002	-0.012
$1x10^{-1}$	-0.059	-0.079	-0.056	-0.055	-0.059	-0.054	-0.057	-0.055	-0.065	-0.076
$1x10^{-2}$	-0.112	-0.112	-0.121	-0.120	-0.109	-0.131	-0.131	-0.116	-0.110	-0.109
$1x10^{-3}$	-0.136	-0.135	-0.151	-0.153	-0.140	-0.155	-0.156	-0.136	-0.139	-0.139
$1x10^{-4}$	-0.156	-0.156	-0.151	-0.155	-0.140	-0.156	-0.166	-0.166	-0.140	-0.168

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. The negative selectivity co-efficient values indicative better selectivity of the electrode over other ions (Farzad Deyhimi,1999).

Table 4

CATIONS	SELECTIVITY CO-EFFICIENT VALUES
Na+	$-3.2X10^{-5}$
K+	$-9.6x10^{-5}$

4. Temperaturestudy: The E.M.F values of Calcium ion selective electrode using the cell, Ca, Caionophore//Ag/AgCl was measured at different temperature ranging from 5-40^{0}C &Tabulated in Table-5

Table 5. Effect of Temperature on Calcium- ion Selective Electrode

MEDIUM	278K	283K	288K	293K	298K	303K	308K	313K	$(\partial E/\partial T)p$ V/K^0
Aqueous	0.183	0.188	0.199	0.209	0.219	0.224	0.229	0.234	0.0012
Aqueous+50% acetone	0.175	0.179	0.190	0.197	0.207	0.217	0.227	0.234	0.0016
Aqueous+75% acetone	0.182	0.187	0.197	0.205	0.218	0.226	0.229	0.235	0.0014
Aqueous+25% DMA	0.188	0.193	0.205	0.213	0.227	0.234	0.244	0.251	0.0017
Aqueous+50% DMA	0.185	0.189	0.197	0.207	0.217	0.220	0.227	0.232	0.0013
Aqueous+25% DMF	0.181	0.186	0.197	0.207	0.218	0.220	0.227	0.232	0.0014
50%DMF	0.183	0.189	0.199	0.205	0.219	0.225	0.229	0.236	0.0014
75%DMF	0.187	0.190	0.195	0.208	0.218	0.225	0.230	0.237	0.0014
Aqueous+ pH3.43	0.200	0.208	0.212	0.219	0.225	0.229	0.231	0.235	0.0009
pH4.64	0.203	0.209	0.214	0.220	0.226	0.231	0.235	0.239	0.001
pH5.54	0.205	0.211	0.215	0.222	0.228	0.233	0.239	0.241	0.0015
pH6.24	0.207	0.213	0.216	0.224	0.230	0.235	0.239	0.247	0.0013

The relation was linear in all the cases in accordance with the equation

$$E=-\Delta H/nF+T(\partial E/\partial T)p$$

The value of Temperature co-efficient $(\partial E/\partial T)p$ in Table-5 have been used in the calculation of $\Delta G,\Delta H,\Delta S$ at 5-40^{0}C for the calcium ion selective electrode &the results are presented in Table 6.

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Table 6. Thermodynamic parameter values of ΔG, ΔH & ΔS

MEDIUM	-ΔG K.cal/mole	ΔH K.cal/mole	ΔS e.u
Aqueous	40.6506	37.0801	265.37
Aqueous+50%Acetone	39.2273	51.9755	308/8
75% Acetone	40.5059	41.7069	279.85
25% DMA	42.3394	55.8110	332.92
50% DMA	40.5783	36.1006	260.55
25% DMF	40.2164	40.5830	275.05
50% DMF	40.6024	41.7080	279.8
75% DMF	40.7713	39.1211	270.2
pH 3.42	42.4359	12.6270	188.175
pH 4.27	42.8701	13.8477	193
pH 5.57	43.2803	20.9646	217.125
pH 6.24	43.6904	32.6121	255.725

4. Electrochemical study:

The impedence value varies depending on the frequencies & can be plotted as a function of frequency. Since the impedence values are complex numbers, they can be represented in two different manner *i.e*, Nyquist (fig-5) & and Bode plot (fig-6). From the impedence measurements (Slobodan Brinic *et al.;* 2012) Super-Nernstian response was due to Charge transfer become low rate process & mainly independent of diffusion.

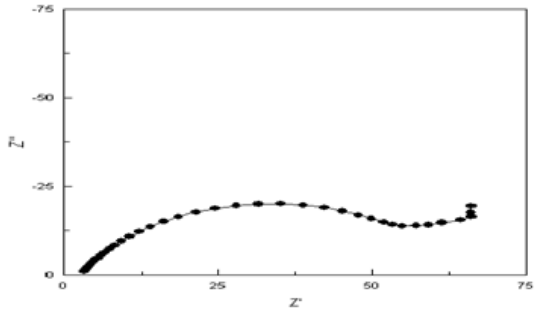

Fig-5-Nyquist plot

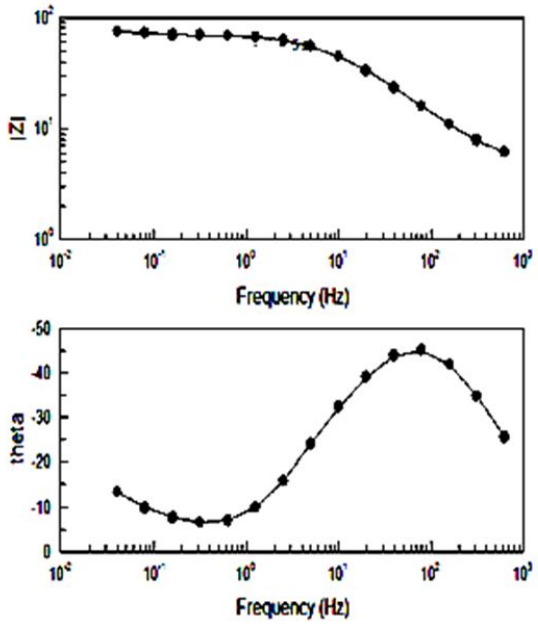

Fig-6-Bode Plot

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. 7&8) with Ca^{2+} ions in the laboratory. From the analysis it was found that the recovery of calcium ion in samples were 97%.

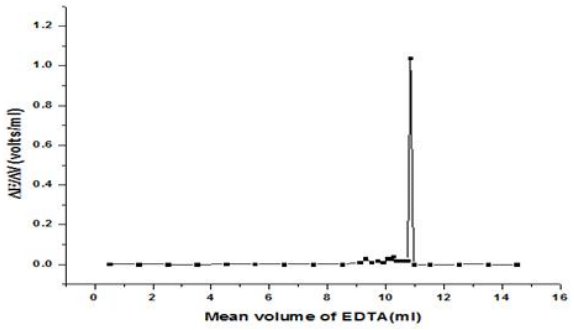

Fig-7-Potentiometric titration with ED

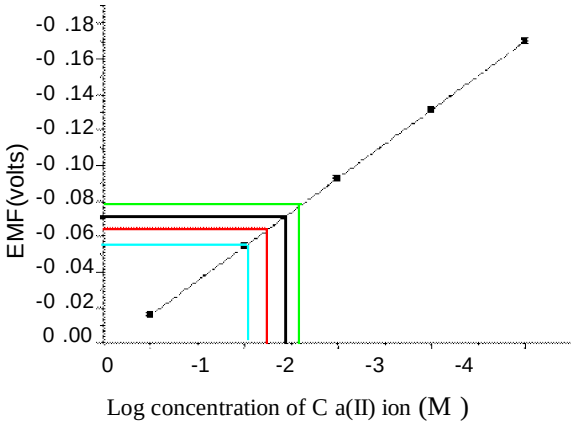

Fig-8-Potentiometric Titrations with real samples

6. Conclusion

A new simple, highlyspecific & 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.

7. Acknowledgement

I thank Avinashilingam University for women-Coimbatore, for providing facility to carried the work out successfully.

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