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Calcium Ion Selective Electrode Based On Surface Modified Zeolite Based Ionophore & Its Analytical Application

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ABSTRACT

A new, efficient Calcium ion selective electrode has been prepared using Surface modified Zeolite 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 1.0×10^{-4} 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 found to give a better response. . It was also successfully used in the analysis of concentration of Calcium ion in various real samples.

Keywords: Calcium (II),Surface modified Zeolite, Potentiometry, Selectivity coefficient.

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[9,10], 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 & membrane permeability. In plants it helps in transpiration which leads to growth of the plant.

Bedlechowicz *et al*; 2002 developed calcium ion selective electrode using ETH1001 as an ionophore. In 2004 Kumar & Mittal developed a new Calcium ion selective electrode based on PVC membrane modified by a new ionophore dibenzo-18-crown-6(DB18C6).

Taking into consideration of all the above facts that a new simple ionophore such as surface modified zeolite 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.

EXPERIMENTAL METHOD

Chemicals used

Silicic acid, 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.

Synthesis of ionophore

2g of Silicic acid was mixed with 3.5g of tetrapropyl ammonium bromide and 0.514g of NaOH & 50 ml of water. The above mixture was heated at 100^{0}C for 5 hours. The white precipitate was obtained. The silica content of the precipitate was determined by evaporation method & found to be 1.1 ML^{-1}. 1g of the above precipitate was dissolved in 2 ml of water and was mixed with a1.15 M aluminate solution (1 ml) to adjust the Si/Al molar ratio to 0.5M. The mixed solution was heated at 80^{0}C for 24 hours. The resulting reaction mixture was dried in a oven

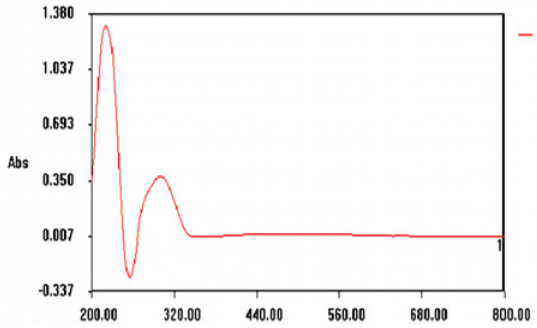

Fig 1: UV spectrum of the ionophore

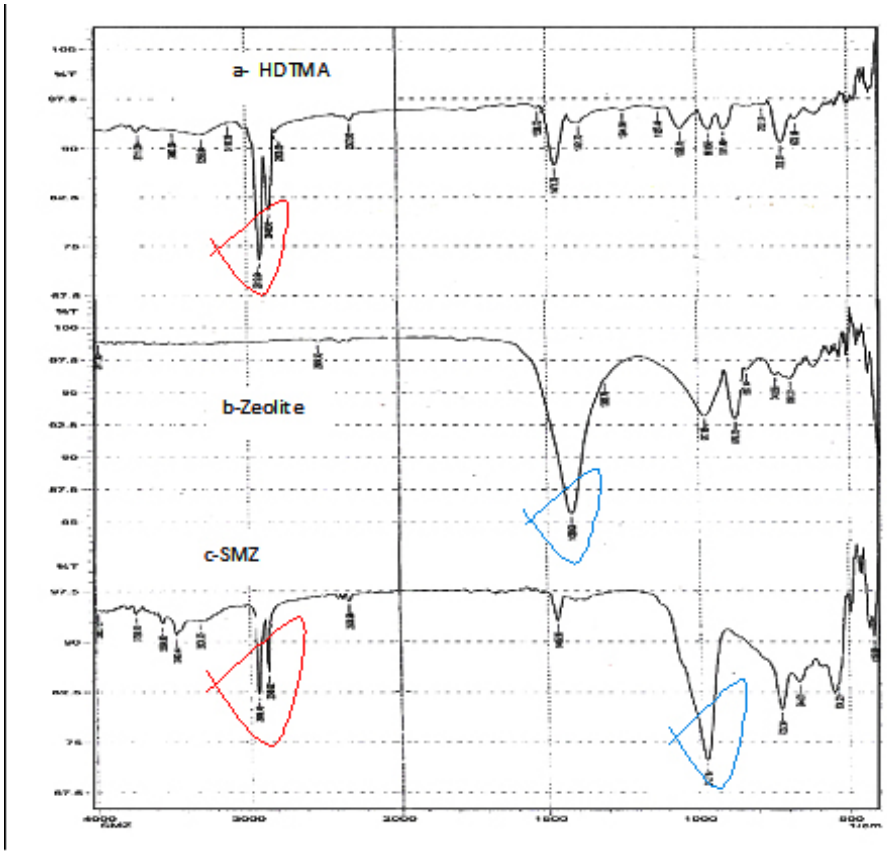

Fig. 2: FT-IR Spectrum of the ionophore

at 60^{0}C overnight. The surface modified Zeolite was prepared by mixing the above mixture with 100 mM HDTMA solution & stirred for 24 hours. The mixture was then centrifuged at 5000 rpm for 20 min & finally the mixture was dried.
Yield:2.5g,Melting point:201^{0}C

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

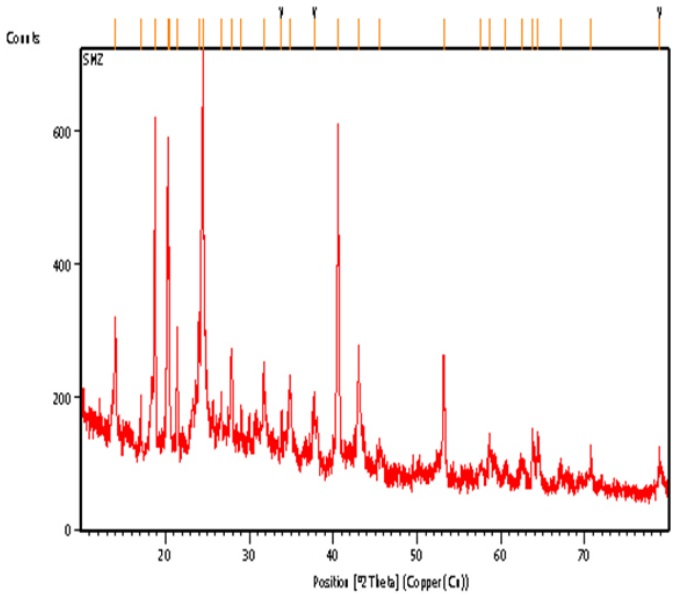

Fig. 3: XRD Spectrum of the ionophore

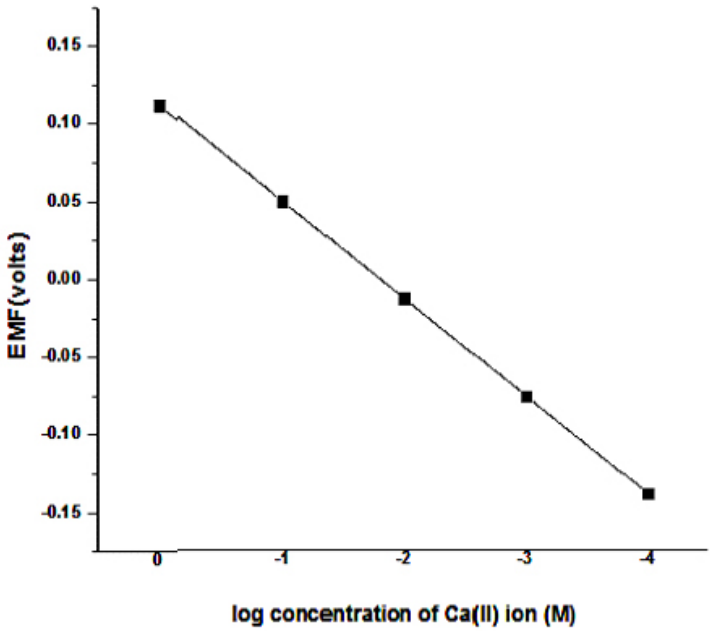

Fig. 4: Electrode response

using PAN analytical x-Pert pro diffractometer from CuKá radiation (X-Ray tube PW 3050/60), In UV spectrum the peak at 221nm corresponds to CN group (Pavian *et al*; 2001) fig-1. In FT-IR HDTMA Surfactant, Zeolite & SMZ are shown in fig-2, The Zeolite absorbed frequencies are 501, 802, 1064, 1465, 1635, 2376, 2970, 3788 & 3842 cm^{-1}

SMZ showed frequencies are 462, 794, 1095, 1435, 1627, 2376, 2854, 2924, 3425, 3749, 3842 which indicate the incorporation of HDTMA on the Zeolite Surface.There was a slight shift in peaks at each wave numbere speically in the peaks at 1435, 2854 & 2924 cm^{-1} in the SMZ spectrum. This data confirmed the loading of HDTMA onto the Zeolite surface. (Nezamzadeh-Ejhieh and Mirzaeyan,2011)

Table 1: Electrode response

Concentration of $CaCl_2$ (M)	EMF (Half Cell Potential) volts
1	0.135
$1x10^{-1}$	0.044
$1x10^{-2}$	-0.033
$1x10^{-3}$	-0.083
$1x10^{-4}$	-0.116
$1x10^{-5}$	-0.116

From X-ray diffraction study the composition was found to be C_{12} H_8Cl_4 $O_{48}Si_{24}$ in fig-3

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$CaCl_2$. The electrode was kept in distilled water when not in use.

Potential measurements

All the membrane electrode potential measurements were performed at constant temperature (30°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 (Immobilised Cu wire)	Internal reference (1M $CACL_2$ Solution)	External reference electrode (AG/AGCL)

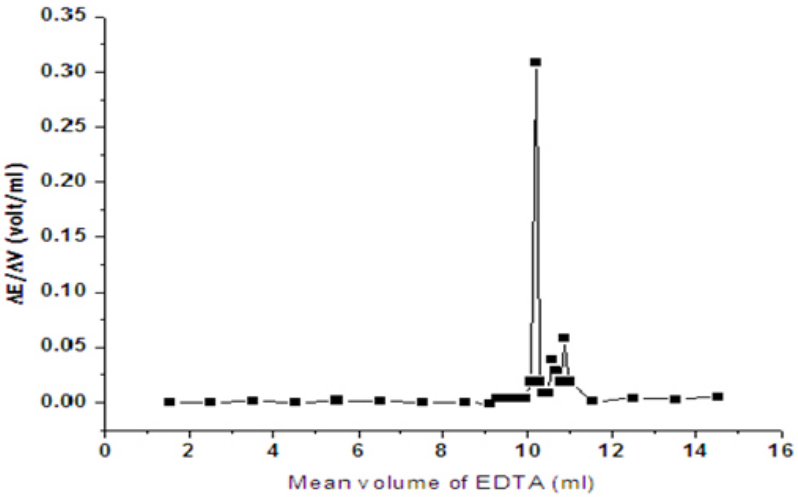

Fig. 5: EDTA Titration With Calcium

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	0.135	-0.067	0.109	0.133	0.139
$1x10^{-1}$	0.044	-0.037	-0.006	0.041	0.048
$1x10^{-2}$	-0.033	-0.114	-0.094	-0.04	-0.028
$1x10^{-3}$	-0.083	-0.117	-0.096	-0.008	-0.080
$1x10^{-4}$	-0.116	-0.117	-0.101	-0.090	-0.080

Table 3 :

Conc. Ca^{2+} Solution (M)	E.M.F	Acetone 25% (Volts)	Acetone 50%	Acetone 75%	Ethanol 25%	Ethanol 25%	Ethanol 75%	DMA 25%	DMA 50%	DMA 75%
1	0.135	0.129	0.146	0.195	0.013	0.136	0.140	0.137	0.145	0.164
$1x10^{-1}$	0.044	0.038	0.022	-0.103	-0.036	-0.042	0.051	0.050	0.067	0.0981
$1x10^{-2}$	-0.033	-0.034	-0.030	-0.063	-0.114	-0.033	-0.029	-0.031	-0.025	-0.021
$1x10^{-3}$	-0.083	-0.083	-0.121	-0.038	-0.078	-0.110	-0.089	-0.081	-0.083	-0.012
$1x10^{-4}$	-0.116	-0.121	-0.056	-0.091	-0.042	-0.102	-0.081	-0.119	-0.051	0.002

Table 4:

Cations	Selectivity co-efficient values
Na+	$3.2X10^{-5}$
K+	$6x10^{-5}$

RESULTS AND DISCUSSION

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 $1x10^{-4}$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 0.023V. The slope value was obtained from the calibration curve fig-4 & it was found to be 33 mv/ decade.

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 5.57to 6.24 Table 2.

Effect of Medium

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% acetone medium, DMA medium in the conc of 10^{-4}M Ca^{2+} ion. 50% of ethanol medium in the concentration range of 10-2 M of Ca^{2+} ion.

Selectivity

The potential response of the prospoed electrode to common cations were investigated by fixed interference method. (Semi-empirical Nicolski-Eisenmans equation). It was found that the potential remains unaffected in the presence of Na^+ & K^+ cation.

Analytical applications

The new prepared electrode was successfully used as an indicator electrode for EDTA titration with Ca^{2+} ions in the laboratory. (Fig-5).

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