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A New Simple Ester Ionophore Based Calcium Ion Selective Electrode – Preparation and its Analytical Application

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Abstract

A new simple efficient calcium ion selective electrode has been prepared using simple ester. A heterogeneous precipitate has been used as ion carriers for the preparation of Ca (II) selective membrane sensor. The sensor exhibits a near Nernstian response for Ca(II) ion over a concentration range of 1.0 x 10^{-4}M to 1.0x10^{-1}M. The proposed sensors revealed relatively good selectively and high sensitivity for Ca(II)over a mono and divalent cations and anions . It can be used within the pH range of 3.42 to 6.24. The effect of medium and the selectivity coefficient values were evaluated using fixed interference method found to give a better response. It was also successfully used in the analysis of concentration of calcium in various real samples.

Keywords: Calcium (II), potentiometry, polyvinylchloride (PVC), ester.

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 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 non-destructive analysis and inexpensive sample preparation, applicability to coloured sample and turbid solution. Calcium is an essential nutrient in plants. It plays an important structural role in the cell wall and membranes is a counter-cation for inorganic and organic anions, is a main intracellular messenger and helps to harvest and process nitrates for protein metabolism[11]. In addition to the effects calcium level (0-150mg/L) exceeds the limit in water leads to many problem in industry including scale formation. According to nutrition committee the recommended level of calcium intake in human is 1000 – 1500 mg, but the level increasing or decreasing may cause severe health hazarders. The increasing level of calcium may cause kidney stones, blood vessels, and heart attack, Hyperparathyroidism and damage cells. Lack of calcium causes Osteoporosis, Hypocalcaemia, blood coagulation, signal transduction, muscle pains, tingling of the hands and feet and also low calcium causes acidic pH in soils[12].

Lakshminarayanaiah[13] reported calcium ion selective electrodes based on diester. α-furildioxime has been used as ion carriers for the determination of Ca(II) ion by Ashok Kumar Singh et al[14]. Akyilmaz et al[15] developed Ca (II) electrode by using activation of the enzyme. H.Fujita et al[16] developed Ca^{2+} sensitive fluorescent dye.

Taking into consideration of all the above facts that a new simple ionophores such as esters have been used as an electro active phase in PVC matrix for the fabrication of Ca^{2+} ion selective electrode. In the present study the electrode show good selectivity and reproducibility over Ca^{2+} ion and the results are presented in this paper.

Methodology

Chemicals Used: Reagent grade high molecular weight PVC, Dioctyl phthalate (DOP), sodium tetra phenyl borate (NATBP), tetra hydro furan (THF), ferulic acid were obtained from E.Merck and can be used without further purification. All other reagents such as calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) and sodium chloride (NaCl) were of analytical grade. The standard stock solutions (1M $CaCl_2$) were prepared using distilled water; working solutions were made by dilution of the stock solution.

Physical measurements: IR spectra were recorded on a FTIR spectrometer; Model Shimadzu prestige – 21 series. UV spectra were recorded using PC based Double beam spectrometer 2202.

Synthesis of Ionophore: 2 g of ferulic acid was taken in a RB flask. 7 ml of methanol and 0.8 ml of Conc.H_2SO_4 was added to ferulic acid. It was attached into a air condenser and refluxed for 6 hours. The solution was cooled and added into crushed ice in a beaker. The obtained precipitate was filtered and washed with sodium carbonate solution and cold water. The precipitate was dried and powdered. It was recrystallized from methanol.

Preparation of membrane Ion selective electrode: 0.3 g of precipitate along with 0.1g of PVC, DOP and NaTPB was dissolved in 3 ml THF and the clear solution was evaporated

slowly. Then it was spread uniformly over whatmann filter paper No.42. The electro active membrane was formed then the membrane was air dried for 48 h.

A circular piece from each of the membrane was cut and fixed with resin at one end of hollow glass tubes of diameter 2 cm and length 10 cm. The tubes were filled with 1M solution of calcium chloride. Reference copper metal wire of diameter 0.5 mm and length 12 cm was inserted through the other end of tube in such a way, that it remains dipped in the 1 M solution of calcium Chloride. The electrodes were conditioned for 2 days to attain equilibrium in 1M $CaCl_2$ solution.

Ester: Yield = 0.6 g; and FT – IR; γ (C – H)1000 – 3339 cm^{-1}; γ (C=O) 1713; γ(C-C)1504; γ(C-O-C) 1155.UV –Vis ; the peak at 301 (methoxy substituted benzene); 316(π-π* of C=O)

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

Internal Reference Electrode (Cu wire)	Internal Reference(1M $CaCl_2$ Solution)	Electro Active Membrane	Sample Solution	External Reference Electrode (Ag/AgCl)

The membrane was prepared using the basic method given by Craggs et al[17] with PVC, ionophore, and plasticizers/solvent mediators like DOP, NATBP and THF.

Results and Discussion

Working concentration range and slope of Ca^{2+} sensor: The plasticized PVC- based membrane electrode contains as the neutral ion carrier generated stable potential response in solutions containing calcium. Therefore we studied in detail the performance of the membrane electrodes based on their carrier for calcium (II) ion in aqueous solutions and the electrode shows slope value was 21 mv/decade.

Electrode response: The electrode was first conditioned in 1M solution of $CaCl_2$ for 3 days till it attained stable equilibrium which are then used for the determination of their characteristic study. The potential of the electrode was studied by noting its E.M.F from the series of standard solutions of $CaCl_2$ of concentration ranging from 1M to $1x10^{-4}$M. The obtained E.M.F values are tabulated in (Table 1).

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 wide pH range of 3.42 – 6.24.

Table-1
Electrode response for Ca^{2+} ions

S.No	Concentration of $CaCl_2$ solution (M)	EMF (volts)
1	1	0.186
2	$1x10^{-1}$	0.154
3	$1x10^{-2}$	0.146
4	$1x10^{-3}$	0.121
5	$1x10^{-4}$	0.099
6	$1x10^{-5}$	0.099

Standard electrode potential (E^0) determined by extrapolation method was found to be-0.013V. The slope value was found to be 21mV/decade (figure 1).

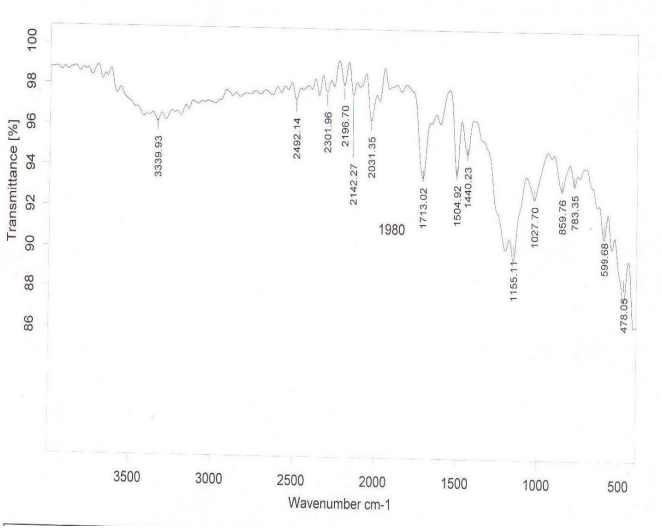


Figure-1
IR spectrum of Ester

Effect of Medium: To study the effect of medium, a standard solution containing 1M Ca (II) ion in a series of 25%, 50%, 75% Ethanol, acetone and dimethyl formamide,was added. It was found that the potential of electrode remains unchanged in the above medium (table 2).

Potentiometric Selectivity: Selectivity is one of the most important characteristics of a chemical sensor. The influence of interfering ion on the response behavior of ion selective electrode is usually described in terms of selectivity coefficient. The potential response of the calcium ion sensor to different cations and anions have been investigated by determining the selectivity coefficient of the electrode using Fixed Interference method (FIM) based on semi empirical Nicolskii-Eisenman equation and the concentration of interfering ions was set to 1 M. It was found that the potential remains unaffected in the presence of a series of various cations like Na^+ , K^+, $Ce^{2+}$and anions like I^-, Br^-, NO^{3-} and Cl^-.

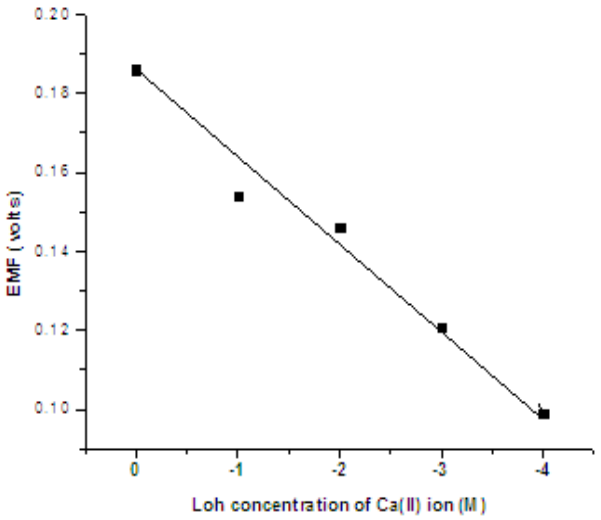
Table-2
Effect of medium for Ca^{2+}ions

S.No	Conc of the Ca^{2+} solution (M)	Acetone			Ethanol			DMF		
		25%	50%	75%	25%	50%	75%	25%	50%	75%
1	1	0.184	0.188	0.191	0.185	0.189	0.195	0.180	0.183	0.186
2	$1x10^{-1}$	0.155	0.153	0.155	0.158	0.159	0.183	0.140	0.148	0.151
3	$1x10^{-2}$	0.147	0.149	0.150	0.139	0.140	0.138	0.121	0.131	0.135
4	$1x10^{-3}$	0.129	0.125	0.131	0.120	0.141	0.129	0.115	0.127	0.125
5	$1x10^{-4}$	0.129	0.125	0.133	0.118	0.139	0.118	0.114	0.125	0.126

Response and life time: The static response time of the electrode was found to 1min. The electrode was used over a period of 1 month with good reproducibility.

Analytical Application: Determination of Calcium by direct potentiometric methods: The practical significance of the sensor was tested by using as an indicator electrode for potentiometric titrations of Ca^{2+} with EDTA solution. Before the end point, the potential shows usual logarithmic change with the volume of the titrant added while the potential response after the end point remains almost constant. It is shown in figure-4.

The proposed electrodes were found to work well under the laboratory conditions. To assess the applicability of the sensors to real sample an attempt was made to determine calcium ion in milk. The recovery of calcium ion for milk analysis was formed to be quantitative with the maximum recovery of 94%.



Figuire-3
Plot of log concentration of Ca(II) ion (M) Vs EMF (volts)

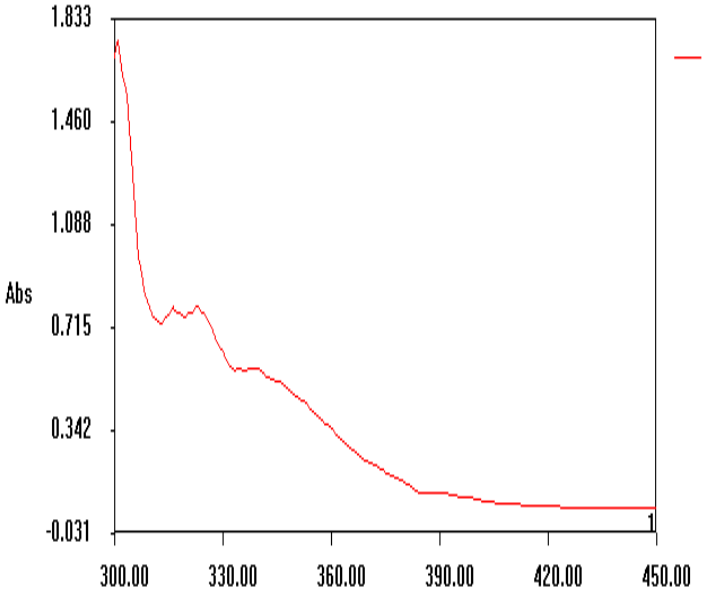


Figure-2
UV-Vis spectrum of Ester

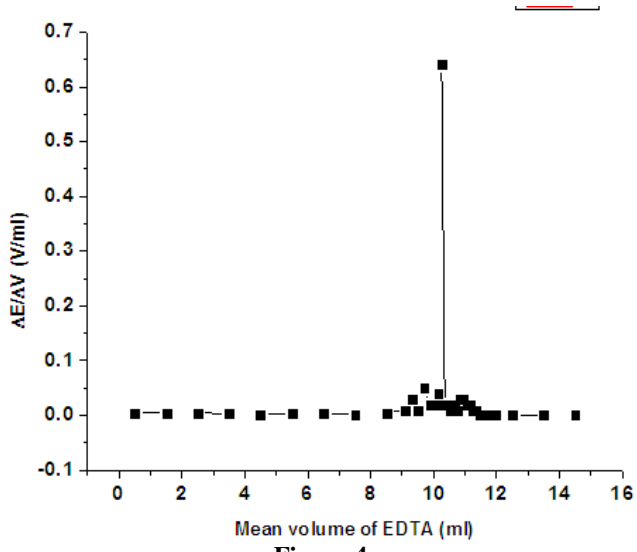


Figure-4
Plot of Mean volume of EDTA (ml) Vs ΔE/ΔV (v/ml)

Conclusion

The plasticized PVC- based membrane incorporating ester as an ionophore, DOP as solvent mediator and NATBP as anion excluder in a PVC matrix could be used to determine Ca^{2+} ion in the concentration range of 1.0 X 10^{-4} M to 1.0 X 10^{-1} M for electrode with a slope value was found to 21 mv/decade. It was found that the electrode worked well in the acidic pH range from 3.42 to 6.24. The selectivity of the electrode towards Ca^{2+} ion is quite well understood over the other cations. The lifetime of the assembly is 1 months in both aqueous and nonaqueous medium. In addition, the membrane sensor can also be used in the analysis of concentration of calcium in milk sample.

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