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Calcium Ion Selective Electrode Based on Vinyl Acetic Acid Grafted PVC Ionophore & Determination of Thermodynamic Functions & Its Analytical Application

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Abstract

A new, efficient Calcium ion selective electrode has been prepared using Vinyl acetic acid grafted PVC based ionophore. The influence of temperature on electrode potential was studied & it can be used in the determination of thermodynamic function like ΔG, ΔH & ΔS. The electrochemical impedance spectroscopy (EIS) technique is also employed to study the electrochemical & surface reactions. It was also successfully used in the analysis of concentration of Calcium ion in various real samples.

Key words: Calcium (II), Vinyl acetic acid, PVC, Potentiometry, Electrochemical impedance spectroscopy.

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[9,10], easy handling, nondestructive analysis and in expensive sample preparation, applicability to coloured sample and turbid solution. Calcium 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). All solid state miniature Calcium ion selective electrode using Poly(3,4-ethylenedi-oxythiophene) doped with poly (styrenesulphonate) was carried out by Hui *et al*; 2013. All solid -state Calcium ion selective electrode prepared of soluble electrically conducting polyaniline. (Lindfors, T and Ivaska, A, 2000).

Taking into consideration of all the above facts that a new simple ionophore such as Vinyl acetic acid grafted Pvc have been used as an electroactive phase for the fabrication of Ca^{2+} ion selective electrodes. In the present study the influence of temperature on electrode potential was studied & it can be used in the determination of thermodynamic function like ΔG, ΔH & ΔS. The electrochemical impedance spectroscopy (EIS) technique is also employed to study the electrochemical & surface reactions and the results are presented in this paper.

2. Experimental Method

2.1 Chemicals used:

Vinyl acetic 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.

2.2 Synthesis of ionophore & Fabrication of the electrode:

A Co^{60} gamma irradiator (model GC5000) with gamma dose rate of 2.5 KGY/hr was used for irradiation of PVC powder. 0.1 g of pvc powder sample was irradiated in the dose of 150 $KGY^{.0.5}$ ml of Vinyl acetic acid was taken in a stoppered glass tube bubbled with nitrogen gas [11]& this ionophore is used in the fabrication of the electrode.

3. Temperature study : The E.M.F values of Calcium ion selective electrode using the cell, Ca, Ca ionophore//Ag/AgCl was measured at different temperature ranging from 5-40^{0}C & Tabulated in Table 1.

The influence of the temperature on electrode potential was also studied (By standard procedure **(Gurtu and Gurtu, 2011))** for the prepared electrode in different calcium ion concentrations at various temperature ranges from 5 – 40^{o}C.

Effect of temperature on electrode potential of the calcium ion selective electrode in the presence of aqueous, aquo-solvent and aqueous-buffer (pH) solution was used for the determination of thermodynamic functions like ΔG, ΔH and ΔS.

Effect of temperature on Ca – ISE(Table-1)

Medium	Ca-Ion Selective Electrode								(δE/δT)
	EMF (volts) at different temperature								p v/K^0
	278K	283K	288K	293K	298K	303K	308K	313K	
Aqueous	0.157	0.168	0.181	0.189	0.196	0.208	0.212	0.226	0.0021
Aqueous+									
25% of acetone	0.160	0.169	0.181	0.189	0.196	0.200	0.206	0.214	0.0014
50% of acetone	0.167	0.171	0.185	0.193	0.198	0.203	0.207	0.217	0.0013
75% of acetone	0.170	0.178	0.189	0.195	0.199	0.205	0.209	0.219	0.0013
25% of ethanol	0.162	0.171	0.185	0.191	0.198	0.205	0.210	0.216	0.0014
50% of ethanol	0.170	0.174	0.189	0.196	0.201	0.206	0.210	0.221	0.0013
75% of ethanol	0.174	0.183	0.193	0.196	0.200	0.209	0.213	0.224	0.0013
25% of DMA	0.165	0.174	0.183	0.197	0.202	0.208	0.213	0.219	0.0015
50% of DMA	0.173	0.177	0.193	0.199	0.205	0.210	0.214	0.224	0.0014
75% of DMA	0.178	0.188	0.197	0.200	0.205	0.213	0.218	0.229	0.0013
25% of DMA	0.169	0.177	0.186	0.191	0.199	0.213	0.217	0.223	0.0014
50% of DMA	0.176	0.181	0.189	0.193	0.197	0.214	0.218	0.227	0.0014
75% of DMA	0.183	0.185	0.188	0.194	0.198	0.215	0.221	0.232	0.0013
Aqueous+									
pH 3.43	0.175	0.181	0.188	0.192	0.195	0.199	0.205	0.211	0.0015
pH 4.64	0.177	0.183	0.189	0.193	0.196	0.198	0.207	0.214	0.0011
pH 5.54	0.180	0.184	0.191	0.194	0.195	0.198	0.204	0.209	0.0012
pH 6.24	0.182	0.185	0.193	0.197	0.198	0.201	0.215	0.230	0.0014

The relationship between $T(\partial E/\partial T)_p$ and E of calcium ion selective electrode in different media were linear in nature.

The relationship is 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 1 inaqueous, aqueous – solvent, aqueous – buffer solution have been used in the calculation of ΔG, ΔH and ΔS at 5-40°C for the calcium ion selective electrode and the results are presented in the Table 2.

Table 2. Thermodynamic parameter values of ΔG, ΔH and ΔS

Medium	-ΔG K.cal/mole	ΔH K.cal/mole	ΔS e.u
Aqueous	37.0801	84.5099	410.125
Aqueous +			
25% ofacetone	36.5493	46.8844	284.675
50% ofacetone	37.1745	39.4337	260.55
75% ofacetone	37.7271	40.4103	265.3
25% of ethanol	37.7271	46.6993	284.675
50% of ethanol	37.8003	40.3558	260.55
75% of ethanol	38.407	38.0701	260.55
25% of DMA	37.6591	42.5544	289.5
50% of DMA	38.4793	38.5028	270.2
75% of DMA	39.2755	37.3551	260.55
25% of DMA	37.9968	45.7265	284.675
50% of DMA	38.4793	43.0920	275.025
75% of DMA	38.986	37.3889	255.725
Aqueous +			
pH 3.42	37.2972	49.5479	303.975
pH 4.63	37.5626	27.0572	217.125
pH-5.57	37.5867	33.7846	236.425
pH- 6.24	38.6241	43.9605	275.025

4. Electrochemical Impedance Spectroscopy Study : To study the interface phenomena of membrane electrode, impedance spectra were obtained. The impedance spectrum of the electrode was recorded in open circuit voltage at 10 mV in the frequency range of 0.01 Hz – 100 Hz in 1M $CaCl_2$ solution. In the presence of single semi circle implies that single charge transfer process in electrode process.

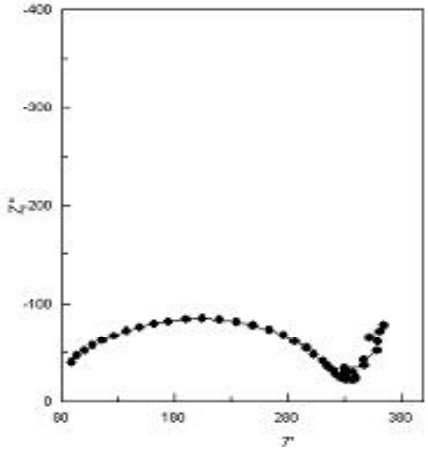

Figure 1. Nyquist plot for vinyl acetic acid based Ca-ISE

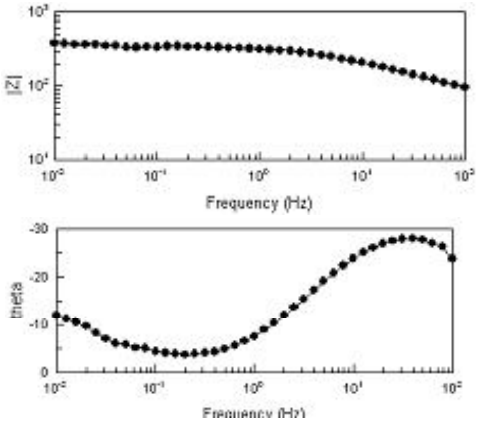

Figure 2. Bode plot for vinyl acetic acid based Ca-ISE

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. 3) with Ca^{2+} ions in the laboratory. From the analysis it was found that the recovery of calcium ion in samples were 97%.(fig. 4).

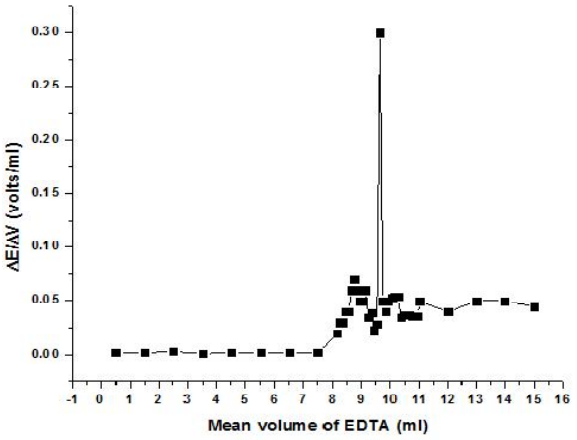

Figure 3. Plot of mean volume of EDTA (ml) Vs ΔE/ΔV (volts/ml)

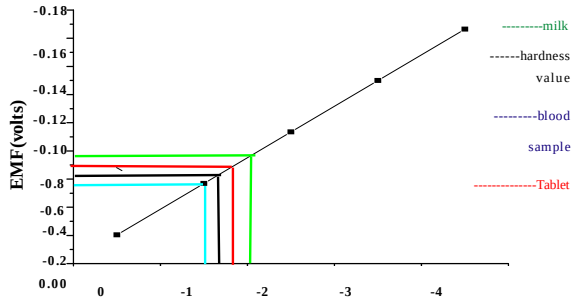

FIG-4-plot of log Conc of Ca(II) ion (M) Vs E.M.F -volts

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. The thermodynamic parameter value ΔG, ΔH, ΔS of the electrode has also successfully determined.

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