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website:- www.journalofchemistry.org**Calcium Ion Selective Electrode Based on Vinyl Acetic Acid Grafted PVC Ionophore & Determination of Thermodynamic Functions & Its Analytical Application**A. VIJAYALAKSHMI¹ and J. THAMARAI SELVI²^{1,2} Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women
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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 assays¹⁻⁸. 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-ethylenedioxythiophene) 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:**

- macrocyclic polyether ligands composed of 1,10-phenanthroline as carriers for primary amine species," *Talanta*, **1994**, *41*, (2); 327–333,
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 13. Rafel Hernandez, Jordi Riu and Xavier Rius, F., Determination of calcium ion in sap using carbon nano tube-based ion selective electrodes, *Analyst*, **2010**, *135*: 1979-1985.

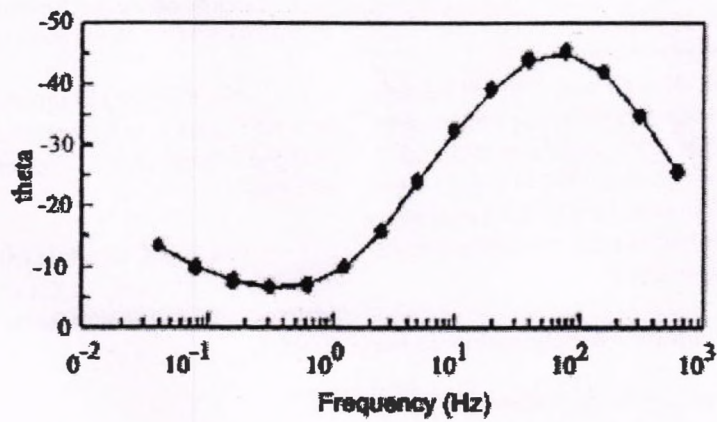
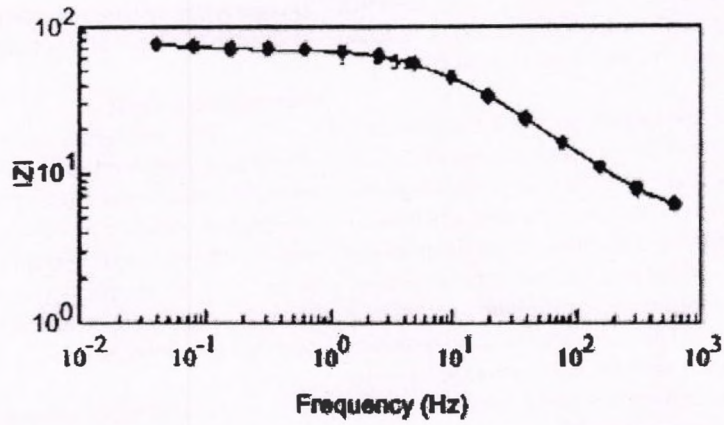


Fig. 2: Bode plot for schiff base based Ca-ISE

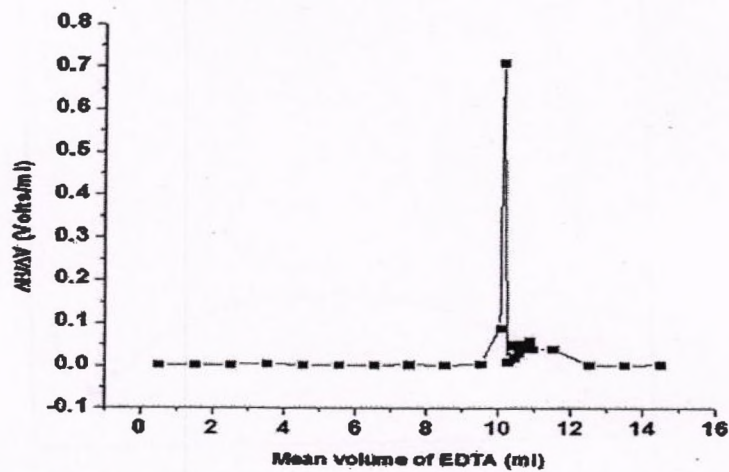


Fig. 3: Calcium ion selective electrode based on schiff base ionophore

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.

EXPERIMENTAL

Chemicals & Reagents used

Glycine, 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 & Fabrication of the electrode

For preparing Schiff base ionophore, 1.1 ml of Salicylaldehyde solution was mixed with 0.75g of

glycine & the mixture was stirred. This ionophore is used in the fabrication of the electrode.

Temperature study

The influence of the temperature on electrode potential was studied by standard procedure (Gurtu and Gurtu, 2011) for the prepared electrode in different calcium ion concentrations at various temperature ranges from 5 – 40°C. Because of the different temperatures, the ionic mobility of the ions which are to be analysed is different, so the potential was change.

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 .

For the study of the effect of temperature on the output response, the temperature was changed in steps of 5°C. The values are tabulated in Table -1

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°C.

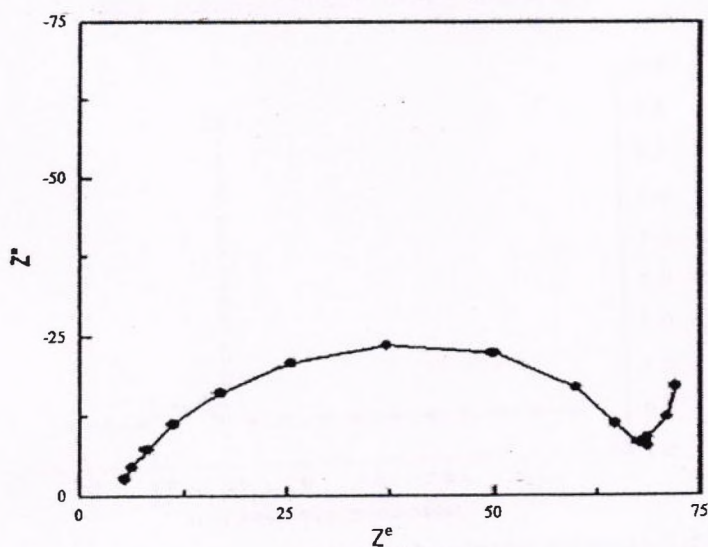


Fig. 1: Nyquist plot for Schiff base based Ca-ISE

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

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

Table 1: Effect of temperature on Ca- ISE

Medium	Ca-Ion Selective Electrode								$(\partial E/\partial T)$ pv/K0
	EMF (volts) at different temperature								
	278K	283K	288K	293K	298K	303K	308K	313K	
Aqueous	0.199	0.216	0.218	0.220	0.228	0.230	0.238	0.250	0.0016
Aqueous+ Solvent									
25% of acetone	0.197	0.203	0.207	0.211	0.214	0.219	0.223	0.228	0.0008
50% of acetone	0.199	0.207	0.210	0.214	0.216	0.221	0.225	0.231	0.0009
75% of acetone	0.203	0.210	0.213	0.216	0.219	0.223	0.227	0.235	0.0009
25% of ethanol	0.196	0.201	0.204	0.209	0.213	0.219	0.221	0.225	0.0008
50% of ethanol	0.198	0.204	0.207	0.212	0.216	0.221	0.224	0.227	0.0008
75% of ethanol	0.201	0.209	0.211	0.215	0.219	0.224	0.229	0.230	0.0008
25% of DMA	0.198	0.202	0.207	0.211	0.215	0.218	0.222	0.227	0.0014
50% of DMA	0.202	0.206	0.211	0.213	0.216	0.220	0.223	0.228	0.0007
75% of DMA	0.204	0.206	0.207	0.212	0.217	0.223	0.226	0.231	0.0007
25% of DMA	0.199	0.203	0.205	0.209	0.214	0.219	0.221	0.226	0.0007
50% of DMA	0.203	0.207	0.211	0.213	0.218	0.221	0.225	0.228	0.0007
75% of DMA	0.206	0.209	0.212	0.216	0.219	0.223	0.227	0.231	0.0007
Aqueous+ pH 3.43	0.155	0.167	0.181	0.190	0.205	0.210	0.216	0.225	0.0018
pH 4.64	0.159	0.170	0.186	0.193	0.208	0.213	0.221	0.228	0.0018
pH 5.54	0.162	0.173	0.188	0.195	0.209	0.215	0.225	0.229	0.0020
pH 6.24	0.165	0.179	0.192	0.201	0.210	0.219	0.229	0.230	0.0019

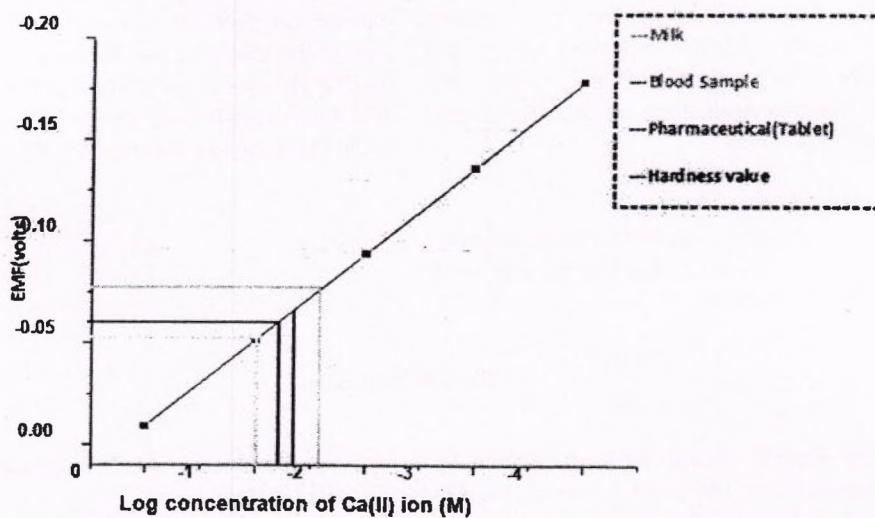


Fig. 4: Plot of log concentration of Ca(II) ion (M) Vs E.M.F (volts)

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

Medium	$-\Delta G$ K.cal/mole	ΔH K.cal/mole	ΔS e.u
Aqueous	43.4009	7.4835	178.525
Aqueous + solvent	41.0586	8.7594	168.87
25% of acetone	41.5638	9.6522	173.70
50% of acetone	42.1173	9.3065	173.60
75% of acetone	40.7230	4.7815	154.40
25% of ethanol	41.2296	4.7236	159.22
50% of ethanol	41.8328	3.4547	154.40
75% of ethanol	41.0125	4.5162	154.40
25% of DMA	41.4709	1.3510	144.75
50% of DMA	41.6398	1.4067	144.75
75% of DMA	40.9138	1.8846	144.75
25% of DMF	41.6350	4.2305	135.10
50% of DMF	42.0455	0.8450	144.75
75% of DMF			
Aqueous+			
pH 3.43	37.3675	68.430	361.875
pH 4.64	38.0643	67.8075	361.875
pH-5.57	38.5035	79.3181	400.475
pH- 6.24	39.1994	68.145	366.70

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

CONCLUSION

The value of temperature co-efficient $(\partial E/\partial T)_p$ in Table-1 in aqueous, 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 were presented in the Table -2

A new simple ,highly specific&selective calcium ion electrode has been prepared.The life time of the prepared electrode was found to be 3 months with good reproducibility of E.M.F values. The thermodynamic parameter value ΔG , ΔH , ΔS of the electrode has successfully determined.

Electrochemical Study

The impedance spectrum of the electrode was recorded at 10 mV amplitude in the frequency range of 0.01 to 1000 Hz.

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