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Research Paper

Preparation of Strontium Ion Selective Electrodes and its Analytical Applications

Chemistry

KEYWORDS : Strontium (II), Araldite –matrix, Potentiometry, Polyvinyl-chloride, Semicarbozone, strontium phthalocyanine.

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ABSTRACT

A new, efficient strontium ion selective electrode(I) has been prepared using strontium phthalocyanine and electrode(II) was prepared using semicarbazone. A heterogeneous precipitates have been used as an ion carriers for the preparation of strontium (II) selective membrane sensor.The sensor exhibits a near Nernstian response for Sr(II) ion over a concentration range of 1.0 X 10-5 M to1.0 X 10-1 M for electrode(I) and for electrode (II) over a concentration range of 1.0 X 10-6 M to 1.0 X 10-1 M. The proposed sensors revealed relatively good selectivity and high sensitivity for Sr(II) over a mono and divalent cations. It can be used with in the pH range of 3 to 5 for electrode(I) and 4 – 6 for electrode(II) . 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 Strontium ion in various real samples.

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 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 inexpensive sample preparation, applicability to coloured sample and turbid solution. Schiff bases which can form strong complexes with certain metal ion due to its geometric size [11,12]. Strontium is present in small quantities in most plant tissues though it has not been shown to be essential for their growth and development [13]. In addition to the effects exerted on bones Strontium can also have some physiological process such as heart and other skeletal muscle contraction and ionic transport across red blood cell membrane and nerve cells[14].

Mojtaba shamsipur et al.,[15] reported Strontium selective electrode based on 1,10-diaza-5,6-benzo-4,7-dioxahexadecane-2,9 dione. ZnO nanorods are used for the determination of Sr2+ ion by khun et al.,[16]Mohammad et al.,[17] developed electrodes using Dibenzo-18-crown ether. Kiaetal.,[18] reported PVC based Sr2+ ion selective electrodeusing 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl. 3,5-diazobicyclo[3,1,0]hex-2-ene(NPDBH) used as an ionophore.

Taking into consideration of all the above facts that a new simple ionophores such as strontium phthalocyanine(I), phenyl substituted Semicarbazone(II) have been used as an electroactive phase in PVC matrix for the fabrication ofSr2+ ion selective electrodes . In the present study both the electrodes show good selectivity and reproducibility over Sr2+ ion and the results are presented in this paper.

2. Experimental Method

2.1 Chemicals used:

Reagent grade high molecular weight PVC, Dioctyl phthalate (DOP), sodium tetra phenyl borate (NATBP), tetra hydro furan (THF) were obtained from E.Merck and can be used without further purification. All other reagents such asPhthalic anhydride, urea, strontium chloride, sodium molybdate , Ethanol, Benzophenone, Semicarbazide hydrochloride , sodium acetate and nitrate of all metal used were of analytical grade. Throughout double distilled ionized water was used.

2.2 Physical measurements:

1H NMR spectra were recorded on a Hitachi FT-NMR; Model R-600 spectrophotometer using DMSO as solvent. Chemical shift is given in ppm relative to Tetra methyl silane (for ionophore-II). IR spectrometer were recorded on a FTIR spectrometer; Model Shimadzu prestige – 21 series.

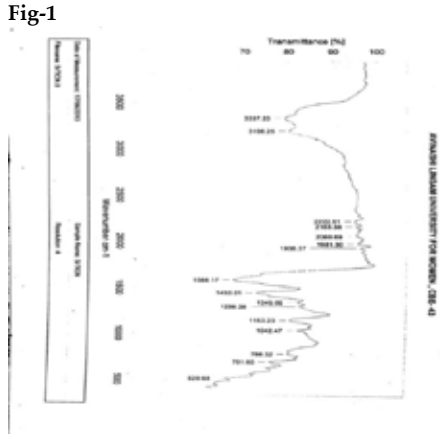
2.3 Synthesis of Ionophore:

6g of Phthalic anhydride, 8g of urea and 2g of hydrated strontium (II) chloride and a predetermined ratio of Sodium molybdate (catalyst). All are powered in a mortar and it is taken in a 100ml beaker and the beaker is heated very gently with a small Bunsen flame and the beaker should be 25 cm above the flame. The slower the heating is done better is the product. The product is cooled and weighed(fig-1).

The hot Ethanolic solution (10 mL) of Benzo phenone (1.82 g 1M), Semicarbazide hydrochloride (1.12 g 0.01 mol), and Sodiumacetate (0.82 g, 0.01 mol) were mixed with constant stirring. On cooling a pale yellow colored compound has separated out. It was filtered, washed several times with cold Ethanol and dried, recrystallized from ethanol (fig-2).

2.4Strontium phthalocyanineyield = 12.52g; Phenyl substituted semicarbazone yield = 2.36g and FT-IR; γ (C-H) 1000 – 3337.23; γ (pyrrole ring) 1153; γ (coupling of isoindole) 1042.47; γ (C-N) 1588.17; γ (N-H) 3337 and 3198.1H NMR (DMSO; 1000 MHZ);δ ppm=3.34 (2H1S1-NH2);6.48-7.79 (Ar-H);7.756-7.753(2CH2)

Fig-1



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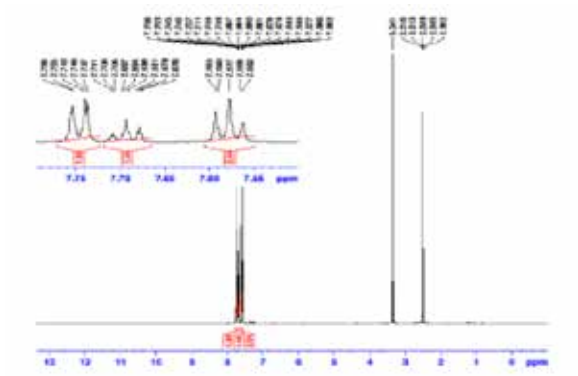

Fig-2

2.5 Potential measurements:
All the membrane electrode potential measurements were performed at constant temperature (300 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 (Cu wire)	Internal Reference(1M $SrCl_2$ Solution)	Electro Active Membrane	Sample Solution	External Reference Electrode (Ag/AgCl)

Preparation of membrane(I):
A number of membrane were prepared using varying amount of powered strontium phthalocyanine precipitates(0.2g,0.3g,0.4g,0.5g), 0.1g polyvinyl chloride, 0.1g sodium teraphenyl borite, 3drops of di-n-butylphthalate and predetermined ratio of terahydrofuran are taken and the mixtures are allowed to heat in a steam bath still evaporate the liquids.The precipitate was thoroughly mixed with Araldite(epoxy adhersive)(Huntsman advanced materials, India pvt Ltd) to make a homogeneous paste which was then applied on a clean watch glass.The paste was spread uniformly to obtain 0.9mm thickness of the electron active membrane were obtained.The membranes were air dried for 48 hours.

Preparation of membrane(II):
A number of membrane were prepared using varying amount of powered semicarbazone precipitates(0.2g,0.3g,0.35g),0.1g polyvinyl chloride, 0.1g sodium tetra phenyl borite, 3drops of di-n-butyl phthalate and predetermined ratio of terahydrofuran are taken and the mixtures are allowed to heat in a steam bath still evaporate the liquids. The precipitate was thoroughly mixed with Araldite(epoxy adhersive)(Huntsman advanced materials, India pvt Ltd) to make a homogeneous paste which was then applied on a clean watch glass.The paste was spread uniformly to obtain 0.7mm thickness of the electron active membrane were obtained.The membranes were air dried for 48 hours.

3.Results and Discussion:
3.1 Working concentration range and slope of Sr2+ sensor:
The plasticized PVC- based membrane electrode contains as the neutral ion carrier generated stable potential response in solutions containing Strontium. Therefore we studied in detail the performance of the membrane electrodes based on their carrier for Strontium(II) ion in aqueous solutions and the two electrodes shows near Nernstain slope value for electrode-I(21 mv/decade) for electrode (II) was 22mv/decade.

ELECTRODE RESPONSE:
The two electrodes were first conditioned in 1M solution of SrCl2 for 7 days till it attained stable equilibrium which are then used for the determination of their characteristic study. The potential of the electrodes were studied by noting its E.M.F from the series of standard solutions of SrCl2 of concentration ranging from 1M to 1x10-6M. The following are the E.M.F values obtained for electrode I (Table.1), electrode II (Table.2) and fig (III & IV)

Electrode response
Table – 1

Concentration of $SrCl_2$ solution(M)	EMF In volts
1	0.265
$1x10^{-1}$	0.244
$1x10^{-2}$	0.232
$1x10^{-3}$	0.192
$1x10^{-4}$	0.184
$1x10^{-5}$	0.184

Electrode response
Table – 2

S.No	Concentration of $SrCl_2$ solution (M)	EMF (Volts)
1	1	0.192
2	$1x10^{-1}$	0.16
3	$1x10^{-2}$	0.145
4	$1x10^{-3}$	0.128
5	$1x10^{-4}$	0.105
6	$1x10^{-5}$	0.092
7	$1x10^{-6}$	0.092

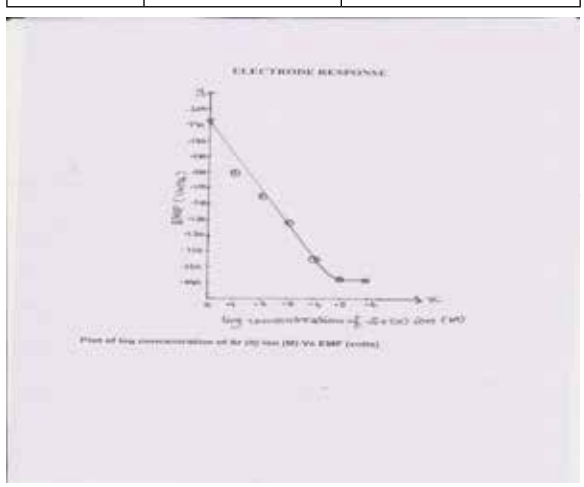

Fig-4

Plot of Log concentration of Sr (II) ion (M) Vs EMF (volts)
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 Sr(II) solution of varying pH had been measured. It was found that the electrode(I) worked well over a wide pH range of 3 to 5 and electrode(II) worked well over a wide pH range of 4 to 6.(Table III & IV).

Table – III
Effect of pH for Sr2+ions

Concentration of $SrCl_2$(M)	pH3	pH5
1M	0.266	0.265
$1x10^{-1}$ M	0.249	0.246

$1x10^{-2}$ M	0.231	0.229
$1x10^{-3}$ M	0.193	0.193
$1x10^{-4}$ M	0.183	0.183
$1x10^{-5}$M	0.183	0.183

Table IV
Effect of pH for Sr2+ions

S.No	Concentration of the $SrCl_2$ solution (M)	pH 4	pH 5	pH 6
1.	1	0.192	0.194	0.192
2.	$1x10^{-1}$	0.162	0.162	0.165
3.	$1x10^{-2}$	0.145	0.143	0.146
4.	$1x10^{-3}$	0.133	0.13	0.132
5.	$1x10^{-4}$	0.105	0.106	0.107
6.	$1x10^{-5}$	0.092	0.091	0.092
7.	$1x10^{-6}$	0.092	0.091	0.092

3.4. EFFECT OF MEDIUM :

To study the effect of medium, a standard solution containing 1M Sr (II) ion in a series of 25%,50% Ethanol, acetone and dimethyl formamide was added. It was found that the potential of electrode I and II remains unchanged in the above medium.(Table V &VI)

Table V
Effect of medium for Sr2+ions

S.No	Concentration of the Sr^{2+} solution (M)	Acetone		Ethanol		DMF	
		25%	50%	25%	50%	25%	50%
1	1	0.265	0.263	0.264	0.262	0.26	0.258
2	$1x10^{-1}$	0.245	0.241	0.244	0.241	0.247	0.243
3	$1x10^{-2}$	0.232	0.23	0.23	0.228	0.222	0.22
4	$1x10^{-3}$	0.192	0.192	0.19	0.188	0.192	0.191
5	$1x10^{-4}$	0.184	0.182	0.184	0.18	0.184	0.18
6	$1x10^{-5}$	0.184	0.178	0.183	0.178	0.18	0.174

Table VI
Effect of medium for Sr2+ions

S.No	Concentration of the Sr^{2+} solution (M)	Acetone		Ethanol		DMF	
		25%	50%	25%	50%	25%	50%
1	1	0.192	0.192	0.19	0.188	0.192	0.19
2	$1x10^{-1}$	0.16	0.161	0.16	0.158	0.161	0.161
3	$1x10^{-2}$	0.143	0.14	0.145	0.141	0.143	0.141
4	$1x10^{-3}$	0.13	0.128	0.132	0.13	0.132	0.13
5	$1x10^{-4}$	0.106	0.104	0.104	0.1	0.105	0.103
6	$1x10^{-5}$	0.091	0.087	0.09	0.085	0.09	0.086
7	$1x10^{-6}$	0.088	0.085	0.085	0.07	0.088	0.085

3.4 POTENTIOMETRIC SELECTIVITY:

Selectivity is one of the most important characteristic of a chemical sensor. The influence of interfering ion and response behaviour of ion selective electrode is usually described in terms of selectivity coefficient. The potential response of the strontium ion selective electrode to different ion 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 ion was set to 1M. It was found that the potential of electrode I remains unaffected in the presence of a serious of various cations likeMn2+, K+, Mg2+, Na+, Cu2+, Ca2+, Zn2+, Ba2+, Ni2+, and anions like NO32-,I-, Cr2O72-,Br-and Cl and also found that the potential of electrode II remains unaffected in the presence of various cations like Mn2+, K+, Mg2+, Na+, Cu2+, Ca2+, Zn2+, Ba2+, Ni2+, and anions like NO32-,I-, Cr2O72-,Br-and Cl- .

3.5 RESPONSE AND LIFE TIME:

The static response time of the electrode (I) was 40 secand for the electrode (II) was 55 sec. The electrodes(I&II) were used over a period of 3 months with good reproducibility.

4.ANALYTICAL APPLICATION

Determination of strontium by direct potentiometric methods

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 strontium ion in vegetables.

The recovery of strontium ion in electrode (I) for sample analysis was formed to be quantitative with the maximum recovery of 96% and in electrode (II) for sample analysis was formed to be quantitative with the maximum recovery of 98%.

5. CONCLUSION:

The plastizied PVC- based membrane incorporating Strontium phthalocyanine, phenyl substituted Semicarbazone as an ionophore, DOP as solvent mediator and NATBP as anion excluder in a PVC matrix could be used to determine Sr2+ in the concentration range of strontium phthalocyanine (electrode-I) and phenyl substituted Semicarbozone (electrode-II). The detection limit was found to be concentration range of 1.0 X 10-5 M to1.0 X 10-1 M for electrode(I) and for electrode (II) over a concentration range of 1.0 X 10-6 M to 1.0 X 10-1 Mwith a slope value was found to the electrode(I) was 21 mv/decade and electrode (II) was 22mv/decade.The sensor works in a wide pH range was found that the electrodes(I&II) worked well in the acidic pH range. pH range of electrode(I) from 3 to 5 and electrode(II) from 4 t0 6.The selectivity of the electrode towards Sr2+ is quite well understood over the other cations. The lifetime of the assembly is 3 months in both aqueous and nonaqueous medium. In addition, the membrane sensor can also be used used in the analysis of concentration of Strontium in various real samples.

Reference:

[1] **M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, and A. R. Massah, "Uranyl selective PVC membrane electrodes based on some recently synthesized benzo-substituted macrocyclic diamides,"** *Talanta*, **vol. 58, no. 2, pp. 237–246, 2002.**

[2] **Z. R. Zhang and R. Q. Yu, "The synthesis and membrane transport characteristics of macrocyclic polyether ligands composed of 1,10-phenanthroline as carriers for primary amine species,"** *Talanta*, **vol. 41, no. 2, pp. 327–333, 1994.**

[3] **A. K. Singh, P. Saxena, S. Mehtab, and B. Gupta, "Strontium(II)- selective electrode based on a macrocyclic tetraamide,"** *Talanta*, **vol. 69, no. 2, pp. 521–526, 2006.**

[4] **A. K. Singh, P. Saxena, and A. Panwar, "Manganese(II)-selective PVC membrane electrode based on a pentaazamacrocyclic manganese complex,"** *Sensors and Actuators B*, **vol. 110, no. 2,pp. 377–381, 2005.**

[5] **M. R. Ganjali, T. Razavi, R. Dinarvand, S. Riahi, and P. Norouzi, "New diltiazem potentiometric membrane sensor stands on theoretical calculations as a useful device for diltiazem hydrochloride analysis in pharmaceutical formulation and urine,"** *International Journal of Electrochemical Science*, **vol. 3, pp. 1543–1558, 2008.**

[6] **M. R Ganjali, Z. Memari, F. Faridbod, and P. Norouzi, "Samarium microsensor: an asymetric potentiometric membrane sensor,"***International Journal of Electrochemical Science*, **vol. 3, pp.1169–1179, 2008.**

[7] **S. S. Beheshti and M. K. Amini, "A simple and selective flowinjection**

potentiometric method for determination of iodide based on a coated glassy carbon electrode sensor,"*InternationalJournal of Electrochemical Science*, **vol. 2, pp. 778–787, 2007.**

[8] H. Zhang, Z. Zhang, J. Li, and Sh. Cai, "Effects of Mg2+ on supported bilayer lipid membrane on a glassy carbon electrode during membrane formation," *International Journal of Electrochemical Science*, **vol. 2, pp. 788–796, 2007.**

[9] P. Paker, *McGraw-Hill Concise Encyclopaedia of Science and Technology*, **McGraw-Hill, New York, NY, USA, 1994.**

[10] S. F. D'Souza, "Microbial biosensors," *Biosensors and Bioelectronics*, **vol. 16, no. 6, pp. 337–353, 2001.**

[11] J. Reglinski, S. Morris, and D. E. Stevenson, "Supporting conformational change at metal centres. Part 2: four and five coordinate geometry," Polyhedron, vol. 21, no. 21, pp. 2175–2182, 2002.

[12] S. Yamada, "Advancement in stereochemical aspects of Schiff base metal complexes," Coordination Chemistry Reviews, vol. 190, pp. 537–555, 1999.

[13] Boumann, E.W. Anal. Chem. 1975, 47, 959.

[14] Akami, N.; Zimmer, H.; Mark, H.B. Anal. Lett. 1991, 24, 1431–1443.

[15] Mojtaba Shamsipur , Sayed Yahya Kazemi and Hashem Sharghi (2007)"design of a selective and sensitive PVC-membranepotentiometric sensor for strontium ion based on 1,10-Diaza-5,6-Benzo 4,7 Dioxacyclohexadecane-2,9-DIone as a neutral ionophore",*sensor*,*7*(4):438-447.

[16] Khun.K,Ibupoto.Z.H, Chey.C.O, Jun. Lu, Nur.O, Willander.M(2013) "Comparative study of ZnO nanorods and thin films for chemical and biosensing applications and the development of ZnO nanorods based potentiometric strontium ion sensor", *Applied Surface Science*, 268: 37–43.

[17] Mohammad hossein arbab-zavar, gholam hossein rounaghi and elham fahmideh-rad (2009)." Strontium Ion-Selective Electrode Based on 18-Crown-6 in PVC Matrix" *Asian Journal of Chemistry* 21(3): 2224-2232.

[18] Kia.M, A. Islamnezhad.A and Shariati.Sh(2011) "Construction of Sr2+-Selective Electrode and Thermodynamic Study of the Ternary Aqueous Mixed Electrolyte System (SrCl2, KCl, H2O) Using Potentiometric Method" *Journal of Physical and Theoretical Chemistry*, 8 (2) 79-83.