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DEVELOPMENT OF PERCHLORATE AND THIOCYANATE SELECTIVE MEMBRANE ELECTRODES BASED ON SCHIFF BASE MACROCYLIC COMPLEXES IN BIOLOGICAL WASTES

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ABSTRACT

A new copper (II) ion selective PVC membrane electrode based on the two molecules of the bis-N, O bidentate Schiff base has been developed .The electrode exhibits a good potentiometric response for Cu (II) over the range $4X10^{-6}$-$1.0X10^{-1}$ for perchlorate and $5X10^{-6}$-$1.0X10^{-1}$M for thiocyanate anions with slope 58.4±5 and 57.0±5mV per decade over a wide pH range of 2.0–12.0 respectively. The proposed electrode has a response time 10 sec. The electrode possesses fast response time, satisfactory reproducibility appropriate life time and most important good selectivity towards perchlorate and thiocyanate relative to other common inorganic anions. The electrodes are successfully applied to the Potentiometric determination of perchlorate and thiocyanate biological samples (e.g. human urine, saliva waste water and mineral water).

Keywords: Perchlorate selective electrode, Thiocyante selective electrode, PVC membrane electrode, Schiff base complex, Potentiometry, Ionophore, Plasticizer

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1.0 INTRODUCTION

A number of ion selective electrodes that can be recognize specific anions by chemical methods have been developed. Perchlorate (ClO_4^-) is regarded as an emerging persistent inorganic contaminant because of its specific properties such as high water solubility, mobility and considerable stability. Perchlorate have been use extensively as missile propellants, organic synthesis, electro polishing of metals, animal feed additives etc. Moreover perchlorate is a human health concern at high doses due to its ability to interface with iodide uptake and ability of the thyroid to regulate hormone production and metabolism. In mineral water the excess supply of chlorine combines with oxygen to form perchlorate ions, which is harmful to human health. Thiocyanate (SCN^-) is the major metabolite of hydrogen cyanide, a toxic substance that organism may be exposed to as a result of cigarette smoking or industrial pollution.

2.0 EXPERIMENTAL

2.1 Material

Regent grade o-nitrophnyl octyl ether (NPOE) dioctyl sebacate (DOS), dibutyl sebacate (DBS), dimethyl sebacate (DMS), dibutyl phthalate (DBP), dioctyl phthalate (DOP) are used as plasticizers. PVC of high molecular weight was obtained (from Merck). Trioctyl-methyl ammonium chloride (NaTPB), tetra hydro furan (THF) as additive was used (from Merck).All aqueous solution was prepared with salts of the highest available purity. The sample solutions for Potentiometric measurements consisted of sodium and potassium salts of anions (all from S D fine chemical).Double distilled water was used through out for preparing all aqueous solutions. The pH adjustment was made with dilute hydrochloric acid or KOH solution as required. The Schiff base complex of Cu (II) were synthesized and purified according to the previous reported procedures.

2.2 Ion Selective membrane preparation

The general procedure to prepare PVC membrane, powered PVC was dissolved in 1% by weight of ionophore, additive (NaTPB) in 5 ml THF. The appropriate amount of plasticizers was added .Then the mixture was shaken vigorously. The THF was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm I'd. on top) was dipped into the solution for about 10 sec. so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 5 hours. The electrode was finally conditioned for 24 hours by soaking $NaClO_4$ and NaSCN at 22 ± 2^0C.A silver / silver chloride electrode was used as an internal reference electrode. The ratio of various ingredients, concentration of equilibrant solution and time of contact optimized to provide membranes.

Ag/ AgCl/ KCl (3M) internal solution $NaClO_4$ ($1X10^{-2}$ to 10^{-4}) PVC Membrane test solution Ag/ AgCl/ KCl (3M) or NaSCN

3.0 RESULT AND DISCUSSION

The response of ion selective electrodes in relation to selectivity, stability etc depends not only on the ionophore but also on the use of certain plasticizer and in the preparation of the different membrane ingredients. Thus the influence of the membrane composition, amount of plasticizer, lipophilic additives and ionophore on the potential was prepared with different composition of plasticizers.

Table: 1 Optimization ingredients of the preparation of perchlorate selective membrane electrode

No.	PVC (mg)	Plasticizer	Ionophore (mg)	NaTPB (Additive)	Slope	Linear range
1.	33.0	o-NPOE-	1.0	0.0	-57.1	$4.0X10^{-6}$-1.0M
2.	32.4	66.0mg	3.2	0.2	-58.7	$4.3X10^{-6}$-1.0M
3.	29.5	o-NPOE-	3.5	1.0	-44.2	$3.7X10^{-5}$-$7.6X10^{-2}$
4.	31.5	64.4mg	2.5	0.2	-45.1	$4.3X10^{-6}$-$1.0X10^{-1}$
5.	31.0	DOS-66.0mg	2.0	1.0	-60.5	$3.0X10^{-5}$-$2.5X10^{-1}$
6.	32.3	DOS-65.8mg	2.0	0.3	-61.4	$2.8X10^{-5}$-$2.0X10^{-1}$
7.	33.0	DOP-66.0mg	3.2	0.4	-41.2	$1.8X10^{-5}$-$1.0X10^{-1}$
8.	32.0	DOP-65.4mg	3.0	0.6	-71.0	$7.4X10^{-5}$-$1.0X10^{-1}$
		DBP-64.4mg				
		DBS-64.4mg				

Table: 2 Optimization ingredients of the preparation of thiocyanate selective membrane electrode

No.	PVC (mg)	Plasticizer	Ionophore (mg)	NaTPB (Additive)	Slope	Linear range
1.	32.1	o-NPOE-	2.9	0.2	-59.9	$1.0X10^{-4}$-$1.0X10^{-1}$
2.	29.9	64.8mg	3.5	1.0	-57.7	$5.0X10^{-6}$-$1.0X10^{-1}$
3.	32.0	o-NPOE-	2.0	0.0	-41.2	$5.7X10^{-5}$-$4.5X10^{-2}$
4.	30.8	65.6mg	4.0	0.4	-40.8	$5.8X10^{-5}$-$4.5X10^{-2}$
5.	32.0	DOS-66.0mg	0.5	0.9	-60.3	$7.2X10^{-5}$-$6.0X10^{-2}$
6.	31.0	DOS-64.8mg	2.5	0.6	-64.3	$8.0X10^{-5}$-$6.9X10^{-2}$
7.	33.0	DOP-66.6mg	1.0	0.0	-43.2	$1.0X10^{-6}$-$1.0X10^{-2}$
8.	32.5	DOP-65.9mg	2.0	0.5	-72.3	$6.3X10^{-5}$-$1.0X10^{-1}$
		DBP-66.0mg				
		DBS-65.0mg				

3.1 SELECTIVITY COEFFICIENT OF THE ELECTRODES

The selectivity coefficients for the each electrode were determined by mixed solution method for two anion selective electrodes. The potential measurements of the solution prepared with different concentrations of perchlorate and thiocyanate 1X 10^{-4}, 1X 10^{-3} and 1X 10^{-2} respectively by interference method for several anions F^-, Cl^-, Br^-, SCN^-, CH_3COO^-, NO_2^-, HSO_3^-, ClO_4^- monovalent ions.

Table-3 Potentiometric selectivity coefficient for various anions with the perchlorate and thiocyanate selective electrode

Anion	K_{ClO4^-}, X	K_{SCN^-}, X
F^-	1.2X 10^{-2}	1.0X 10^{-2}
Cl^-	7.9 X 10^{-3}	6.5 X 10^{-3}
Br^-	7.4X 10^{-3}	6.0 X 10^{-2}
I^-	2.0X 10^{-1}	2.0 X 10^{-1}
SCN^-	1.5X 10^{-1}	-----
CH_3COO^-	1.5 X 10^{-2}	5.0 X 10^{-3}
NO_2^-	7.0X 10^{-2}	1.2 X 10^{-3}
HSO_3^-	9.0X 10^{-3}	5.5 X 10^{-3}
ClO_4^-	-----	2.5 X 10^{-1}

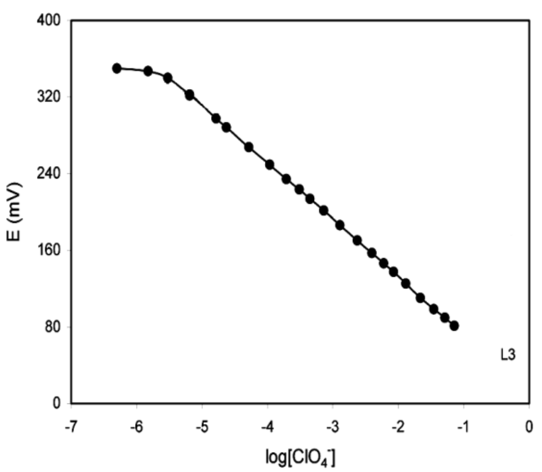

Fig.-1Potential response of various copper (II) complexes to perchlorate

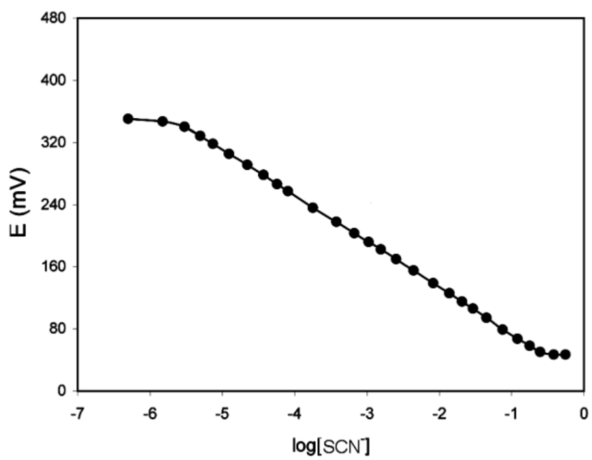

Fig.-2Potential response of various copper (II) complexes to thiocyanate ions.

Thiocyante represents a by product of tobacco that accumulated in blood and tissue of smokers. Besides, it is also one of the major constituents of waste water from the gasification of coal factories.

A lot of perchlorate and thiocyanate sensors based on different ionospheres were reported for the selective determination of these compounds from biological samples- saliva,urine,mineral water and waste water for example-5,10,15,20 tetra polyporhine manganese(III) chloride bis[N-(2 hydroxy ethyl salisyaldehydimino)]copper (II). The aim of this paper, the potentiometric response of ion selective electrodes for selecting the perchlorate and thiocyanate by using the different plasticizers (membrane solvent) based on Cu (II) complex of a Schiff base.

3.2 Effect of pH-The pH dependence of the potential response of the membrane electrode was tested in the pH range 1-12 at three concentrations of perchlorate and thiocyanate ($1X10^{-4}$, $1X10^{-3}$, $1X10^{-2}$). The ph was adjusted with HCl and NaOH required the result shown in figure

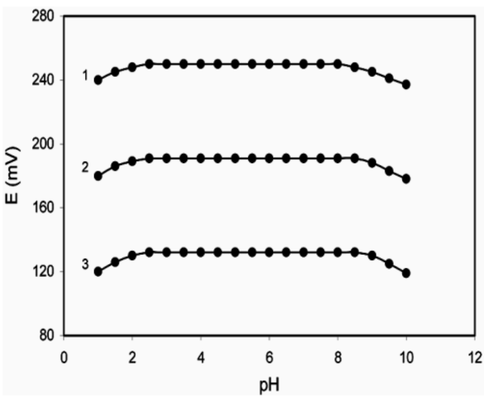

Fig.-3 The effect of pH of the test solution on the potential response of the perchlorate-selective electrode at three different ClO_4^- concentrations: (1) $1.0X10^{-4}$ M (2) $1.0X10^{-3}$ M, (3) $1.0X10^{-2}$ M

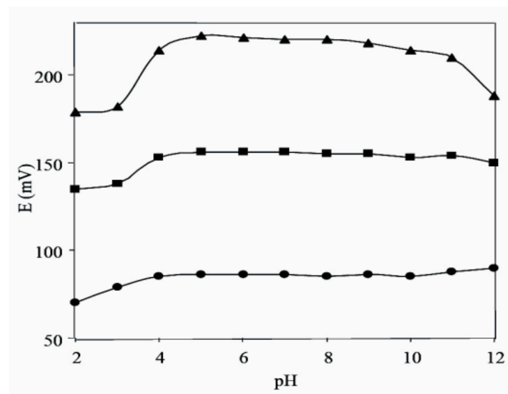

Fig.-4 The effect of pH on the potential response of thiocyanate selective electrode (▲) 1.0×10^{-4}M, (■) 1.0×10^{-3}M and (●) 1.0×10^{-2} M.

As seen the electrode potential was independent of pH in the range 2.0-12. the observed potential at low pH value is due to the concentration of perchlorate and chloride ions and variation of the potential at pH<4 could be related to protonation of ionophore in the membrane phase which results in the loss of its ability to interact with thiocyanate ions and chloride ions . While at higher pH values drift could be due to perchlorate and hydroxide anions and not for thiocyanate ions.

3.3 Analytical applications of ion selective electrodes

To assess the applicability of the membrane electrode for selecting perchlorate and thiocyanate in the biological samples (urine, saliva of smoker and non smoker humans), mineral water and waste water were found to important because of human health. The high selectivity of ClO_4^- and SCN^- of the proposed electrodes makes it potentially useful for monitoring the concentration of perchlorate and thiocyanate in different concentration of samples and different concentration of different plasticizers. The result of analysis of the s amples are given in Table-4

Table-4Determination of perchlorate and thiocyanate in biological samples of mineral water

Sample	Perchlorate(μgmL^{-1})	Thiocyante (μgmL^{-1})
Urine (Non smoker)	10.8 ± 0.5	0.89 ± 0.02
Urine (smoker)	97.6 ± 0.7	7.9 ± 0.3
Saliva (Non smoker)	10.02 ± 0.02	1.03 ± 0.4
Saliva (smoker)	97.9 ± 0.5	7.1 ± 0.01
Mineral water	9.7 ± 0.4	1.03 ± 0.05
Waste water	1.01 ± 0.05	0.99 ± 0.02

4.0 CONCLUSION

The result of present study show that electrode based on binuclear copper (II) complex of bis-N, O- bidentate Schiff base may provide tool for the determination of perchlorate and thiocyanate. The proposed sensor is very easily to prepare and show high sensitivity, selectivity, long life time, low detection time and very wide pH range. High selectivity and rapid response make these electrodes suitable for measuring the concentration of perchlorate and thiocyanate ions in a wide variety of samples (e.g. biological samples) with out the need of pretreatment steps and without significant interactions from other anionic species present in the sample.

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