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A NEW ION SELECTIVE AND SENSITIVE PVC MEMBRANE ELECTRODE BASED ON PRECIPITATED NITRON-NITRATE AND NITRON-THIOCYANATE

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Abstract : The present work describes the preparation of new PVC membrane electrodes for NO_3^- and SCN^- ions based on precipitated nitron-nitrate, nitron-thiocyanate mixed with PVC in tetrahydrofuran along with dibutyl phthalate as an electroactive material. The nitrate selective electrode shows linear response in the concentration range of 1 x 10^{-1} M to 1 x 10^{-5} M with pH working range of 2 to 10 and dynamic response time of 20 seconds at the concentration of 1 x 10^{-2} M, 1 x 10^{-3} M and 1 x 10^{-4} M. The thiocyanate selective electrode shows linear response in the concentration range of 1x10^{-1} M to 5x10^{-6} M with a pH working range of 3 to 8 and dynamic response time of 15 seconds at the concentration of 1 x 10^{-2} M, 1 x 10^{-3} M and 1 x 10^{-4} M. The selectivity coefficients (K_{ij}^{pot}) for the two electrodes have been evaluated using mixed solution method. The sensors are found to be useful in potentiometric titrations and have been successfully used in the analysis of real sample.

IndexTerms **- Ion selective electrodes, ISE, nitron, PVC membrane, sensors.**

I. INTRODUCTION

In the recent years the analytical chemists have developed interest in designing novel ion selective electrode (ISEs), synthesizing electroactive material and studying the applications of ISEs in field of environmental, agricultural and medical analysis, In the past few decades considerable efforts have led to the development of selective electrodes for alkali, alkaline earth and heavy metals. In this laboratory we have synthesized nitron-nitrate and nitron-thiocyanate ions selective electrode1. The nitron (N,1,4-triphenyl-4-aza-1-azonia-2-azanidacyclopent-5-en-3-imine) can be precipitated by various monovalent anions (Fig. 1.).[1]

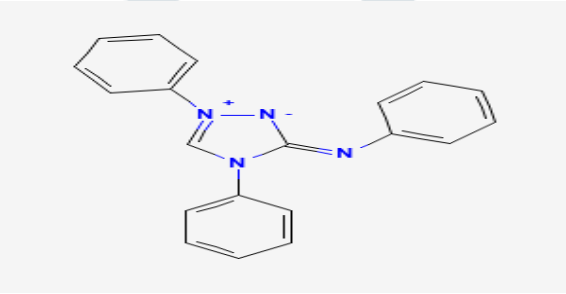

Fig. 1. Structure of nitron

The present work was undertaken to see if precipitated nitron-nitrate and nitron-thiocyanate could be used for the preparation of ion selective PVC membrane electrodes for the determination of NO_3^- and SCN^-, respectively and to see to what extent other halides and other anions interfere in the working of such electrodes. The characteristics of these electrodes have been examined in detail.[2-6]

II. RESEARCH METHODOLOGY

2.1 Procedure

2.1.1 Preparation of master membranes

A solution of nitron (0.5g) in 20% acetic acid is added separately to KNO_3 and KSCN solution to obtain nitron-nitrate yellow color precipitate and nitron-thiocyanate black color precipitate.

After washing and drying the precipitates,
(a) master membrane of nitron-nitrate was fabricated by mixing with PVC dissolved in 6 cm^3 of tetrahydrofuran and 100 mg of electroactive material (nitron-nitrate) along with 4 drops of dibutyl phthalate as plasticizer was spread on a glass plate to obtain a membrane of 0.1 mm thickness and dried it well and
(b) Similarly, master membrane of nitron-thiocyanate was fabricated over another glass plate to obtain a membrane of 0.1 mm thickness and dried it well.

2.1.2 Preparation of electrodes

A small portion from nitron-nitrate PVC membrane and nitron-thiocyanate PVC membrane was cut and plugged at one end of two separate glass tubes (outer diameter 0.8 cm, inner diameter 0.5 cm) with the help of a suitable adhesive. Before studying the characteristics and applications of NO_3^- ISE and SCN^- ISE, each electrode system was kept immersed for a week in 0.1M solution of KNO_3 and KSCN respectively. A 0.1M solution of KCI was added to each of the tubes and a saturated calomel electrode was inserted for electrical contact. A separate saturated calomel electrode was used as an external reference electrode. Thus, the two electrode systems can be represented as follows:

SCE CI^- (0.1M) NO_3^- (0.1M) Membrane Sample SCE
SCE CI^- (0.1M) SCN^- (0.1M) Membrane Sample SCE

III. RESULTS AND DISCUSSION

The pH was measured by using a pH meter (Equiptronics EQ 615) and the electrode potential was measured by the potentiometer (Equiptronics EQ 555). A magnetic stirrer was used for the stirring purpose. All physiochemical measurements were performed at room temperature ($25^0 \pm 2^0$ C).
Two separate sets of solutions of KNO_3 and KSCN were prepared in which the concentration was varied in the range of 1 x 10^{-1} M to 1 x 10^{-6} M and the potential was recorded with respective ion selective electrodes. Potassium salts of iodide, nitrate, sulphate, chloride, oxalate, nickel nitrate, cobalt nitrate, cadmium nitrate, potassium hydrogen phosphate, phosphoric acid, PVC, tetrahydrofuran and dibutyl phthalate were used during the study.

3.1 Characteristics of ISE

3.1.1 Working pH range

The effect of pH of test solutions of KSCN (1×10^{-3}M) and KNO_3 (1×10^{-3}M) on the potential response of SCN^- ISE and NO_3^- ISE was studied. The pH was maintained by adding NaOH or HCl solutions to it. A plot was made between the pH and electrode potential. For SCN^- ISE, there is an increase in electrode potential up to pH 3.0. The potential remains constant up to pH 8.0 and falls after pH 8.0. Hence, the working pH range was 3-8 [Fig. 2., Table (I)].
In case of NO_3^- ISE electrode, there was an increase in electrode potential up to pH 2 and remained constant until pH 10. After pH 10, an increase in potential was found [Fig. 2., Table (1)]. Hence, the working pH range was 2-10.

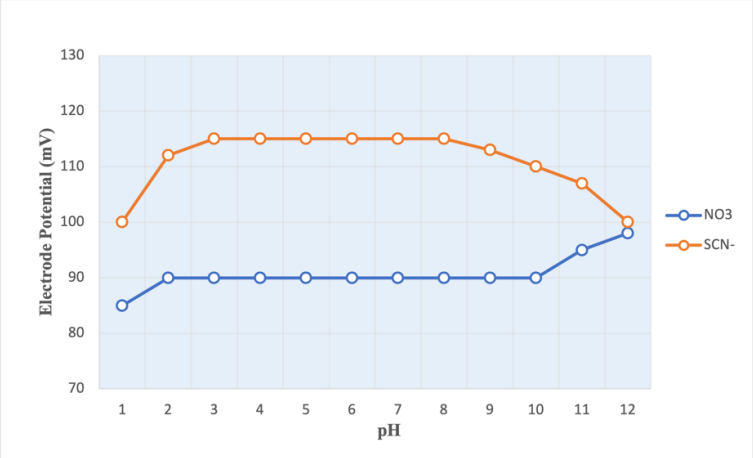

Fig. 2. The effect of PH of test solutions, KSCN (1×10^{-3}M) and KNO_3 (1×10^{-3}M) on the potential response.

3.1.2 Response Time

The dynamic response time behaviour of SCN^- ISE and NO_3^- ISE was recorded by changing the concentration of the solution from 1×10^{-2} M to 1×10^{-4} M in both the electrodes. To determine the response time of the electrodes, each was subjected to rapid changes in the concentration. The corresponding change in potential was recorded at intervals of 5 seconds and 10 seconds. The period required to attain a steady potential was read. (Fig. 3.a. and Fig. 3.b.)

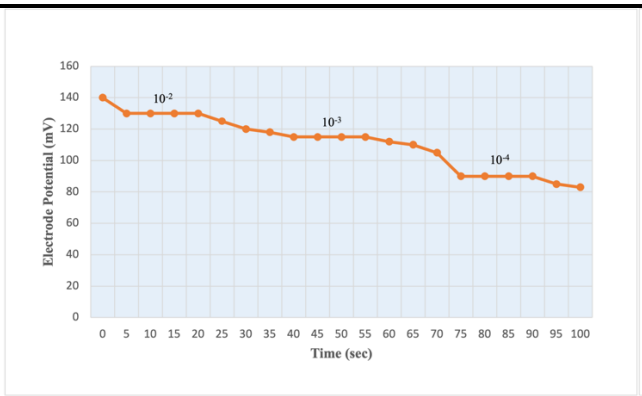

Fig. 3.a. Dynamic response time of SCN^- ISE

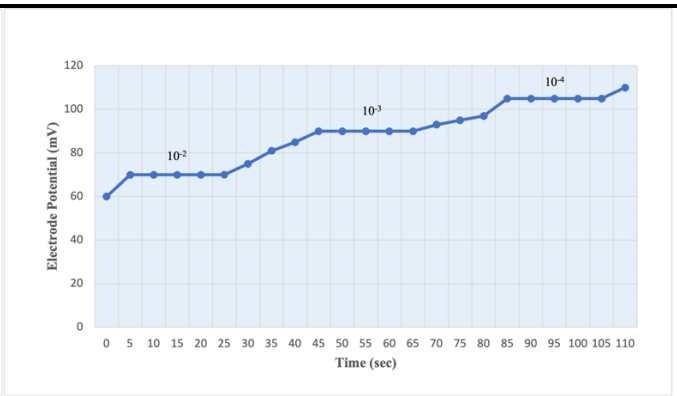

Fig. 3.b. Dynamic response time of NO_3^- ISE

3.1.3 The Linear Response of NO_3^- and SCN^-

Two separate sets of solutions of KNO_3 and KSCN were prepared in which the concentration was varied in the range of 1 x 10^{-1} M to 1 x 10^{-6} M and the potential was recorded with respective ion selective electrode. To measure the response of each electrode, graph was plotted against the SCN^- and NO_3^- ion concentration and the electrode potential. The nitrate selective electrode shows linear response in the concentration range of 1 x 10^{-1} M to 1 x 10^{-5} M. For the thiocyanate selective electrode, linear response was observed down to thiocyanate concentration of 5 x 10^{-6} M. [Table (1)]

Table (1) - Characteristics of ion selective membrane electrodes

Ion selective electrode (ISE)	Lower detection limit (M)	Per decay change in potential (mV)	Response time (sec)	Working pH range	Life of electrode
Nitrate	1 x 10^{-5}	45	20	2 to 10	8 months
Thiocyanate	5 x 10^{-6}	37	15	3 to 8	6 months

3.1.4 Selectivity coefficient

In order to know the interfering ions, the selectivity coefficients were determined for many ions by using mixed solution method using equation 1,

$$K_{ij}^{pot} = \frac{ai}{aj^{z/y}} \qquad \text{Eq. 1}$$

Where, *ai* is activity of primary ion
aj is activity of interfering ion
z and y are charges on primary and interfering ion

To calculate selectivity coefficient, the potential was measured for solution with fixed interfering ion concentration of 1 x 10^{-2} M whereas the concentration of NO_3^- and SCN^- was varied [Table (2)]. Selectivity coefficient value of 1.0 indicates that membrane responds equally to primary as well as interfering ion and a value smaller than 1.0 indicates that the electrode only responds to primary ion over interfering ions.[7-8]

Table (2) - Selectivity coefficient (K_{ij}^{pot}) of ion selective membrane electrodes.

	Selectivity coefficient in presence of interfering anions										
Ion Selective Electrode	Cl^-	Br^-	I^-	NO_3^-	NO_2^-	SCN^-	SO_4^{2-}	CH_3COO^-	CO_3^{2-}	$C_2CO_4^{2-}$	PO_4^{3-}
Nitrate	0.05	0.01	0	Nil	0.05	0	0.003	0.01	0.0032	0.032	0.0005
Thiocyanate	0.05	0.01	0	0	0.01	Nil	0.003	0.01	0.0016	0	0

The selectivity coefficient values are smaller than 1 and therefore, do not cause any significant interference in determination of NO_3^- ions and SCN^- ions in various samples.

3.2 Application

In order to explore utility of these fabricated electrodes in potentiometric titration, the PVC membrane nitron-thiocyanate ISE is successfully employed for determination of thiocyanate in laboratory water sample. The detection limit was decreased when 1 x 10^{-3}M SCN^- was titrated in 4:1 mixture of methanol with water. In non-aqueous medium of methanol, the SCN^- ion is titrated to measure directly with Ni^{2+}, Co^{2+} and Cd^{2+} nitrate by maintaining a pH between 3.5 to 4.0. Measuring the nitrate content in soil water provides important information on its pollution by fertilizer and by decomposition of organic material. In the present work, nitrate was studied in rain water and soil samples. Rain water sample was acidified with diluted H_3PO_4 at pH=3 and the ionic strength was adjusted with 5 ml of 0.5 M of potassium hydrogen phosphate (K_2HPO_4). The NO_3^- ISE was used for end point detection in titration of water sample with diphenyl thallium (III) sulphate.[9-10]

3.3 Conclusion

The constructed PVC based membrane nitron-thiocyanate and nitron-nitrate ion selective and sensitive electrode was found to work well under laboratory conditions, the electrode works in wide pH range 3 to 8 and 2 to 10 respectively. The selectivity of electrodes towards SCN^- and NO_3^- ion is appreciably good and the sensors have fairly wide applications in analysis of real sample.

IV. Acknowledgment

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