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Polymer Membrane Ion-Selective Electrode (PMISE) Based On 2,4-Dinitrophenyl–β – Naphthylamine Conjugate

Vivek Pandey[1]& R.K. Yadav[2]

1 Department of Chemistry, Rajasthan Technical University, Kota, Rajasthan (India)-324010
2 P.G.Department of Environmental Science ,SS Jain Subodh P.G. College Rambagh Circle, Jaipur, Rajasthan (India)302004

ABSTRACT

PVC polymer membrane ion-selective electrode (PMISE) Incorporating 2,4-dinitrophenyl–β– naphthylamine(DNP-β-Naphthylamine) conjugate over the surface of graphite loaded epoxy-resin based solid-state electrode body has been reported. The new conjugate shows good ionophoric behavior within the membrane and responses for NH_4^+ , Na^+ ,K^+& Mg^{++} ions have been studied. The order of selectivity for various ions is NH_4^+ > Na^+ ,> K^+> Mg^{++} . The electrode has good operational stability upto 30 days with lowest detection limit of 10^{-5} M range. For NH^+_4.

Keywords: PMISE, 2,4-Dinitrophenyl–β – Naphthylamine

INTRODUCTION

The field of polymer membrane ion-selective electrode (PMISE) is one of the most eminent area of interdisciplinary research in Analytical Chemistry. Number of publications is available on plasticized PVC [1-3] polymer membrane ion-selective electrode based on selective ionophoric materials. Application of ionophores within the polymer membrane plays significant role as the selectivity, stability, & responsive behavior of ion-selective electrode depends upon its nature. Lot of attention has been made on the use of ionophoric species such as neutral carriers (nonactin [4], valinomycin [5]& crown ethers [6]) and ion exchangers [7, 8] in the construction of PMISEs. More efforts are still needed in the development of PIMSEs with longer life time, high selectivity and fast response time. Researches have shown the incorporation of 2 , 4-dinitrophenyl-bovine serum albumin (DNP-BSA) conjugate as an antigenic ionophores [9, 10] within the PMISEs. Pandey & Pandey [11] have reported ion-selective electrode using 2 , 4-dinitrophenyl -alanine conjugate (DNP-Ala.) as ionophoric material where the DNP group[12] has strong affinity for monovalent cations. The poor operational life time of the electrode is due to the leaching of DNP-Ala conjugate from the PVC membrane to the aqueous solution is reported and there still exist a scope to exploit the use of DNP based conjugates in the construction of PMISEs.

In this paper, application of 2,4-dinitrophenyl–β–naphthylamine(DNP-2,4-dinitrophenyl–β–naphthylamine) conjugate as an ionophore for PMISE is reported. Response curves obtained for NH^+_4, K^+, Na^+ & Mg^{++} ions, effect of ionic strength along with the data showing operational stability of graphite loaded solid-state epoxy resin based PMISE incorporating DNP-B-naphthylamine conjugate is reported.

MATERIALS

PVC fine powder was obtained from Aldrich. All other chemicals used were of AR grade. All solutions were made in deionized distilled water.

Synthesisof2, 4-dinitrophenyl-B–naphthylamineconjugate:

The conjugate was prepared by using the classical protein sequencing agent, fluorodinitrobenzene [13] . β- naphthylamine and fluorodinitrobenzene were added in stoichiometric amount followed by the addition of equimolar amount of triethylamine to complex the released fluoride ion. The mixture was stirred for one hour and the solution turned reddish orange in colour. To this distilled water was added and the reddish orange precipitate was separated by filtration. The precipitate was dissolved in dichloromethane followed by the addition of saturated solution of sodium hydrogen carbonate in order to remove the free amine and the weakly acidic phenolic products. Finally the dichloromethane extract was dried using anhydrous sodium sulphate for overnight and the product was isolated by rotator evaporation. The structure was confirmed by NMR spectroscopy.

Preparation of graphite loaded epoxy-resin based solid-state PMISE

The solid-state graphite loaded epoxy-resin PMISE was prepared as described in earlier publication by replacing DNP-Ala with DNP-β-naphthylamine conjugate. The PMISEs were stored in 10^{-3} M solution of the appropriate salt when not in use.

Potentiometric measurement

The potential measurements using PMISE were made in a cell with a working volume of 10 mL equipped with a magnetic stirrer and thermostated at 25°C (Townson& Mercer Ltd. U.K. bath). The potential was recorded with a Radiometer PHM 64 pH meter connected to a digital electronic recorder No. 5000. The reference electrode was a Radiometer double junction (ds 10) calomel electrode containing 0.1 M Tris-HCl buffer (pH 7.5) into the second junction. The PMISE along with reference electrode was placed in a recation cell containing 10 mL of working buffer and the base line potential was recorded. Following the establishment of steady base line potential (E_1) , varying concentrations of the cations were added and the new steady state potential (E_2) was recorded. The difference of these two potentials $E_2 - E_1$ ($\Delta\phi$) is logarithmically correlated to the concentration of analyte present in the sample solution.

RESULTS AND DISCUSSION

Solid-state electrode body [13-16] has been widely used in the construction of ion-selective electrode because of their added advantages over conventional double barrel electrode body. Newly constructed PMISE with DNP-β-Naphthylamine conjugate is ease to design and handle because of its small size and the recovery of base line potential is very fast. The electrical potential noise during the measurement is very low (< 0.1 mV) as the impedance of the electrode is very small.

The potentiometric response of the PMISE for various ions of activity a_i is given by the following equation:

$$E = k + 2.303\ RT/F \log \{a_i + k_{i\ j} (a_j)^{1/y}\}$$

Where E is the measured potential, R is the gas constant, T is the absolute temperature in Kelvin, F is the Faraday constant and $k_{i\ j}$ is the selectivity coefficient of the PMISE in the presence of interfering ion (j) of activity (a_j) and charge (y).

Figure 1 shows the effect of buffer concentration of the response of PMISE. The response increases when the buffer concentration decreases. 0.005 Tris-Hcl buffer (pH 7.5) was found suitable as the wording buffer for taking the potentiometric data. Figure 2 shows the relative responsive nature of electrode for various cations(NH_4^+ > Na^+ > K^+> Mg^{++}) at 25^0. The electrode has maximum linear response for ammonium ion with a slope of 40 Mv/decade, while the lowest response is obtained in the case of magnesium ion which may be because of high affinity of DNP group for monovalent cations. Sodium and potassium ion also shows reasonable Nertian response having short linearity range attained at higher concentration (10^{-3} M). Table 1 revels significant feature of using this conjugate in PMISE as it is highly selective for ammonium ion in comparison to other cations. The operational life time of the electrode is very good as evidenced from the data (Table 2) of potentiometric response obtained for10^{-2} M ammonium ion on the successive days. This added stability of PMISE may be because of the strong binding of DNP-B-Naphthylamine conjugate within the plasticized PVC membrane as no leaching of conjugate was observed during the course of investigation. The electrode loses only 21% of its initial response after 35 days may be due to leaching of plasticizer[17] from the plasticized PVC polymer membrane. The PMISE was stored in 10^{-3} M solution of ammonium chloride when not in use.

Table 1:- Data on selectivity coefficient of PMISE made from DNP-B-Naphthylamine conjugate for various cations at 25^0 C in Tris-HCl buffer (.005 M pH 7.5).

Sr. No.	Interferying ion	Selectivity factor
1.	Sodium	0.45
2.	Potassium	0.17
3.	Magnesium	0.01
4.	Ammonium	1.00

Table 2:- Data on stability of PMISE made from DNP-B-Naphthylamine conjugate for 10^{-2} M ammonium ion at 25^0 C in Tris-HClbuffer(.005 M pH 7.5).

Sr. No.	Days	Response / \ 0 (mV)
1.	5	98
2.	10	95
3.	15	93
4.	20	88
5.	25	84
6.	30	80
7.	35	78

Figure 1:- Effect of ionic strength (Tris-HCl buffer pH 7.5) on PMISE made from DNP-B-Naphthylamine conjugate at 25^0 C.

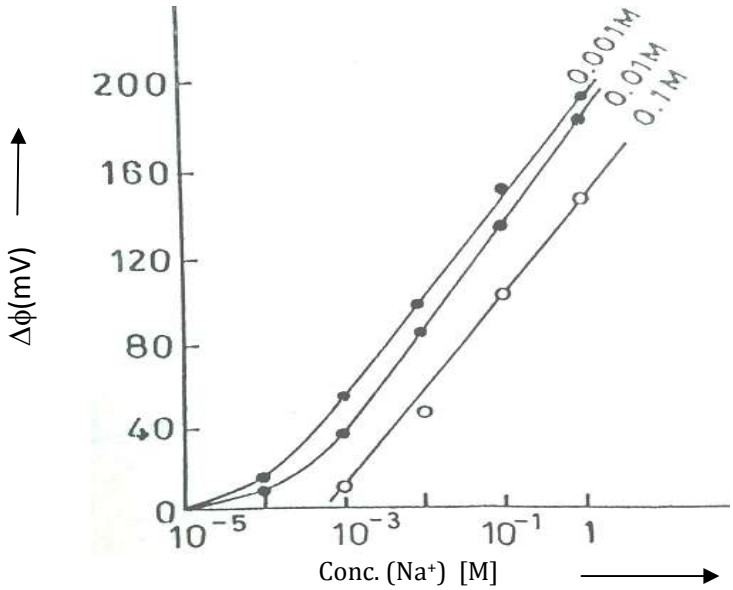
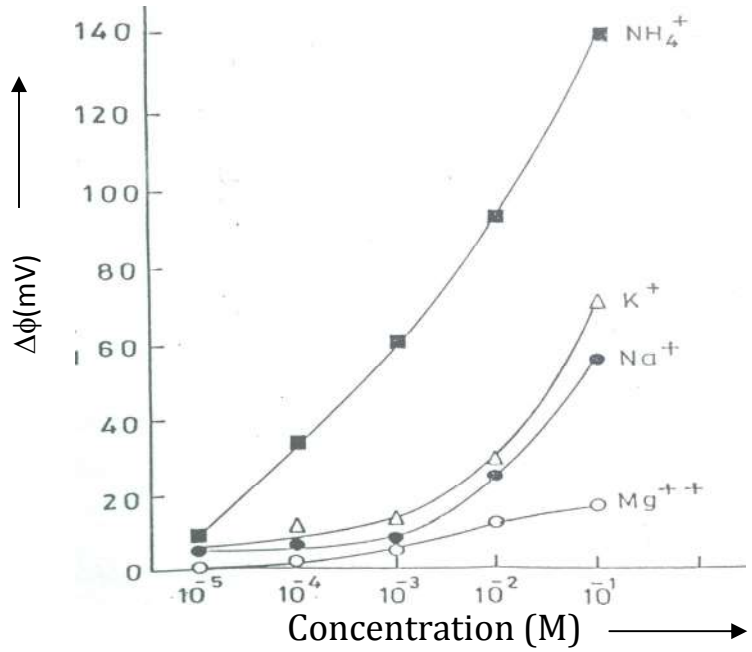


Figure 2:- Response curve of PMISE made from DNP-B-Naphthylamine conjugate to ammonium, sodium, potassium and Magnesium ions at 25^0 C in Tris-HCl buffer (.005 M pH 7.5).



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