

Sn (II) selective 2-Amino-1,4-Naphthoquinone Derived poly(vinyl chloride) Membrane Sensors

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The two quinone derivatives, 2-(N-alkenyl) amino-1,4-naphthoquinone (M_1) and 2-(N-1-butenyl)amino-1,4-naphthoquinone (M_2), have been synthesized and explored as ionophores for preparing PVC-based membrane sensors selective to stannous ion. The influences of membrane compositions on the potentiometric response of the electrodes have been found to substantially improve the performance characteristics. The best performance was obtained with the electrode having a membrane composition (w/w; mg) of (M_1): PVC: NaTPB: *o*-NPOE in the ratio 5: 150: 5: 150. The sensor shows a linear potential response for Sn^{2+} over a wide concentration range 1.4×10^{-7} to 1.0×10^{-2} M with Nernstian compliance (30.0 ± 0.2 mVdecade⁻¹ of activity) within pH range 2.5 to 7.5 and a fast response time of 10 s. The sensor has been found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of methanol, ethanol, and acetone. The analytical usefulness of the proposed electrode has been evaluated by its application in the determination of stannous in artificially made samples.

Keywords: Ion Selective Electrodes; Sn (II); 2-Amino-1, 4-Naphthoquinone; Sensors

1. INTRODUCTION

Tin is a natural element in the earth's crust. Tin metal is used to line cans for food, beverages, and aerosols. It can combine with chemicals like chlorine, sulfur, or oxygen to form inorganic tin compounds (i.e., stannous chloride, stannous sulfide, stannic oxide). These compounds are used in toothpaste, perfumes, soaps, food additives and dyes. Tin can also combine with carbon to form organotin compounds (i.e., dibutyltin, tributyltin, triphenyltin), which are used to make plastics, food packages, plastic pipes, pesticides, paints, and pest repellents [1]. Inorganic tin compounds are used as pigments in the ceramic and textile industry [2]. In addition, stannous chloride, SnCl_2 , is widely used in daily human life to conserve soft drinks, in food manufacturing, processing and packaging, and in biocidal preparations. In nuclear medicine, SnCl_2 is used as a reducing agent of Technetium-99m (as

sodium pertechnetate), a radionuclide used to label different cells and molecules [3]. As result of the use of tinplate for packaging of food and beverages, there is a probability that traces of tin dissolve in the food content [4]. According to Food and Agriculture Organization and the World Health Organization (UN-FAO/UN-WHO), the maximum limit for tin in canned foods is 250mgkg^{-1} [5], but there is evidence suggesting that consumption of food or beverages containing tin above 200mg kg^{-1} has caused gastrointestinal effects [6]. Moreover, when the contamination reaches this level the organoleptic properties of the food can be seriously affected. The biological effects of SnCl_2 include stimulation followed by depression of the central nervous system in laboratory animals [6]. Early reports showed toxicity of tin chloride in rats, i.e. pathological changes in liver and kidney, brain edema, pancreatic atrophy, increased incidence of changes in fatty acids and vacuoles in the proximal convoluted tubules [7]. The determination of strontium thus, assumes importance and various instrumental methods for its detection used are atomic absorption spectrometry [8], flame photometry [9], ICP-AES [10], etc. Though these methods do provide an accurate determination, they are not very appropriate for large scale monitoring in view of high cost and requirement of sample pretreatment. In such situations, a potentiometric determination by ion-selective electrodes (ISEs) is desirable. It provides an easy, convenient and low cost procedure of analysis in short time. The analysis by ISEs can be nondestructive, requires low sample volumes and generally no sample pretreatment, and is also applicable to turbid and colored samples. Thus, the analysis by ISEs is a preferred procedure for those ions for which good ISEs are available. In the present study the two different quinone derivatives of 2-Amino-1,4-Naphthoquinone were synthesized and explored as poly(vinyl chloride) based membrane sensors for the quantitative estimation of Sn^{2+} in different samples.

2. EXPERIMENTAL PART

2.1. Reagents

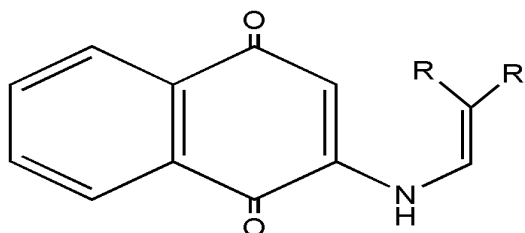
High molecular weight poly (vinyl chloride) (PVC) Aldrich (Wisconsin, USA), dioctylphthalate (DOP), Renkem (Gurgaon, India), tri-n-butylphosphate (TBP), BDH (Poole, England), orthonitrophenyloctyl ether (*o*-NPOE), dibutylphthalate (DBP) and dibutyl (butyl) phosphate (DBBP), Mobile (Alabama, USA), sodium tetraphenyl borate (NaTPB), BDH (Poole, UK) were used as obtained. Analytical reagent-grade tetrahydrofuran (THF), nitric acid, sodium hydroxide were obtained from Ranbaxy (Gurgaon, India). 2-Amino-1,4-Naphthoquinone, stannous chloride and aldehydes were from Avon Organics Limited (Greenland, Hyderabad, India). Solution of metal salt (chloride) was prepared in double-distilled water. Working solution of different concentrations was prepared by diluting 0.1 M stock solutions.

2.2. Synthesis of ionophore

2.2.1 General procedure for preparing 2-(*N*-alkenyl) amino-1,4-naphthoquinone

In 100 mL round bottom flask fitted with Dean Stark apparatus and a reflux condenser, 50 ml of benzene along with 250mg (1.45 mmol) of 2-Amino-1,4-Naphthoquinone, and 2 ml (excess) of the

aldehyde (butanaldehyde for M_1 and pentanaldehyde for M_2) were added. The reaction mixture was refluxed for 5 days. The solvent was removed and the residue was chromatographed on silica-gel using dichloromethane as eluant. The product was recrystallized from ether-hexane mixture to yield dark red needle crystals.



R = H, R' = C₂H₅ (M_1) and R = H and R' = C₃H₇ (M_2)

Figure 1. The structure of ligand M_1 and M_2 .

2-(N-1-propenyl)amino-1,4-naphthoquinone (M_1):

Yield: (145mg, 47%), m.p: 149-151°C. IR (KBr): 3250(m), 1678(s), 1602(s), 1566(s), 1502(s), 1344(m), and 1276(m) cm⁻¹. ¹HNMR δ_H(CDCl₃) for the E isomer: 1.70 (dd, J₁=7.0 Hz, J₂=1.45 Hz, 3H), 5.37 (two overlapped quartets, J₁=7Hz, J₂=14Hz, 1H), 5.88 (s, 1H), 6.20 (m, 1H), 7.35 (br, NH), 7.52(m, 1H), 7.63 (m, 1H), 7.95 (m, 1H); Non-overlapping peaks for the minor Z isomer were present at 5.02 (pentet, 1H). The ratio of the E and Z isomers was 6 determined to be 88: 12 respectively, by integration. Anal. Calcd. For C₁₃H₁₁NO₂: C, 69. 83; H, 5.86; N,7.40. Found: C, 69.64; H, 5.72; N, 7.32. The observed elemental analysis of the compound was consistent with the theoretical data obtained on the basis of the structure as given in the Fig. 1

2-(N-1-butenyl)amino-1,4-naphthoquinone (M_2):

Yield: (160mg,49%), mp: 155-157. IR (KBr): 3210(m), 3157(m), 2963(m), 1680(m), 1603(s), 1571 (s), 1509 (s), and 1275 (m) cm⁻¹. ¹HNMR δ_H (CDCl₃) for the E isomer: 1.04 (t, J = 7.4 Hz, 3H), 2.13 (pentet of doublet, J₁ = 7 Hz, J₂ = 1.5 Hz, 2H), 5.48 (td, J₁ = 14 Hz, J₂ = 7 Hz, 1H), 5.95 (s, 1H), 6.26 (m, 1H), 7.37 (br, NH), 7.61 (td, J₁ = 7.5 Hz, J₂ = 1.3 Hz, 1H), 7.72 (td, J₁= 7.5 Hz, J₂ = 1.3 Hz, 1 H), 8.03 (dd, J₁ = 7.5 Hz, J₂ = 1.1 Hz, 1H), 8.08 (dd, J₁= 7.5 Hz, J₂ = 1.1Hz, 1H). Non-overlapping peaks for the minor Z isomer were present at 1.08 (t, J=7.5 Hz, 3H), 2.19 (pentet of doublet, J₁= 7.5 Hz, J₂=1.5 Hz, 1H), 5.01 (q, J=7.5 Hz, 1H), 6.18 (m, 1H), 7.34 (br, NH). The ratio of the E and Z isomers was determined to be 90: 10 respectively, by integration. C-13NMR δ(CDCl₃): 13.83, 23.28, 102.01, 119.91, 121.82, 126.21, 126.38, 130.29, 132.22, 133.40, 134.85, 143.15, 181.73, 182.98. m/z: 227 (M⁺, 100%). Anal. Calcd. For C₁₄H₁₃NO₂: C, 73.99; H, 5.77; N, 6.16. Found; C, 73.87; H, 5.49; N, 5.98. The observed elemental analysis of the compound was consistent with the theoretical data obtained on the basis of the structure as given in the Fig. 1

2.3. Fabrication of electrodes

The PVC-based membranes were prepared by dissolving appropriate amounts of Schiff bases (M_1 or M_2), anion excluder NaTPB, solvent mediators, dioctyl phthalate (DOP), tri-*n*-butylphosphate (TBP), 1-chloronaphthalene (CN), dibutyl(butyl)phosphonate (DBBP) and (orthonitrophenyloctyl ether) *o*-NPOE and appropriate amounts of PVC in THF (5 mL). After complete dissolution of all components and thorough mixing, the resulting mixture was poured into polyacrylate rings placed on a smooth glass plate. THF was allowed to evaporate for about 24 h at 25°C. To obtain membranes with reproducible characteristics, the viscosity of the solution and solvent evaporation were carefully controlled; otherwise morphology and thickness of the membranes have shown a drastic variation, which ultimately affected the sensor response. The transparent membranes of 0.4 mm thickness were removed carefully from the glass plate. A 5.0 mm diameter piece was cut out and glued to one end of a “Pyrex” glass tube. [11].

2.4. Conditioning of membranes and potential measurements

The membranes were equilibrated for 2 days in 0.1 M SnCl_2 solutions. The potential have been measured by varying the concentration of SnCl_2 in test solution in the range 1.0×10^{-8} to 1.0×10^{-2} . The standard SnCl_2 solutions of metal salts have been obtained by gradual dilution of 0.1 M SnCl_2 solution. Membranes of different compositions were prepared, equilibrated and investigated. Those that gave reproducible results and best performance characteristics were selected for detailed studies. The potential measurements were carried out at $25 \pm 1^\circ\text{C}$ using saturated calomel electrodes (SCE) as reference electrodes with the following cell assembly:



3. RESULTS AND DISCUSSION

3.1. Determination of formation constant

Formation constant of the ion–ionophore complex within the membrane phase is a very important parameter that dictates the practical selectivity of the sensor. In this method, two membrane segments are fused together, with only one containing the ionophore, to give a concentration-polarized sandwich membrane. A membrane potential measurement of this transient condition reveals the ion activity ratio at both interfaces, which translates into the apparent binding constants of the ion–ionophore complex [12]. In this method complex formation constants obtained by neglecting ion pairing. As reported, the membrane potential E_M is determined by subtracting the cell potential for a membrane without ionophore from that for the sandwich membrane. The formation constant is then calculated from the following equation:

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_I} \right)^{-n} \exp \left(\frac{E_M z_I F}{RT} \right) \quad (1)$$

Where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion-ionophore complex stoichiometry, and R , T and F are the gas constant, the absolute temperature, and the Faraday constant. The ion I carries a charge of z_I . The determined formation constants ($\log \beta_{IL_n}$) for the examined different complexes were recorded in Table 1. The elapsed time between sandwich fusion and exposure to electrolyte was typically <1 min. The potential was recorded as the mean of the last minute of a 5 min measurement period in the appropriate salt solution. The potential of such sandwich membranes remains free of diffusion-induced potential drifts for about 20 min. A careful analysis of the data in Table1 reveals that Sn^{2+} ion has significant cation-binding characteristics.

Table 1. The formation constant of ligands-metal complexes

	M ₁	M ₂
Cation	Formation constant ($\log \beta_{IL_n}$)* \pm SD	Formation constant ($\log \beta_{IL_n}$)* \pm SD
Al ³⁺	3.25 \pm 0.4	3.11 \pm 0.3
In ³⁺	3.15 \pm 0.3	3.05 \pm 0.5
Sn ²⁺	7.25 \pm 0.2	7.14 \pm 0.4
Co ²⁺	4.16 \pm 0.4	3.33 \pm 0.5
Cu ²⁺	3.65 \pm 0.2	2.85 \pm 0.6
Cr ³⁺	3.43 \pm 0.6	2.35 \pm 0.3
Fe ³⁺	3.32 \pm 0.4	2.12 \pm 0.4
Ca ²⁺	2.23 \pm 0.6	1.89 \pm 0.5
Ag ⁺	1.12 \pm 0.8	0.98 \pm 0.6
Mg ²⁺	2.25 \pm 0.7	0.74 \pm 0.3
Na ⁺	0.85 \pm 0.6	0.65 \pm 0.2
K ⁺	0.73 \pm 0.2	0.45 \pm 0.3
Ga ³⁺	2.35 \pm 0.5	2.15 \pm 0.4

*Mean value \pm standard deviation (three measurements)

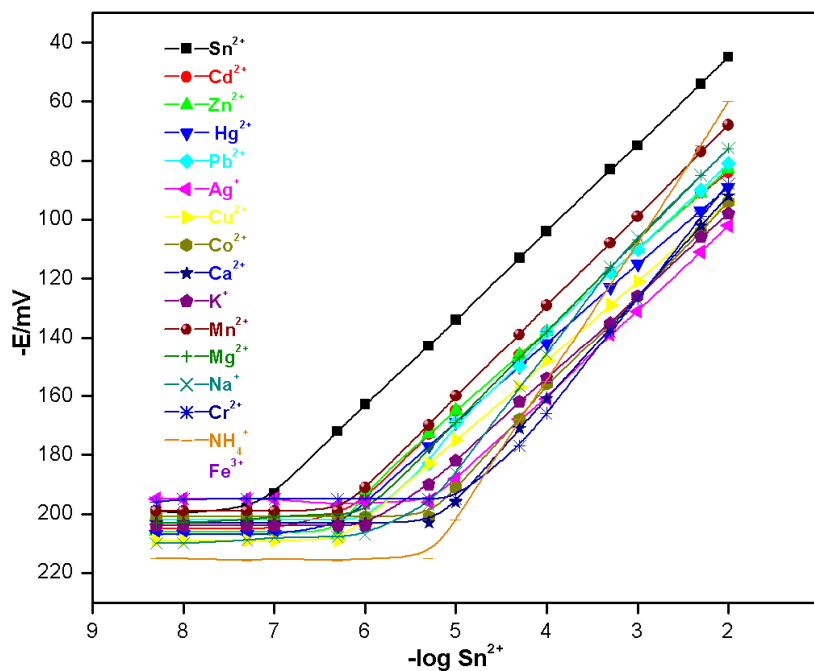


Figure 2. The response characteristic study of sensor no. 2 against different metal ions.

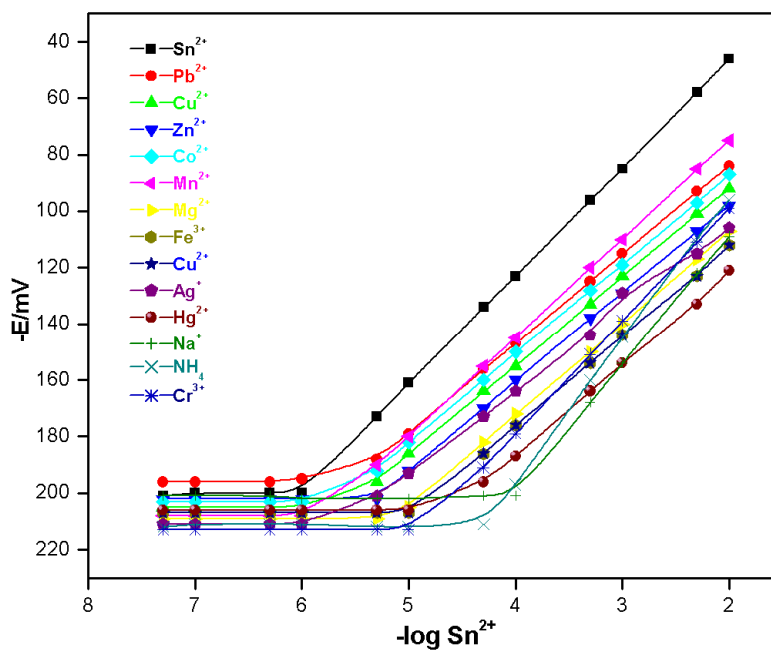


Figure 3. The response characteristic study of sensor no. 7 against different metal ions.

Table 2. The composition of ionophore (M₁) based PVC membrane sensors selective to Sn²⁺.

Sensor no.	Composition of membrane w/w, mg							Working concentration range (M)	Detection limit (M)	Slope (± 0.2 mV/decade of activity)	Response time (s)
	M ₁	PVC	NaTPB	DOP	TEP	o-NPOE	DBBP				
1	5	150	-	-	-	-	-	1.0 × 10 ⁻⁴ - 1.0 × 10 ⁻²	6.3 × 10 ⁻⁵	33.3	12
2	5	150	5	-	-	150	-	1.4 × 10 ⁻⁷ - 1.0 × 10 ⁻²	1.0 × 10 ⁻⁷	30.0	10
3	5	150	5	150	-	-	-	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻²	5.0 × 10 ⁻⁷	29.0	13
4	5	150	5	-	150	-	-	5.0 × 10 ⁻⁵ -1.0 × 10 ⁻²	5.0 × 10 ⁻⁶	28.0	16
5	5	150	5	-	-	-	150	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻²	3.0 × 10 ⁻⁷	26.0	14

Table 3. The composition of ionophore (M₂) based PVC membrane sensors selective to Sn²⁺.

Sensor no.	Composition of membranes (w/w; mg)							Working concentration range (M)	Detection limit (M)	Slope (± 0.2 mV/decade of activity)	Response time (s)
	M ₂	PVC	NaTPB	DOP	TEP	o-NPOE	DBBP				
6	5	150	-	-	-	-	-	5.9×10^{-2} - 1.0×10^{-2}	9.9×10^{-3}	.32.5	15
7	5	150	5	-	-	150	-	1.3×10^{-6} - 1.0×10^{-2}	1.0×10^{-6}	29.8	12
8	5	150	5	150	-	-	-	1.0×10^{-5} - 1.0×10^{-2}	7.0×10^{-7}	30.0	12
9	5	150	5	-	150	-	-	5.8×10^{-4} - 1.0×10^{-2}	4.1×10^{-4}	32.8	11
10	5	150	5	-	-	-	150	1.8×10^{-4} - 1.0×10^{-2}	1.1×10^{-4}	28.0	14

3.2. Response of the electrode based on Schiff bases to Sn(II)

To investigate the suitability of the ionophores for comparison purposes, ligands were used as neutral ionophores to prepare several PVC membrane ion selective electrodes under identical conditions for a variety of metal cations, including alkali, alkaline earth, transition and heavy metal ions. It has been observed from Figs. 2 and Figs.3, respectively, except for the Sn^{2+} ion for all other cations, the slope of the corresponding potential plot is much lower than the expected Nernstian slopes of 59, 29.5 and 20 mV decade^{-1} of activity for the univalent, bivalent and trivalent cations, respectively, although over limited concentration range. As is obvious from the obtained results, the Sn^{2+} ion with the most Nernstian response over a wide concentration range seems to be suitably determined with the PVC membrane electrode based on ligand M_1 . The results might indicate that the selectivity towards this ion is masked by the low detection limit of the electrode, which is most probably due to the transport of Sn^{2+} ions from the measuring solution to the boundary between membrane and the solution as discussed by Bakker [13].

3.3. Optimization of membrane composition

The sensitivities and selectivities obtained for a given membranes depend significantly on the membrane ingredients and the nature of plasticizer and additives used. Therefore, 10 membranes with different compositions (Tables 2 and 3) have been prepared and their response characteristics were evaluated according to the IUPAC recommendation [14]. In order to guarantee a good membrane performance, an adequate plasticizer must show sufficient lipophilicity, no crystallization and exudates in the membrane phase. It is now well established that the plasticizer play a vital role in the sensor performance as it is responsible for ionophore solvation and distribution in the membrane matrix, thus controlling the detection limit [15], affecting the selectivity and sensitivity [16] and giving the plastic membrane its proper elasticity and strength. This is achieved by decreasing the zero-current fluxes from the membrane ingredients into the solution through judiciously optimizing the membrane ingredients and inner electrolyte composition. Sn^{2+} selective membranes incorporating ionophores with different constitution showed pronounced variation when using plasticizers of varying polarity, constitution and lipophilicity as solvents and also there is much evidence indicating its responsibility for the mobility of the ion through the membranes. Thus the membranes containing the two ionophores (M_1) and (M_2) plasticized with DOP, TEP, CN, DBBP, *o*-NPOE have been investigated. It is clear from (Tables 2. and 3.) that *o*-NPOE, shows the best performance characteristics with electrode (2) for (M_1) with concentration range of 1.4×10^{-7} to 1×10^{-2} M and electrode 7 for M_2 with concentration range 1.3×10^{-6} to 1×10^{-2} M. This indicates the solvent medium of *o*-NPOE is probably providing the best complexation environment between stannous ions and their respective carriers.

3.4. Dynamic response time

It is well known that the dynamic response time of a sensor is one of the most important factors in its evaluation. To measure the dynamic response time of the proposed sensor the

concentration of the test solution has been successively changed from 1.0×10^{-6} to 1.0×10^{-2} M. The resulting data depicted in Fig. 4, shows that the time needed to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of Sn^{2+} ions, each having a tenfold difference in concentration is, 10 s for M_1 (electrode 2) and 12 seconds (electrode 7). This is most probably due to the fast exchange kinetics of complexation–decomplexation of Sn(II) ions with the M_1 ionophore at the test solution–membrane interface. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from (1.0×10^{-2} to 1.0×10^{-3} M) sample concentrations and the results showed that, the potentiometric response of the electrodes was reversible; although the time needed to reach equilibrium values (50 s) were longer than that of low-to-high sample concentrations [17-21]. Reproducibility of the electrode was examined by using six similar constructed electrodes under the optimum conditions. The result showed good reproducibility (± 0.4 mV) for the electrode.

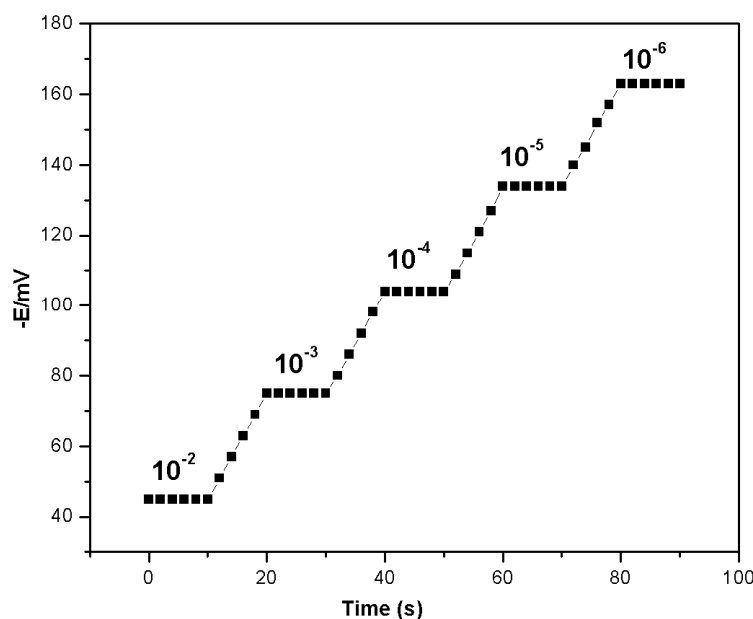


Figure 4. The dynamic response study of best responsive sensor no. 2.

3.5. Potentiometric selectivity

The potentiometric selectivity coefficient of an ISE is commonly used as a quantitative expression of the ability of the electrode to respond primarily ion in the presence of interfering ions. The selectivity studies were carried out only for sensors Nos.2 and 7 at pH 5.4, which exhibited the best performance characteristics in terms of working concentration range, slope, response time and life time. Different methods of selectivity determination have found in the literature. In the present study, the selectivity coefficients were determined using the fixed interference method (FIM) [22-40]. In this method selectivity coefficient was evaluated by potential measurement on solutions containing fixed concentration of interfering ion (1.0×10^{-2} M) and varying concentration of primary ion Sn(II)[41-122]. It is given by expression:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \quad (2)$$

Where a_A is the activity of primary ion A (Sn^{2+}) at the lower detection limit in the presence of interfering ion B and z_A and z_B are their respective charges. The selectivity coefficient is expressed as the logarithm mode and the negative value indicate a preference for the target ion relative to the interfering ion, while positive value indicate the preference of an electrode for the interfering ion. Of the two sensors, selectivity of the sensor no. 2 was found to be better (Table 4) and it has been seen that the selectivity of the proposed sensor toward stannous is better for most of the cations as compared to all reported sensors and thus it is superior to all of them. As sensor no. 2 is better than the sensor no. 7 in terms of wider working concentration range, lower response time, high selectivity and Nernstian compliance, further studies have been carried out with it only.

Table 4. Selectivity coefficients of sensor no.2 and 7 on the membranes of M_1 and M_2 , respectively.

Interfering ion	Sensor no. 2 Selectivity coefficient ($K_{Ni,x}^{Pot}$)	Sensor no. 7 Selectivity coefficient ($K_{Ni,x}^{Pot}$)
Li^+	9.5×10^{-3}	6.0×10^{-3}
Na^+	1.7×10^{-3}	1.0×10^{-2}
K^+	6.7×10^{-3}	6.5×10^{-3}
NH_4^+	3.6×10^{-4}	1.5×10^{-4}
Cs^+	3.3×10^{-3}	1.2×10^{-3}
Tl^+	2.4×10^{-3}	1.9×10^{-3}
Ag^+	6.3×10^{-3}	5.8×10^{-3}
Ca^{2+}	4.2×10^{-2}	3.9×10^{-2}
Sr^{2+}	6.3×10^{-2}	2.6×10^{-2}
Zn^{2+}	2.4×10^{-2}	1.5×10^{-2}
Cd^{2+}	6.5×10^{-2}	4.2×10^{-2}
Hg^{2+}	1.8×10^{-2}	9.5×10^{-3}
Co^{2+}	4.6×10^{-2}	1.6×10^{-2}
Pb^{2+}	4.6×10^{-2}	6.7×10^{-2}
Mn^{2+}	3.5×10^{-2}	4.6×10^{-2}
Cu^{2+}	2.4×10^{-2}	3.6×10^{-2}
Fe^{3+}	4.3×10^{-4}	5.6×10^{-4}
Cr^{3+}	3.6×10^{-4}	4.5×10^{-4}

3.6. PH and non-aqueous effect

One of the ions present in the aqueous solution is the hydrogen ion. It interferes in many instances, in the functioning of the electrode. In view of this, it is necessary to find the optimum pH range where the electrode functions without interference from the hydrogen ions. The pH dependence of the sensor (2) has been tested over the pH range 1.0 - 12.0 at two fixed concentrations (1.0×10^{-2}

and 1.0×10^{-3}) of Sn^{2+} . The pH was adjusted with dilute nitric acid or sodium hydroxide solutions. The potential of the sensor was determined as a function of pH and the results were illustrated in Fig. 5. The potential remained constant over the pH range of 2.5-7.5, which may be taken as the working pH range of the sensor assembly. The performance of the sensor no.2 was further assessed in partial non-aqueous media, i.e. methanol – water, ethanol – water and acetonitrile – water mixture. The results obtained are compiled in Table 5 and show that up to 20 % non-aqueous content no significant change occurs in the slope and working concentration of the sensor. However, above 20 % non-aqueous content, the working concentration of the sensor is significantly reduced, and thus the sensor can only be utilized in mixtures containing up to 20 % non-aqueous content.

Table 5. Effect of partially non-aqueous medium on the working of Sn^{2+} sensor (sensor No. 2)

Non-aqueous content (%, v/v)	Slope (mV/decade of activity)	Working concentration range (M)
0	30.0	1.0×10^{-7} - 1.0×10^{-2}
Methanol		
10	30.0	1.4×10^{-7} - 1.0×10^{-2}
15	30.0	1.4×10^{-7} - 1.0×10^{-2}
20	29.4	1.6×10^{-7} - 1.0×10^{-2}
25	28.2	7.0×10^{-7} - 1.0×10^{-2}
Ethanol		
10	30.0	1.4×10^{-7} - 1.0×10^{-2}
15	30.2	1.4×10^{-7} - 1.0×10^{-2}
20	29.4	1.7×10^{-7} - 1.0×10^{-2}
25	28.1	8.1×10^{-7} - 1.0×10^{-2}
Acetonitrile		
10	30.0	1.4×10^{-7} - 1.0×10^{-2}
15	29.5	1.4×10^{-7} - 1.0×10^{-2}
20	29.0	5.0×10^{-7} - 1.0×10^{-2}
25	27.8	1.2×10^{-6} - 1.0×10^{-2}

4. ANALYTICAL APPLICATIONS

The analytical application of proposed work (sensor no. 2) is evaluated by estimation of Sn^{2+} concentrations in different artificially made samples with simple starch-iodine based titration. Transfer different concentration's samples (56.5 mg, 113 mg, 226 mg, 452 mg) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ accurately weighed, to a 250 ml volumetric flask, dissolve in 25 ml of hydrochloric acid, dilute to volume with water, and mix well. Transfer 50 ml of this solution to a 500 ml conical flask, and add 5 g of potassium sodium tartrate, and then a cold saturated solution of sodium bicarbonate until the solution is alkaline to litmus paper. Titrate at once with 0.1N iodine using starch TS as the indicator. The obtained results were comparatively compiled with sensors no 2 in Table 6. Each ml of 0.1N iodine consumed is equivalent to 11.28 mg of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$

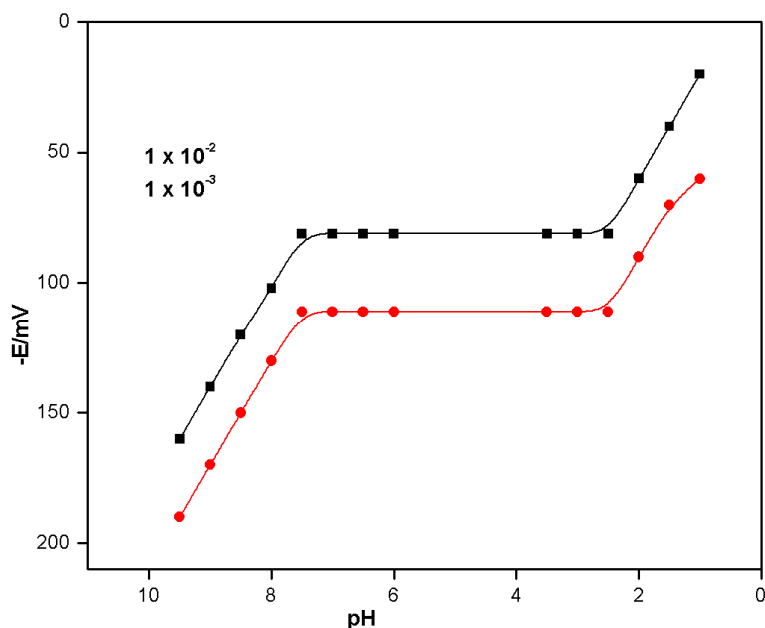


Figure 5. The pH performance study of sensor no. 2.

Table 6. The comparative performances evaluation of sensor 2 and iodine-starch titration.

Sample no.	*Sensor no. 2	*Titration
1 (56.5 mg/500 mL)	56.2 ± 0.5	56.1 ± 0.3
2 (113 mg/500 mL)	112.8 ± 0.4	112.6 ± 0.4
3 (226 mg/500 mL)	225.7 ± 0.3	225.6 ± 0.3
4 (452 mg/500 mL)	451.8 ± 0.5	451.6 ± 0.4

*Mean value ± standard deviation (three measurements)

5. CONCLUSIONS

This work demonstrates that both the sensors (M_1) and (M_2) used for quantification of stannous ions are good selective. The sensor (M_1) exhibits excellent potentiometric performance. The best composition of the proposed electrode was found to be ionophore (M_1): PVC: NaTPB : *o*-NPOE = 5 : 150 : 5 : 150 (w/w). It responds to Sn^{2+} in a Nernstian fashion, presents a good selectivity over most of the cations of conventional Sn^{2+} selective electrodes and showed a low detection limit and working range (1.4×10^{-7} to 1.0×10^{-2}). This is characterized by a relatively fast response, long term and responsive potential stability and was successfully applied to the determination of Sn^{2+} in different environmental samples.

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