

Full Paper

Selective Electrochemical Sensor for Silver(I) Ion Based on Chelating Ionophore *o*-Hydroxyacetophenone Carbohydrazone (OHAC)

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Abstract- Novel polymeric membrane electrode based on *o*-hydroxyacetophenone carbohydrazone (OHAC) as a neutral ionophore carrier has been prepared and explored as silver(I) ion selective electrode. The addition of lipophilic anion excluder (NaTBP) and various plasticizers viz. *o*-nitrophenyl octyl ether (*o*-NPOE), dibutyl phthalate (DBP) and butyl acetate (BA) have found to improve the performance of membrane sensor which have a composition of I:NaTBP:NPOE:PVC in the ratio 3:2:62:33 (w/w; mg). The electrode exhibit Nernstian slope for silver (I) ions over wide concentration ranges from 1.0×10^{-7} M to 1.0×10^{-2} M with limits of detection 1.6×10^{-7} M. The response time was found to be 10 s. The potentiometric responses were independent of the pH of the test solutions in the pH range of 3.0 to 8.0. The proposed electrode revealed good selectivity over a wide variety of other cations including alkali, alkaline earth, transition and heavy metal ions. The proposed PVC electrode was used as an indicator electrode in the potentiometric titration of Ag^+ ions with KI and NaCl solutions and in direct determination in different water samples and urine sample of peoples working as jewelry maker.

Keywords - Polymeric membrane, Carbohydrazone, Silver Selective Electrode, Detection Limit, Selectivity

1. INTRODUCTION

The development of selective chemical sensors has received widespread attention during the past two decades because of their possible use in clinical and environmental monitoring. Ion selective electrodes (ISE) are appropriate for this purpose because they show good selectivity for inorganic ions and they are easy to build. They are relatively of low cost and used in the places of interest. ISEs have found wide spread use for the direct determination of ionic species in complex samples [1]. In the early days, their selectivity was often the limiting factor in determining low levels of analyte ions. In unbuffered samples, the current polymer membranes ISEs show lower detection limits that are much, typically in the micromolar range [2].

Silver is a useful element in many respects, its role in physiological processes has not been proved, but its presence in some part of the human body, such as human hair, is well known [3]. Silver also has an important role in electrical and electronic applications, photographic film production and the manufacturing of fungicides [4], and as an important ion in some drugs like silver sulfadiazine cream that has been a standard treatment for burns over the past decades and silver deposition has been found in the skin, gingival, cornea, liver, and kidney of patients [5, 6]. The multi-purpose nature of silver makes its analysis in and recovery from waste material, drinking water, and other samples of importance [7]. Thus, the determination of trace amounts of silver ion in various media is necessary .

Based on the chemical recognition principle, several types of carriers of suitable size and specific metal–carrier interaction have been successfully utilized for the construction of Ag^+ -ISEs. [8-15]. In recent years, the design of carrier-based Ag^+ -ISEs has gained importance, mainly due to the neutral ionophore-based Ag^+ -ISEs with better selectivity.

It is well known that the soft heavy metal ions, Ag^+ , Pb^{2+} , and Hg^{2+} display great affinity for soft coordination centers like oxygen, sulfur and nitrogen. By using ionophores containing oxygen and nitrogen atoms in ion-selective electrodes, it is expected that the electrodes are sensitive to soft heavy metal ions and the selectivity for soft heavy metal ions against alkali metal ions is significantly increased [16].

In this respect, carbohydrazones with nitrogen and oxygen donor atoms have attracted much interest owing to the unique properties of the compounds. The carbohydrazone derivatives are highly versatile chelating agents for metal cations. This type of compounds forms selective complexes with metal cations due to their flexible structure. Taking this advantage into consideration, in the present work, we designed and synthesized a new ligand *o*-hydroxyacetophenone carbohydrazone (OHAC) as neutral ionophore in Ag(I) selective membrane electrodes. This ligand which is easily synthesized and have different C-shaped cavity with three donor atoms, are expected to form selective complexes with transition-metal ions and to give an improved selectivity for the silver ions. The effect of several parameters such as the ionophore concentration and pH was investigated and the optimized membranes

were used to obtain the response characteristics and selectivity. In addition, the electrodes were used in titration experiments and for the determination of silver ion concentrations in real samples.

2. EXPERIMENTAL

2. 1. Reagents and Apparatus

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueous solutions. *o*-Hydroxy acetophenone, carbohydrazide, high molecular weight poly(vinylchloride) powder (PVC), dibutyl phthalate (DBP), butyl acetate (BA) and tetrahydrofuran (THF) were obtained from Sigma. Sodium tetraphenyl borate (NaTPB) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. Salts of metal nitrates or chlorides (all from Merck) were of the highest purity available and used without any further purification. All the metal nitrate solutions were freshly prepared by accurate dilution from their stock solution of 0.1 M, with distilled, de-ionized water.

The carriers or ionophores used in electrode preparation were synthesized in the laboratory and then were characterized. The C, H, and N contents were analyzed on a Carlo-Erba 1106 elemental analyzer. IR spectra (KBr) were recorded on a Perkin-Elmer Fourier transform infrared spectroscopy (FTIR) spectrum BX-II spectrophotometer. The ¹H NMR spectrum was recorded with a model Bruker Advance DPX-300 spectrometer operating at 300 MHz using DMSO-d₆ as a solvent and TMS as an internal standard.

2. 2. Synthesis of ionophore

An aqueous ethanolic solution of carbohydrazide (0.01 mol, 0.9g) was treated with 1 ml glacial acetic acid followed by slow addition of a solution of *o*-hydroxy acetophenone (0.01 mol, 1.04 ml) in 20 ml ethanol. The resulting mixture was heated under reflux for about 12 h. On cooling overnight at 0°C, yellowish crystalline precipitate of ionophore (Fig.1) was separated out, which was filtered, washed with cold ethanol and dried under vacuum. Yield 72 %, m.p. 203 °C.

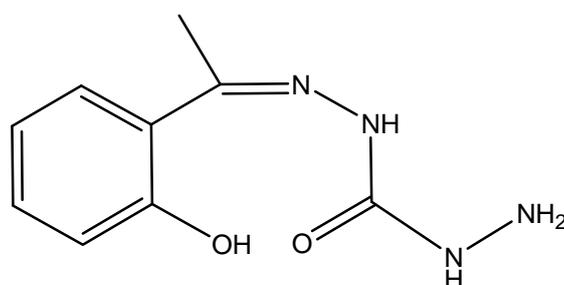


Fig. 1. *o*-Hydroxyacetophenone carbohydrazone (OHAC)

Elemental analysis: $C_9H_{12}N_4O_2$, Found (Calc.) C: 35.01(34.76), H: 3.78(3.39), N: 18.29 (18.01). IR bands ($KBr\ cm^{-1}$) 3482 $\nu(OH)$, 3237 $\nu(NH)$, 1705 $\nu(C=O)$, 1550 $\nu(C=N)$, 738 $\phi(C=O)$ shown in Fig. 2 (a). 1H NMR (300 MHz, DMSO d_6), δ (ppm); 2.1(s, 3H, $-CH_3$), 3.4(s, br, 2H, $-NH_2$), 6.5(s, br, 1H, $-NH$), 6.8-7.8(m, 4H, $-arH$), 12.9(s, 1H, $-OH$), 13.3(s, 1H, $-NH$) shown in Fig.2 (b).

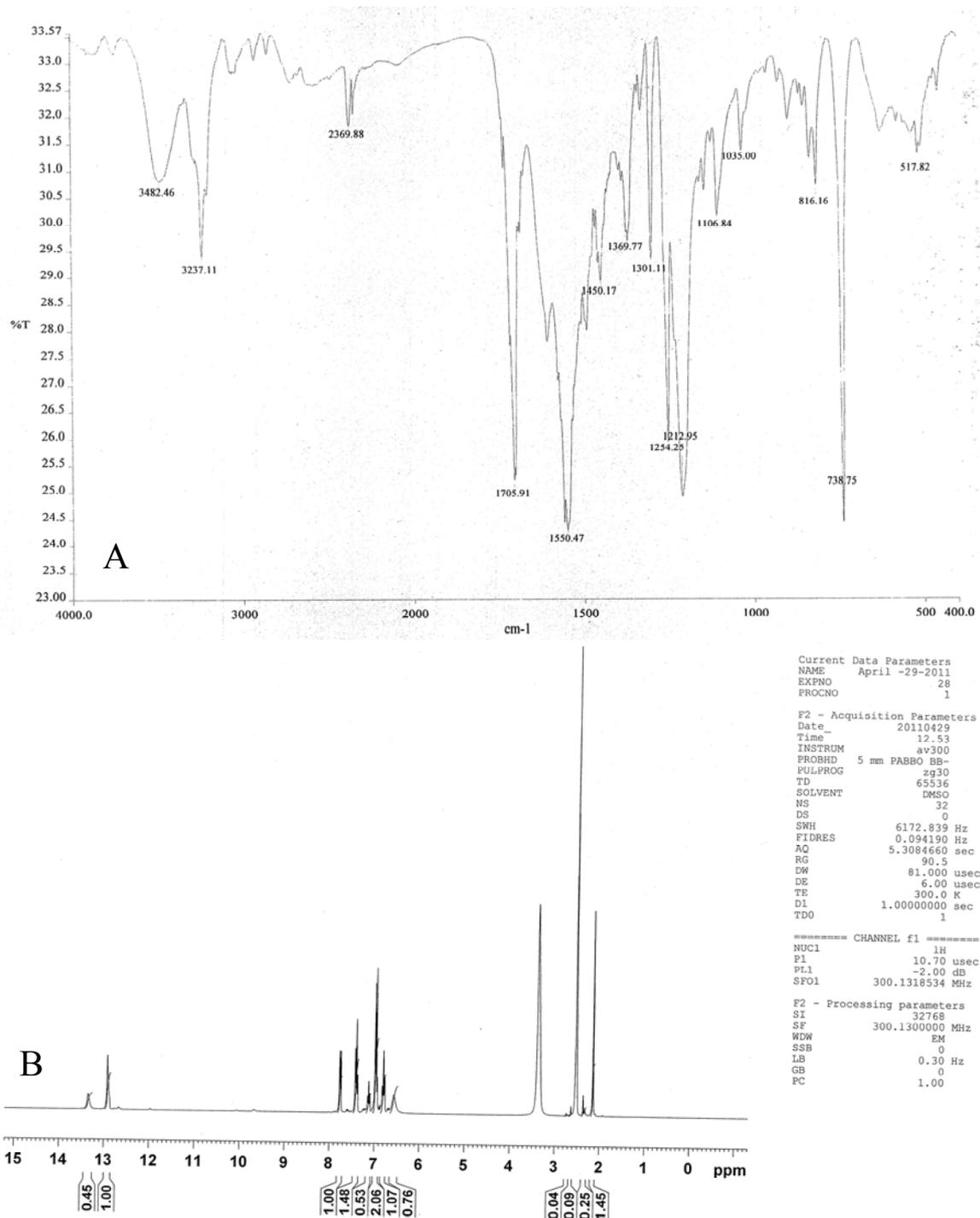


Fig. 2. (A) IR Spectra of ionophore OHAC (B) 1H NMR of ionophore OHAC

2. 3. Fabrication of electrodes

Beside the critical role of the nature of ion carrier in preparing membrane-selective sensor, some other important features of the PVC based membrane electrode, such as amount of ionophore, nature of solvent mediator, plasticizer/PVC ratio and especially the nature of additive used are significantly influence the sensitivity and selectivity [17]. The membranes have been fabricated as suggested by Craggs et. al [18].

Membranes of 0.2 mm thickness were obtained by pouring a solution of the membrane components of PVC 33%, ionophore 2-6%, plasticizer 58-63% dissolved in 3-5 mL of tetrahydrofuran (THF). The viscous solution thus obtained was poured in a glass ring of 30 mm diameter placed on a dust free pyrex glass plate. The solvent was allowed to evaporate slowly for about 24 h at room temperature. To obtain membrane with similar characteristics, viscosity of the casting solution and the rate of solvent evaporation were controlled so that the thickness and the morphology of the membranes remained almost unchanged and the appearance of the film looked like pale yellow color. The membrane were then removed from the glass plate and circular pieces of 1.50 cm diameter were cut and mounted on the ground end of pyrex glass tube with araldite. The picture of membrane taken by optical microscope is shown in Fig. 3.

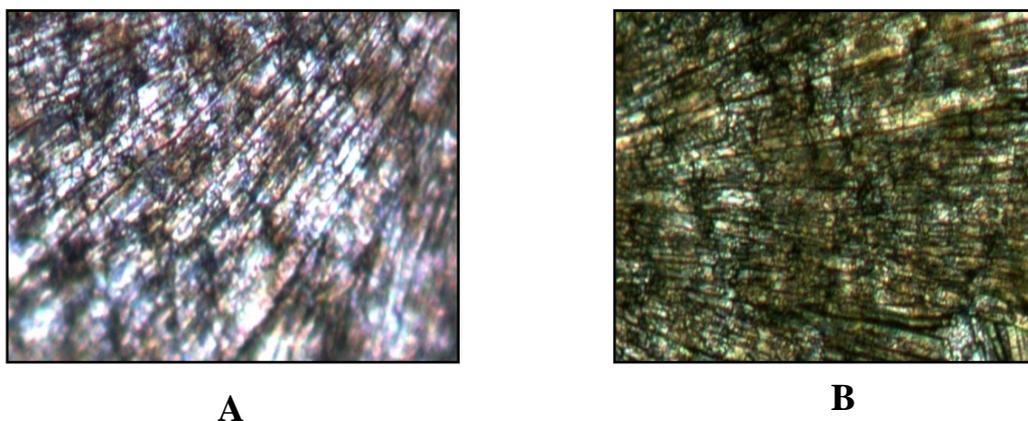
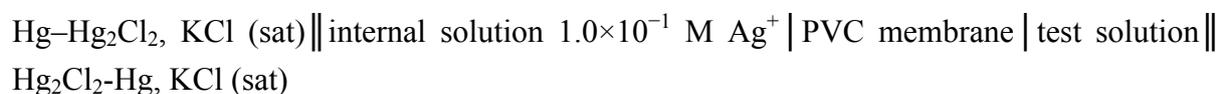


Fig. 3. Optical microscopic picture of membrane (A) before use as a sensor, (B) after use as a sensor

2.4. Equilibration of membrane and potential measurement

The time of contact and concentration of equilibrating solution were optimized so that the sensors generated stable and reproducible potential at relatively short response time. The polymeric membrane electrode was equilibrated for ~2 days in 1.0×10^{-1} M AgNO_3 solution. The potentials were measured by varying the concentration of AgNO_3 in test solution in the range 1×10^{-8} M to 1.0×10^{-2} M. Standard AgNO_3 solutions were obtained by gradual dilution of 10^{-1} M AgNO_3 solution.

The emf measurements with the polymeric membrane electrode were carried out on digital potentiometer (Equiptronic Model no. EQ-609) at 25 ± 1 °C using saturated calomel electrode (SCE) as reference electrode with the following cell assemblies:



3. RESULT AND DISCUSSION

3. 1. Study of internal solution

In order to study the ion sensor response formalism, the influence of the concentration of internal solution on the potential response of the polymeric membrane electrode for Ag^+ ion based on proposed ionophore were studied. The concentration was varied from 1.0×10^{-1} M to 1.0×10^{-4} M and the potential response of the sensor has been observed. It was found that the most effective results in terms of slope and working concentration range which was quite appropriate for the smooth functioning of proposed sensor has been obtained with internal solution of concentration 1.0×10^{-1} M .

3. 2. Optimization of the membrane composition

The sensitivity and selectivity of an electrode are significantly affected by the nature of plasticizer, the composition of ionophore, internal solution etc. [19-21]. So, for optimization of the membrane, effect of the electrode like the slope of the calibration curve, measurement range and detection limit were studied.

The optimum membrane ingredients showing the most sensitive, reproducible and stable result was obtained with a plasticizer/PVC ratio 64/33 together with 3 mg of ionophore. This ratio exhibits the best response with a Nerstian slope of ~ 60 mV per decade. A study of influence of the plasticizer on the potentiometric response was conducted by *o*-NPOE, DBP and BA and results are shown in Table 1. It was shown that among various solvent medium, *o*-NPOE is the most effective plasticizer.

Table1. Optimization of membrane composition

S.N.	PVC (wt.%)	Plasticizer (wt.%)	Ligand (wt.%)	NaTPB (wt.%)	Slope (mV/decade)	Detection Limit (M)	Linear range(M)
1.	33	65(NPOE)	2	-	50	1.0×10^{-5}	$1.0 \times 10^{-2} - 1.0 \times 10^{-5}$
2.	33	64(NPOE)	3	-	60	1.6×10^{-7}	$1.0 \times 10^{-2} - 1.0 \times 10^{-7}$
3.	33	63(NPOE)	4	-	61	6.0×10^{-5}	$1.0 \times 10^{-2} - 1.0 \times 10^{-7}$
4.	33	62(NPOE)	5	-	52	5.0×10^{-4}	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
5.	33	61(NPOE)	6	-	57	5.0×10^{-4}	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
6.	33	60(NPOE)	7	-	65	1.0×10^{-4}	$1.0 \times 10^{-3} - 1.0 \times 10^{-6}$
7.	33	59(NPOE)	8	-	50	5.0×10^{-5}	$1.0 \times 10^{-2} - 1.0 \times 10^{-5}$
8.	33	60(NPOE)	6	1	62	1.0×10^{-5}	$1.0 \times 10^{-2} - 1.0 \times 10^{-7}$
9.	33	62(NPOE)	3	2	60	5.0×10^{-7}	$1.0 \times 10^{-2} - 1.0 \times 10^{-7}$
10.	33	61(NPOE)	3	3	51	3.0×10^{-5}	$1.0 \times 10^{-3} - 1.0 \times 10^{-7}$
11.	32	60(DBP)	5	3	52	5.5×10^{-4}	$1.0 \times 10^{-3} - 1.0 \times 10^{-5}$
12.	32	60(BA)	4	4	51	5.0×10^{-4}	$1.0 \times 10^{-2} - 1.0 \times 10^{-7}$
13.	31	63(NPOE)	3	3	54	1.0×10^{-5}	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
14.	31	62(NPOE)	4	2	41	1.5×10^{-4}	$1.0 \times 10^{-3} - 1.0 \times 10^{-6}$
15.	30	65(NPOE)	3	2	48	1.5×10^{-5}	$1.0 \times 10^{-4} - 1.0 \times 10^{-6}$

It has been shown that the presence of lipophilic salt in the ion selective membrane sensor is necessary to introduce perm selectivity [22]. Addition of sodium salt of tetra phenyl borate is known to increase the sensitivity of the membrane as it reduces anionic interferences [23]. It was observed from Table 1 that the addition of this lipophilic cation does not affect the working of electrode response but it decreases the plasticizer/PVC ratio of membrane sensor.

3.3. Working concentration range and detection limit

This Ag^+ ion selective sensor displayed a widest concentration range of 1.0×10^{-2} M to 1.0×10^{-7} M with the Nernstian slope of ~ 60 mV per decade as shown in Fig. 4. The limit of detection was evaluated according to IUPAC recommendations [24] from the intersection of two extrapolated segments of the calibration curve and was found to be 1.5×10^{-7} M.

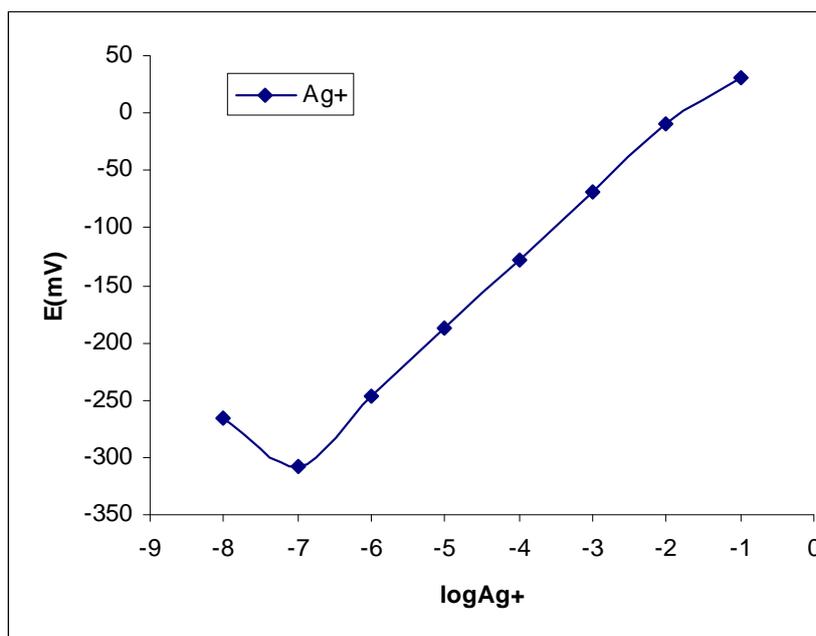


Fig. 4. Potential response of ionophore OHAC to Ag^+ ion

3. 4. pH effect

The effect of pH of the test solution on the response of the membrane electrode was examined at two Ag^+ ion concentrations. As illustrated in Fig. 5, the potentials remained constant from pH of about 3.0 to 8.0. It was shown that the sensor is suitable for Ag^+ ion determination in the pH range of 3.0 to 8.0. The variation of potential at $\text{pH} < 2.5$ could be related to the protonation of the ligand in the membrane phase, which results in a loss of its ability to form complex with Ag^+ ions. At higher pH (> 8), the potential drop may be due to the hydroxylation of Ag^+ ions.

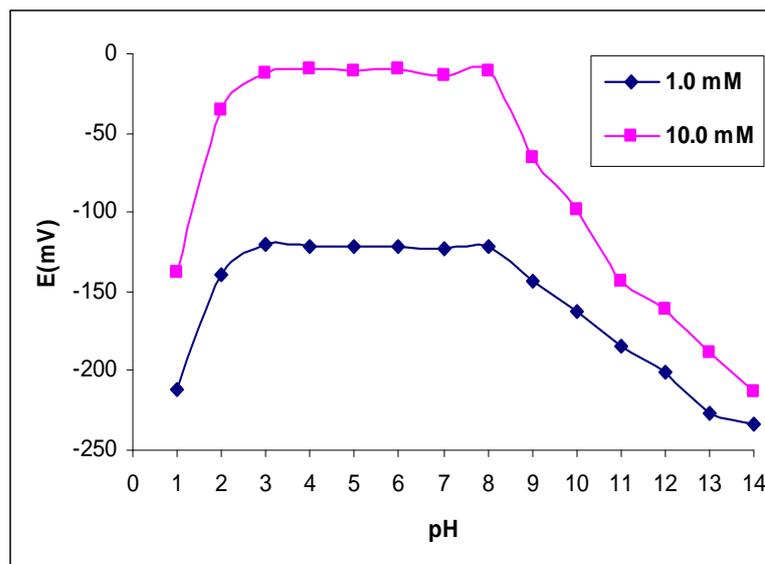


Fig. 5. pH effect on the response of Ag^+ -ISE

3. 5. Response time, reproducibility, repeatability and lifetime study

The IUPAC preferred manner of reporting the response time is now a defined rate of potential i.e. $\Delta E/\Delta T$. The response time is defined as the time between the addition of an analyte to the sample solution and the time when a steady state potential with less than 0.1 mV/min changes has been achieved. For analytical applications, the response time of a sensor is an important factor. The average time for Ag^+ ion selective electrode to reach a potential within ± 1 mV of its final equilibrium value was measured after successive immersion of the electrode in a series of Ag^+ ion solutions, each having a 10 fold increase in Ag^+ ion concentration from 10^{-7} M to 10^{-2} M. The obtained static response time for a PVC membrane electrode is 10 s. The sensing behavior of the membrane electrode remained unchanged when the potential were recorded either from low to high concentration or vice versa. The response time of the proposed electrode with respect to 10^{-3} M Ag^+ ion solutions are shown in Fig. 6.

The stability and reproducibility of the electrode were also studied. It is really apparent that any measurement device must give a result that approximates to the accurate value, and must do this with sufficient reproducibility (precision) for individual readings to be dependable. Statistician says that random errors affect the reproducibility of an experiment. Standard deviation of 20 replicated measurements for the proposed sensor at 10^{-3} and 10^{-4} M concentration of Ag^+ ion were ± 0.5 and ± 0.9 mV respectively. The long term stability of the electrode was studied by periodically recalibrating in standard solutions and calculating the response slope over the range of 1.0×10^{-7} to 1.0×10^{-2} M.

The lifespan of the electrodes was determined by recording their potentials at optimum pH value and plotting their calibration curves each day. It was observed that there was no

significant change in the slope of an electrode on the following day. The proposed sensor electrode was tested over a period of 3 months to investigate its stability. During this 3 month period, electrode was used daily and the parameters like slope, working concentration range and response time of the electrode were found to be reproducible.

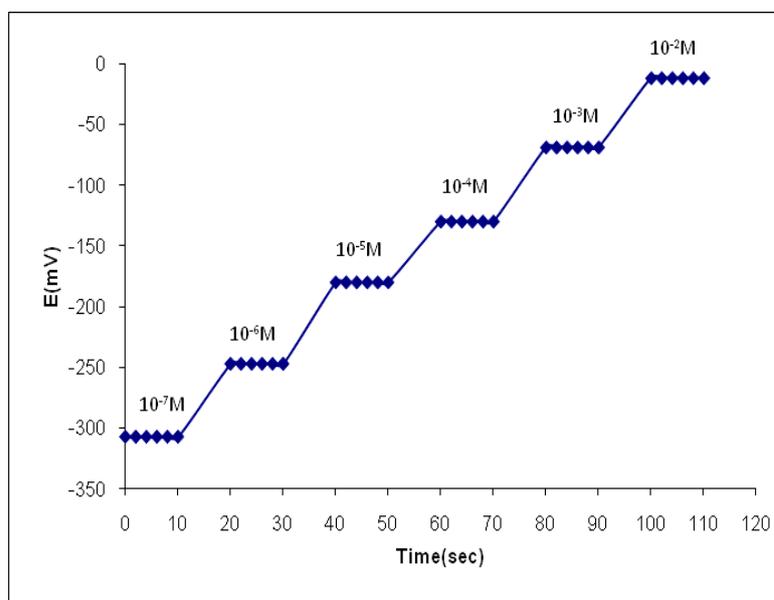


Fig. 6. Dynamic response curve of Ag^+ -ISE

3. 6. Effect of non aqueous content

The real sample may contain non aqueous content, so the performance of the sensor was also studied or tested in partially non aqueous media using 10%, 20% and 30% (v/v) non aqueous content in methanol-water, acetone-water, butane-2-one-water and acetonitrile-water mixtures and results are shown in Table 2 and Fig.7.

It was observed from the potential measurements that the membrane do not show any appreciable change in working concentration range and slope in methanol-water and acetone-water up to 20% (v/v) non aqueous contents. In butane-2-one-water and acetonitrile-water mixtures, membrane could tolerate up to 10% (v/v) non aqueous content. An increase beyond above mentioned non aqueous content causes a significant interference in slope. This may be due to the dynamic complexation and decomplexation of Ag^+ ion with the ligand.

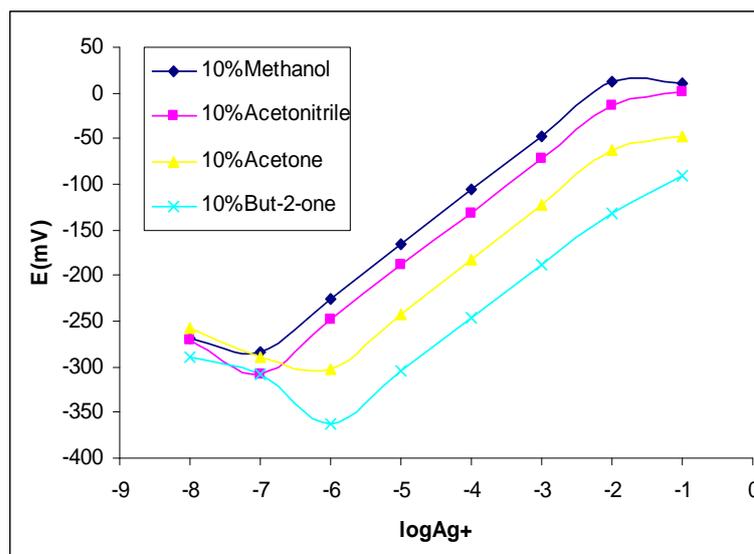


Fig. 7. Potentiometric response of Ag^+ -ISE in partially non-aqueous media

Table 2. Electrode response in mixed solvent media

Solvent	Percentage(%) (v/v)	Slope (mV/decade) (mV per decade)	Detection limit (M)
Methanol	10	59	1.9×10^{-7}
	20	58	4.0×10^{-6}
	30	53	5.0×10^{-5}
Acetone	10	60	1.5×10^{-6}
	20	59	5.0×10^{-6}
	30	54	2.8×10^{-4}
Butane-2-one	10	58	1.9×10^{-6}
	20	50	5.0×10^{-4}
	30	51	5.0×10^{-4}
Acetonitrile	10	59	2.5×10^{-7}
	20	54	4.0×10^{-5}
	30	53	4.8×10^{-4}

3. 7. Influence of interfering ions

Selectivity is the most important characteristic as it determines the utility of any sensor in real sample measurements. Ion selective electrodes are rarely specific. It gives the response of ion sensitive sensor for the primary ion in the presence of other ion present in solution.

In this work, the selectivity coefficient of the sensor towards different cationic species (M^{n+}) was evaluated by using both the matched potential method (MPM) and the fixed interference method (FIM) [25].

In case of MPM, a specified amount of primary ion is added to a reference solution and the membrane potential is measured. In a separate experiment, interfering ions are successively added to an identical reference solution until the membrane potential matches with that one obtained before with the primary ions. It is given by the expression

$$\log K^{\text{pot}}_{\text{Ag}^+, \text{B}} = \log(a'_{\text{Ag}^+} \cdot a_{\text{Ag}^+}) - \log(a_{\text{B}})$$

Where a'_{Ag^+} , is the activity of Ag^+ ions in reference solution, a_{Ag^+} is the activity of Ag^+ ion added in the reference solution and a_{B} is the activity of the interference solution. In the present work, a_{Ag^+} and a'_{Ag^+} were 1.0×10^{-2} and 1.0×10^{-3} M Ag^+ ion and a_{B} was determined experimentally.

In FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2}) and varying amount of Ag^+ ions. It is given by the expression.

$$\log K^{\text{po}}_{\text{tAg}^+, \text{B}} = \log(a_{\text{Ag}^+}) - \log(a_{\text{B}}) Z_{\text{Ag}^+} / Z_{\text{B}}$$

Where, Z_{Ag^+} and Z_{B} is the charge on silver(I) ion and interfering ion.

The resulting value of the selectivity coefficient for FIM and MPM are summarized in Table 3. As the values from this table show that all cations would not affect significantly the selectivity of the proposed sensor.

3. 8. Analytical performance

Polymeric membrane silver ion selective electrodes have potential applications in a variety of fields. We successfully applied the ionophore electrode as an indicator electrode in the potentiometric titration of Ag^+ ions with KI solution and with NaCl solutions. It is also used in the determination of halide ion from the mixture of halide ions. The electrode has also been applied for the direct determination of silver in peoples working in silver jewelry making shops, water samples and fixation solutions. A comparison of the results obtained by proposed sensor with the results obtained by atomic absorption spectrometry (AAS) shows good agreement as shown in Table 4.

Table 3. Potentiometric selectivity coefficient ($K^{\text{pot}}_{\text{Ag}^+/\text{B}}$) for interfering ions

Interfering ion (B)	$\log K^{\text{pot}}_{\text{Ag}^+/\text{B}}$	
	FIM	MPM
Na^+	1.2	2.2
K^+	1.7	2.1
Mg^{2+}	2.8	2.1
Ca^{2+}	2.5	2.2
Sr^{2+}	2.3	2.9
Pb^{2+}	2.0	2.2
Cu^{2+}	2.1	2.5
Co^{2+}	3.1	2.6
Ni^{2+}	2.5	2.1
Zn^{2+}	2.2	2.5
Cd^{2+}	3.0	2.8
Hg^{2+}	2.1	2.5
Fe^{3+}	1.9	2.6

3. 9. Determination of silver in urine sample

The better selectivity for silver ion was exhibited by the electrode based on neutral ionophore OHAC, making it potentially workable for determination of silver concentration level in biological samples. The experiment was conducted to measure silver concentration in human urine samples, obtained from peoples working in silver jewelry making shops. They inhale silver dust while working. The standard addition method was followed according to which the samples were diluted 10 times with 0.05 M phosphate buffer at pH 4.5. The spectrophotometric method was followed as a reference method for comparison of results obtained by the silver selective electrode. The results shown in the Table 4, indicate good agreement with the results obtained from the atomic absorption spectrometry (AAS).

3. 10. Determination of silver in different water samples

To access the applicability of silver selective electrode to real samples, an attempt was made to determine silver in real samples. Silver is added to samples from waste water and tap water and filtered through filter paper and acidified with 1:1 nitric acid to a pH of about 3.0 and then diluted with distilled water to the mark of a calibrated flask. The silver content was

measured using proposed electrode and by atomic absorption spectrometry (AAS), with the standard addition method. The results are given in Table 4 .

Table 4. Determination of silver in physiological samples using OHAC silver selective electrode

Sample	Ag added	ISE study ^a	AAS study ^a
People working as jewelry maker(urine sample)	-	2.1±0.3	2.4±0.2
Tap water	14.4	14.0±0.3	14.2±0.2
Waste water	16.8	16.6±0.3	16.4±0.2

^a Std. deviation calculation for five measurements

Table 5. Comparing various silver ion selective electrodes

pH range	Concentration range (mol L ⁻¹)	Slope (mV/decade)	Detection limit (mol L ⁻¹)	Reference
1.0–6.0	1.0×10 ⁻¹ to 1.0×10 ⁻⁵	58.9	6.3×10 ⁻⁶	[27]
-	1.0×10 ⁻² to 3.6×10 ⁻⁶	-	1.0×10 ⁻⁶	[28]
3.5-7.0	3.1×10 ⁻² to 9.0×10 ⁻⁷	58.4	4.2×10 ⁻⁷	[29]
3.3-8.0	1.0×10 ⁻¹ to 1.0×10 ⁻¹	60.0	6.0×10 ⁻⁵	[30]
2.0-9.0	1.0×10 ⁻³ to 1.0×10 ⁻⁶	55.5	1.0×10 ⁻⁶	[9]
3.0-8.0	1.0×10 ⁻² to 1.0×10 ⁻⁷	60.0	1.0×10 ⁻⁷	proposed electrode

4. CONCLUSION

On the basis of the results discussed in this paper, *o*-hydroxyacetophenone carbohydrazone (OHAC) can be regarded as a potential carrier for the construction of polymeric membrane to determine the low level concentration of Ag⁺ ions. The best performance was obtained for the membrane sensor having a composition of I:NaTBP:NPOE:PVC 3:2:62:33 (w/w; mg). The potentiometric response of Ag⁺-ISE indicate their Nernstian behavior over a wide concentration range i.e., 1.0×10⁻⁷ to 1.0×10⁻². The interference from common ions is not very serious, and the range of pH over which Ag⁺ ion can be measured is 3.0 to 8.0. The proposed method has excellent reproducibility, a wide linear range, good selectivity, time saving and a Nernstian slope and can be used as indicator

electrode as well as for direct determination of Ag^+ ions in physiological samples. These are all important features of the system.

From the results in Table 5, it can be concluded that, present electrode in most of the cases is superior over the previously reported silver selective electrodes.

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