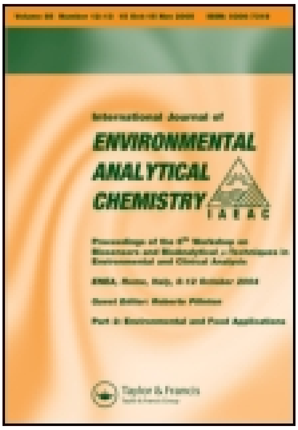


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

Fabrication of a silver (I) ion PVC-membrane sensor based on 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol as a selective sensing material

Mehrorang Ghaedi [a], Ardeshir Shokrollahi [a], Ali Hossain Kianfar [a] & Asma Najibi [a]
[a] Department of Chemistry, University of Yasouj, Yasouj 75914-353, Iran

To cite this article: Mehrorang Ghaedi, Ardeshir Shokrollahi, Ali Hossain Kianfar & Asma Najibi (2012): Fabrication of a silver (I) ion PVC-membrane sensor based on 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol as a selective sensing material, International Journal of Environmental Analytical Chemistry, 92:1, 43-58

To link to this article: http://dx.doi.org/10.1080/03067310903582366

Intern. J. Environ. Anal. Chem.
Vol. 92, No. 1, 15 January 2012, 43–58

Fabrication of a silver (I) ion PVC-membrane sensor based on 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol as a selective sensing material

Mehrorang Ghaedi*, Ardeshir Shokrollahi,
Ali Hossain Kianfar and Asma Najibi

Department of Chemistry, University of Yasouj, Yasouj 75914-353, Iran

(*Received 16 March 2009; final version received 5 December 2009*)

The Schiff-base 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol, was synthesised and explored as a suitable ionophore for preparation of poly(vinyl chloride) based membrane sensor selective to silver(I) ion. The addition of potassium tetraphenyl borate and various plasticisers, viz. o-NPOE, DBP, DMS and DOP was found to substantially improve the performance of the sensor. The electrode revealed a Nernstian behaviour over a wide silver ion concentration range (1.0×10^{-6}–$1.0 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$) with relatively low detection limit ($7.5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$). The potentiometric response was independent of the pH of the solution in the range of 1.8–5.0 with very short response time (< 5 s). The proposed electrode can be used for at least two months without any considerable divergence in potentials. It exhibits very good selectivity relative to a wide variety of alkali, alkaline earth, transition and heavy metal ions. The selectivity of the proposed sensor shows great improvements compared to the previously reported electrodes for silver ions. The sensor was also found to work satisfactorily in partially non-aqueous media up to 25% (v/v) content of acetone with respect to water and can tolerate the concentration 0.05 (w/v%) of non-ionic (Triton X-100) surfactant. The sensor could therefore be used for Ag^+ ion estimation in radiographic films occupationally exposed.

Keywords: silver-selective electrode; potentiometric titration; 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol **(ANPIMMP)**; coated-graphite electrode

1. Introduction

The need for highly sensitive and selective determination of silver ions arises from its economic value and its long-term toxicity for humans and environment [1–4]. It is known that silver deactivates sulfhydryl enzymes and also combines with amine, imidazole and carboxyl groups [5]. These, together with the widespread use of silver in industry and increasing applications in the field of medicine, have led to the development of a relatively large number of silver ion sensors based on different carriers [5–26].

There has been a growing interest in the development and application of potentiometric sensors for monitoring concentration of various species in biological, environmental and industrial fields, because of their unique advantages such as fast

---

*Corresponding author. Email: m_ghaedi@mail.yu.ac.ir

ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067310903582366
http://www.tandfonline.com

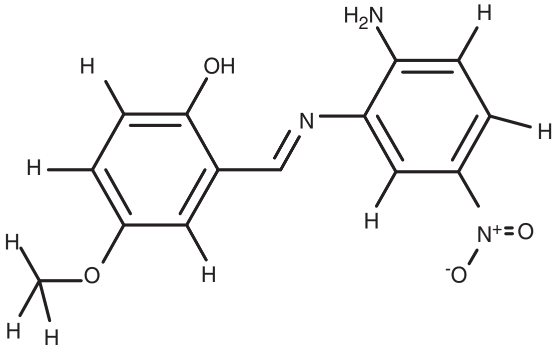
response, easy preparation, low cost, possibility of using in complex and colour media, wide linear dynamic range, relatively low detection limit and adequate selectivity for most analytes. Most of the recently reported potentiometric sensors are carrier-based ion-selective electrodes (ISEs), which presumably act on the basis of chemical recognition principles [27]. Several types of recognition elements such as using carriers of suitable size and specific metal–ligand interactions have been utilised in the selection or synthesis of suitable carriers for construction of ISEs [28]. Several ligand structural features including type and geometrical arrangement of the donor atoms, ability to coordinate with the soft silver ions and the presence of two linear coordination sites to fit the singular coordination is necessary to improve its selectivity for complexation with silver ion. On the basis of the response characteristics of the reported carrier-based silver ISEs, the following points are worth considering: the selectivity of some macrocyclic compounds toward silver ions is not due to the size of their cavity, but is related to the other ligand characteristics, so that non-cyclic carriers with suitable arrangement of donor atoms can show a better discrimination of Ag^+ ion [29]; while the presence of some substituents with п-electrons [30–32] and oxygen atoms of the ligand mostly interact with Ag^+ ion as a soft acid through ion–dipole interactions, which result in fast sensor response and higher sensitivity. Ion-sensors provide analytical procedures that overcome or minimise the drawbacks of liquid membrane electrodes since they are fast, convenient, can be handled easily and do not require sample pretreatment and large infrastructure backup. A review of literature [2,7] reveals that the Schiff bases are the best choice as ionophores for the fabrication of ion sensors due to their peculiar properties. The lipophilic ability of Schiff bases provide geometric and cavity control for host guest complexation modulation and thus produces remarkable selectivity, sensitivity and stability for a specific ion.

Herein, we report the new synthesised highly lipophilic Schiff's bases 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol (ANPIMMP) to exhibit excellent response to silver ion. This sensor has a simple design, a fast response time and a Nernstian slope and shows fairly good discriminating ability towards this ion in comparison with other alkali anions.

2. Experimental

2.1 *Reagents and instruments*

Polyvinyl chloride (PVC) of high relative molecular weight, dibutyl phthalate (DBP), dioctylphthalate (DOP), 4-nitrophenylocthyl ether (NPOE), dimethylsebacate (DMS), tetrahydrofuran (THF), sodium tetraphenylborate (NaTPB), methyltrioctyl ammonium chloride (MTOAC) and methanol (MeOH) were purchased from Aldrich and were used as received, except THF which was distilled before use. All other chemical materials such as Triton X-100, Triton X-114, sodium dodecyl sulfate (SDS), CTAB and DTAB were of highest purity available from E. Merck Darmstadt Germany. All aqueous solutions were prepared with deionised distilled water. The pH adjustments were made with dilute HNO_3 and/or KOH solutions as required. Cyclic voltammetry (CV) was carried out with a Metrohm 746 VA Trace Analyzer, using a multi-mode electrode in the hanging mercury drop electrode (HMDE) mode and SCE as the reference electrode. All potentials are measured and quoted relative to this reference electrode. The three-electrode system was completed by means of a platinum auxiliary electrode. A Shimadzu V-570-atomic absorption spectrometer equipped with deuterium background correction silver



Scheme 1 . The structure of ANPIMMP.

hollow-cathode lamp as the radiation source. The instrumental parameters were adjusted according to the manufacturer's recommendations.

2.2 *Synthesis of 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol (ANPIMMP)*

ANPIMMP was prepared by dissolving 1 mmol (0.152 g) of 5-methoxysalicylaldehyde and 1 mmol (0.153 g) of 4-nitro-1, 2-phenylenediamine in 3 ml methanol and stirred for 3 h, till a yellow precipitate obtained. The product was recrystallised in dichloromethane/methanol (1 : 2) mixed solvent with Yield of 80%. FT-IR (KBr, Cm^{-1}) υ_{max} 3000(NH_2), 2600(C=N), 1300(NO_2), 1200(C-O). Uv-Vis (DMSO): 359 nm, 294 nm. M.P. = 219°C. ^{1}HNMR(DMSO/H_2O): 3.75 (s, 3H), 6.70 (S, 1H), 6.80 (d, 1H), 6.91 (d, 1H), 7.40 (d, 1H), 7.44 (s, 1H), 7.92 (d, 1H) ppm, 8.94 (s, 1H), 11.10 (s, 1H) ppm. ^{13}CNMR (DMSO/H_2O, ppm): $\delta = 161.71$, 154.08, 152.52, 150.61, 136.62, 134.40, 124.69, 121.27, 120.79, 117.95, 114.61, 114.45, 113.61, 111.80.

2.3 *Preparation of electrode*

The coated-graphite electrode was prepared according to our previous publications [31,32]. Graphite rods (3 mm diameter and 10 mm long) were prepared from spectroscopic grade graphite. A shielded copper wire was glued to one end of the graphite rod with silver loaded epoxy resin and the rod was inserted into the end of a PVC tube. The working surface of the electrode was polished with a polishing cloth. The electrode was rinsed with water and methanol and allowed to dry. A mixture of appropriate amount of PVC, plasticiser and the membrane additive, NaTPB was dissolved in about 4 mL of THF. To this mixture suitable amount of ANPIMMP to give a total mass of 100 mg was added and the solution was mixed well. The polished graphite electrodes will be then coated by repeated dipping (several times, a few minutes between dips) into the membranes solutions. A membrane formed on the graphite surface was allowed to set overnight. The electrode was rinsed with water and conditioned for 24 h in 0.1 M silver nitrate ion solution. The coating solutions are stable for several weeks if kept in a refrigerator and can be used for the construction of new membranes.

2.4 *Potential measurement*

The response characteristics of the prepared coated-graphite electrode were determined by recording potential across the membrane as a function of silver concentration at a constant temperature of 25°C. All the potential measurements were carried out with a model 691 (Metrohm) and pH measurements were carried out with a pH/Ion meters model 692 (Metrohm). The potential build up across the membrane electrode was measured using the galvanic cell of the following type: Hg/Hg2Cl2/KCl(sat) || test solution | PVC membrane | Graphite electrode. The performance of each electrode was investigated by measuring its potential in silver solutions in the concentration range of $1.0 \times 10^{-7} - 0.1\,\mathrm{M}$ by serial dilution of the 0.5 M stock solution at constant pH. The pH was adjusted by addition of KOH and/or HNO_3. The solutions were stirred and potential was recorded after reaching steady state values. The data were plotted as observed potential versus the logarithm of the silver ion concentration.

2.5 *Sample pretreatment*

The waste radiographic samples were prepared for the measurement of their silver content as follows. 10 ml of 3 M nitric acid and 40 ml water was added to 20 ml of the sample and the solution was boiled for 60 min until its volume reduced to a half. The resulting solution was neutralised with sodium hydroxide solution to a pH of 4.5 ± 0.2 and filtered. The filtrate was washed and diluted to 100 ml in a volumetric flask and used for potentiometric and atomic absorption measurements.

2.6 *Response time measurement*

Dynamic response time of an ion selective electrode is defined as the length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution and the first instant at which the cell gives a constant potential. The response time of a sensor is measured by changing the concentration of test solution successively from 1.0×10^{-5} to $1.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$, and each time the cell potential is measured. The results depicted in Figure 4 show that the time needed to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Ag^+ ions concentration, each having a tenfold difference in concentration, is 5 s. This indicates fast exchange kinetics of complexation-decomplexation of Ag^+ ions ionophore at the test solution membrane interface.

3. Results and discussion

Ligand used as ionophore in ion-selective electrode should fulfil certain conditions, including high selectivity for Ag^+ ion over other metal cations, rapid exchange kinetics and be sufficiently lipophilic to prevent its leaching into the aqueous solution surrounding the membrane electrode. ANPIMMP (with two oxygen and two nitrogen donating atoms) due to its low solubility in water is susceptible for construction of new cation selective electrode. The Schiff bases ligand stable complexes with transition metal ions have been used for preparation of ion selective electrodes as suitable ionophore [33,34]. In order to investigate the interaction of ANPIMMP with Ag^+ ion, cyclic voltammetrict experiments

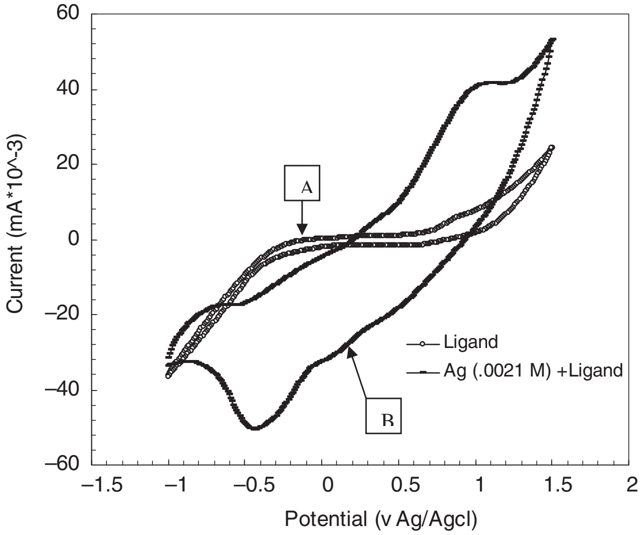


Figure 1. Cyclic voltammogram for complexation of ligand with Ag^+ ions, conditions: (a) 0.0021 M Ag+, (b) 0.0021 M Ag+, 0.2 mM ligand; scan rate 80 mv/s, potential window −1.1–1.5, 0.05 M tetra butyl ammonium perchlorate (TBAP) in 1 : 1 water : ethanol.

were carried out in solution at room temperature, taking into consideration the electrochemical behaviour of the ligand to obtain more details of the electron transfer processes of this complex with Ag^+ ion. A typical cyclic voltammogram of the complex in the potential range of −1.0 to 1.5 V (vs. Ag/AgCl) is shown in Figure 1. An oxidation peak is observed at *ca.* 0.5 V. It seems that this irreversible reduction peak would be ascribed to an intramolecular reductive coupling of the two imine groups in ligand structure. Such a process would involve self-protonation reactions where the phenolic hydroxyl groups act as proton donors. Upon reversal of the scan direction, the Ag (I) complex is reduced to Ag (o) at lower potentials. These results reveal that the redox process for the complex under study is the one-electron transfer reaction.

This ionophore due to its sufficient insolubility in water efficiently, can be used to prepare several PVC membrane ion-selective electrodes under identical conditions for a variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. As it can be seen from (Figure 2), among different tested cations, the Ag^+ ion with Nernstian response seems to be suitably determined while the emf responses obtained for all other cation-selective electrodes are much lower than the predicted by the Nernest equation. The results might indicate that the selectivity towards these ions is masked by the low detection limit of the electrode, which is most probably due to the transport of Ag^{+1} ions from the measuring solution to the boundary between membrane and the solution.

3.1 *Influence of membrane composition*

It is well known that the performance characteristics of the membrane ion-selective electrodes, i.e. sensitivity, working range, selectivity and stability, not only depend on the

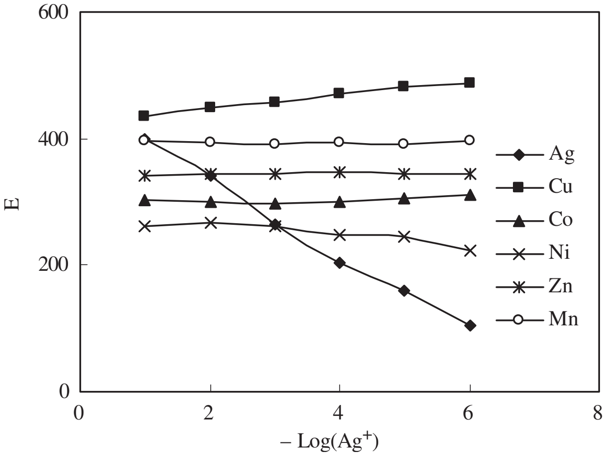


Figure 2. Potential responses of ion-selective electrode based on (E)-[(2-amino-5-nitrophenyl)-imino]methyl}-4-methoxy phenol complex for various cations.

nature of the carrier, but also significantly on the amount and type of polymer matrices, plasticiser and membrane additives. The influence of membrane compositions were investigated by varying the amount of the membrane active material, concentration of NaTPB and type of plasticiser. The response of the electrodes prepared with different amounts of ionophore has been studied taking different concentrations of the Ag^+ ions ranging from 1.0 to 10^{-6} to 1.0 to 10^{-1} M. In all of the membranes the NaTPB/ionophore mole ratio and plasticiser/PVC mass ratio were fixed at 0.5 and 2.0, respectively. The working range and slope of the electrode was improved appreciably on increasing the amount of the ionophore in the membrane matrix from 1 to 7%. The electrodes with low amounts of the ionophore (<2%) show poor perm-selectivity. Further increasing the amount of the ionophore beyond 7%, the response of electrode do not improved. The plasticiser nature influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the ligand state. Therefore it was expected to play a key role in the determination of the selectivity, the working concentration range and the response time of the membrane electrode. The influence of plasticiser type on the characteristics of the Ag^+ ion-selective electrode was investigated by using four plasticisers of different polarity including DOP, DBP, DMS and NPOE. Similar to our previous publications [31,32], in order to obtain best characteristic performance, the plasticiser/PVC mass ratio was kept 2.0. The electrodes based on DBP and DOP showed the best response characteristics, i.e., linear range, detection limit and slope. It seems that DBP and DOP as low polarity plasticisers provide more appropriate conditions for complexation of ANPIMMP with Ag^+ ions. The optimisation of perm-selectivity of membrane sensors is known to be highly dependent on the incorporation of additional membrane components [35]. The presence of such lipophilic anionic species as tetraphenyl borate in cation-selective membrane electrodes is proved to have a beneficial influence on different sensor characteristics. It will not only reduce the ohmic resistance [36,37] and improve the response behaviour and selectivity [38], but also, in cases where the extraction capability of the ionophore is poor, enhance the sensitivity of the membrane electrode [39]. Moreover, the additives may catalyze the exchange kinetics at the sample membrane interface. To further determine how the different lipophilic sites and various amount of NaTPB added to the membrane phase influence the working parameters of the electrode, a series of membranes was studied by using lipophilic additives of NaTPB or MTOACl. In the presence of cationic additive (MTOACl), no remarkable response was observed. It was observed that incorporating NaTPB in the membrane composition with a mole ration of additive to ionophore equal to 0.5 showed best performance characteristics. This is due to fact that NaTPB acts as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction. On the other hand, the membranes without lipophilic salt, showed very narrow concentration range and sub-Nernstian slopes. This observation is likely due to the presence of anionic impurities within the PVC polymer matrix [40]. These observation are indications of the fact that ionophore act as neutral carrier.

3.2 *Response characteristics and selectivity of the electrodes*

The performance of the sensor as a function of time (no. 8) shows adequate life time of 2 months. Over this period the response of the sensor was measured by recording the calibration graph, at 25.0°C at different time intervals, without appreciable change in slope and working concentration range. However, when not in use the sensors were stored in 0.1 M silver nitrate solution. An earlier study on the interaction between metal ions and ionophores containing nitrogen, phosphorus, oxygen and sulfur atoms also showed that such ionophores has the most selectivity to pH changes because of the formation of hydroxo complexes of metal or protonation–deprotonation of the ionophore. The effect of solution pH towards the membrane potential was then evaluated by adding HNO_3 or KOH to Ag^+ ion solution at pH 1.5 up to 11 until a significant EMF change was observed. The pH was measured concurrently with the EMF change. Two kinds of Ag^+ ion concentration (1.0×10^{-3} and 1.0×10^{-2} M) were studied and respective results are shown in Figure 3. It can be seen that the ISE can be used in a wide range of solution pH from pH 1.8 to 5.0 with no significant change in the EMF value. This means that 2-{(E)-[(2-amino-5-nitrophenyl)imino]methyl}-4-methoxy phenol electrodes can be used to measure a wide range of environmental and industrial water samples without pH adjustment The electrode was affected when $pH < 1.8$ probably due to the interference from H^+ and $pH > 5$ due to the precipitation of silver hydroxide. However, the effective pH range found in this study was wide enough to use in the sample without need to critical pH adjustment.

It is well known that the dynamic response time of a sensor is one of the most important factors in its evaluation. The results depicted in Figure 4 show that after 5 s electrode response reach to a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Ag^+ ions, having a tenfold difference in concentration. This indicates fast exchange kinetics of complexation-decomplexation of Ag^{+1} ion with the ionophore at the test solution membrane interface. The reversibility of the sensor was checked by changing the sample concentrations successively from 1.0×10^{-6}–1.0×10^{-1} mol L^{-1} and the results showed that the potentiometric response of the sensor was reversible; although the time needed to reach equilibrium values was a little longer than that of low to high sample concentrations.

Repeated monitoring of potentials and calibration, using the same electrode over several days gave good slope reproducibility as given in Table 3 and respective calibration

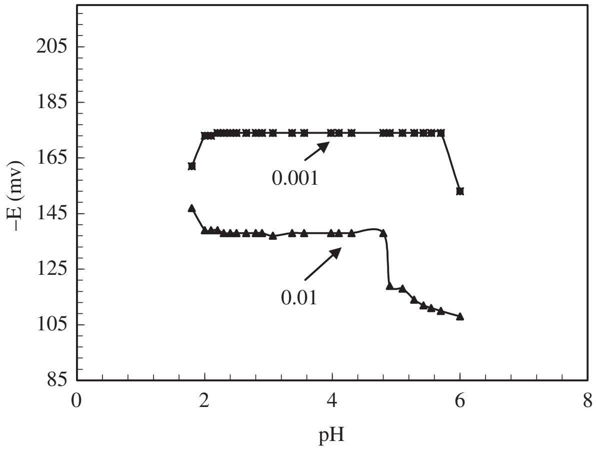


Figure 3. Effect of pH of the text solution on the potential response of the silver ion-selective electrode.

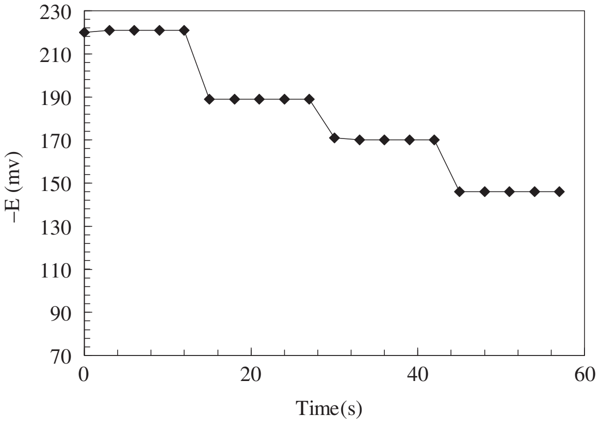


Figure 4. Dynamic response of CGE for step changes in concentration of AG^{+1}.

curve is presented in Figure 5. The standard deviation of 10 identical measurements was 0.5 mV. The sensitivity of the electrode does not change when the potentials are recorded from low to high concentrations and vice versa. The lifetime of the electrodes was studied by periodically measuring the calibration graph over a period of two months. During this period, the electrodes were in weekly use and they were stored at three different conditions when not in use, in conditioning solution (0.1 M $AgNO_3$), out of solution (dry) and in distilled water. It was observed that slope, linear range and detection limit of the electrode which prepared in 0.1 M $AgNO_3$ did not change significantly after two months. Selectivity of an ionophore is the most crucial characteristic of an ISE. The ionophore should have good selectivity for primary ion over interfering ions in order to avoid the bias response from such interfering ions. The selectivity of ISE s was explored based on the so-called 'unbiased selectivity coefficient' proposed by Bakker and co-workers [41].

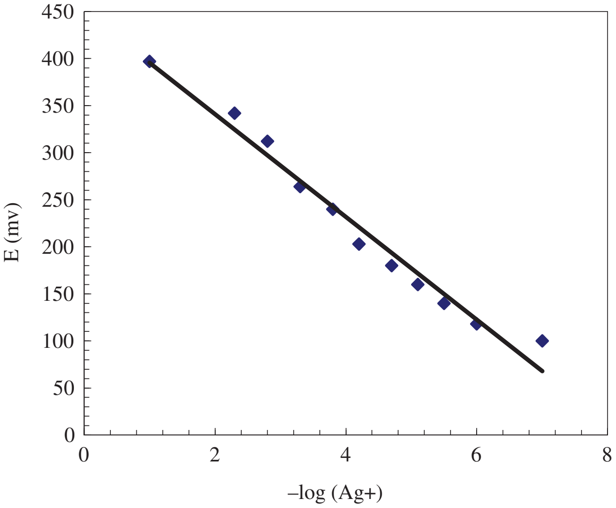


Figure 5. Potential response of the proposed electrode.

The selectivity behaviour determines the accuracy and precision of a reliable measurement of an ion in the sample in the presence of interference. In order to assess the selectivity of the proposed silver ion-selective electrode over other cations the method of fix interference method [FIM] [2,30] and separate solution method [SSM] [5,31] was employed. FIM has generally been the more preferred method because it most closely mimics a practical application of a sensor. In this method, the potentiometric selectivity coefficients, $K_{pot,Ag+1}$, were evaluated by the potential measurements of solutions containing a fixed concentration (0.01 M or 0.001 M) of interfering ion (respective nitrate salts) and varying concentration of silver ion. In SSM, potential of different solutions containing same amount of silver or interfering ion (0.01 M) were measured and the selectivity was calculated according to literature [31,32]. As it is evident from Table 4, most of the interfering ions show low values of selectivity coefficient, indicating no interference in the performance of the membrane electrode assembly in the presence of interfering ion. Such remarkable selectivity of the proposed Ag^+ ion-selective electrode over other metal ions reflects the high affinity of the nitrogen and oxygen coordination sites of the ionophore toward the Ag^+ ion. The smaller the charge of interfering ion, the larger the selectivity coefficient, KPot Ag. Thus, despite their large selectivity coefficients, the thallium and potassium ions would not disturb the functioning of the Ag^+ ion sensor significantly.

The mechanism of silver response shown by the ionophore could be related to the rapid complex formation and exchange of ions at the membrane interface caused by ion exchange processes. The tolerance limit of cations with respect to silver ion was calculated by the following equation, using a maximum of 2% tolerable error: $a_M^{1/z} / a_{Ag} = P/100 \times 1/(K_{Ag,M})$ where z is the charge of the interfering ion and p is the tolerable error in percent due to interference by M. In the case of alkaline earth metal ions with selectivity coefficients in the range of −2.30 to −2.93, as $\log K_{Ag,M}$, and bivalent transition metal ions ($\log K_{Ag,M}$, −2.13 to −3.04) the tolerance limits are highly concentration dependent, due to the superscript of $1/z$ in the above equation. For these groups of metal ions the tolerance ratios ($a_M^{1/2}/a_{Ag}$) are between −522.8 to −1683.2and

Table 1. Characteristic performance of some silver selective electrodes.

Ionophore	L.T (day) [a]	I.[b]	R.T[c]	D.L[d]	PH[e]	L.R.[f]	S[g]	Ref.
polysulfone matrix embedding metallothioneins		(Hg(II)–Cu(I)≈–Cd(II) Pb(II) Zn(II))	–	1000	2–8	10–0.1	61.0	[1]
Schiff-base lariat ether chelates based on 4,13-diaza-18-crown ether			12	0.044	3.0–8.0	0.056−0.1	59.3	[2]
bis-benzilthiocarbohydrazide	9 weeks		<10	0.086	1.6–4.3	0.1–0.01	19.6	[3]
poly(4-vinyl pyridine)	10 days		25	50	3–4	0.1–0.01	30 ± 1	[4]
N-(2-hydroxyethyl) ethylene-diamine-N,N′,Nq-triacetic acid	30 days		10	0.003	1.8–4.5	0.001–0.01	19.5±0.4	[5]
25,27-di(benzothiazolyl)-26,28-hydroxycalix[4]arene		H^+	5	0.0041	2–8	0.008–0.032	59.8±1	[6]
2-[{(2-hydroxyphenyl)imino}-methyl]-phenol and 2-[{(3-hydroxyphenyl)imino}methyl]-phenol		H^+	7	0.02	3.0–8.5	0.0032–0.1	29.5±0.5	[7]
2-mercaptobenzimidazole and 2-mercaptobenzothiazole		$H^+$and Hg^{2+}	10–20s	0.063	5.0	1.0–0.01	57.8	[8]
bis-pyridine tetramide macrocycle	5 months	Na^{+1} and Hg^{+2} in large amount	5	–	–	1.0–0.1	61	[9]
hexathia-18-crown-6	3 months		<10	4.0	2.0–7.5	6.0–0.0032	59	[10]
bis(dialkyldithiophosphates)	–	common ions of alkali metals, alkaline earth metals and transition metals in extremely high concentrations	15	0.6	3.0	1.0–0.1	57.3	[11]
benzothiazolyl calix[4]arene	1 months	Na^{+1}, H^{+1}, Pb^{2+} and Hg^{2+}	<10	3.2	2.5–7.0	1.0–0.1	58.6	[12]
This work			<5	0.8	1.8–5.0	1.0–0.1	59.25	

Notes: [a]Life Time (day); [b]Interference; [c]Response Time (s); [d]Detection Limit (μM); [e]Applicable pH; [f]linear range (μM-M); [g]slope (mV per decade concentration).

Table 2. Response performance of the silver ion-selective electrodes, conditions various membrane: compositions, conditioned 24 h in 0.1 M Ag^+.

No	Plasticizer	PVC	Ionophore	NaTPB	MTOACl	L. R.[a]	S[b]
1	…………	32.3	2.0	1.1	–	10^{-6}–10^{-1}	26.82
2	64.5 (DOP)	32.3	2.0	1.1		10^{-6}–10^{-1}	57.05
3	64.5 (DMS)	32.3	2.0	1.1		10^{-6}–10^{-1}	54.02
4	65.0 (DBP)	32.3	2.0	1.1		10^{-6}–10^{-1}	37
5	65.0 (NPOE)	32.4	2.0	1.1		10^{-6}–10^{-1}	47
6	65.0 (DOP)	…….	2.0	1.1		10^{-6}–10^{-1}	33.07
7	65.9 (DOP)	32.9	1.0	0.59		10^{-6}–10^{-1}	41.6
8	64.5 (DOP)	32.3	2.0	1.1		10^{-6}–10^{-1}	59.25
8	64.5 (DOP)	32.3	2.0	–	1.1	10^{-4}–10^{-2}	12.1
9	63.5 (DOP)	31.7	3.0	1.8	–	10^{-6}–10^{-1}	67.53
10	61.3 (DOP)	30.7	5.0	3		10^{-6}–10^{-1}	45.18
11	61.2 (DOP)	30.6	7.0	4.2		10^{-6}–10^{-1}	32.48
12	65.93	32.97	………	1.1		10^{-6}–10^{-1}	54.52
13	64.5 (DOP)	32.3	2.0	………		10^{-6}–10^{-1}	38.7
14	65.3 (DOP)	32.6	2.0	0.4		10^{-6}–10^{-1}	18.3
15	65.3 (DOP)	31.6	2.0	0.9		10^{-6}–10^{-1}	24.52
16	64.6 (DOP)	31.3	2.0	1.1		10^{-6}–10^{-1}	57.05
17	65.05 (DOP)	32.5	2.0	1.4		10^{-6}–10^{-1}	31.90
18	65.33 (DOP)	32.6	2.0	1.9		10^{-6}–10^{-1}	18.35

Table 3. Response characteristics of the proposed silver selective electrode.

Properties	Values/range
Optimized membrane composition	PVC: plasticizer: ionophore: NaTPB (32.3 : 64.5 : 2 : 1.1)
Electrode type	Coated-graphite electrode
pH range	1.8–5
Conditioning time and concentration	24 hours in 0.1 M $AgNO_3$
Linear range (Ag^{+1}, M)	1.0×10^{-6}–1×10^{-1}
Slope (mV/decade)	59.25 ± 0.91
Detection limit (M)	8×10^{-7}
S.D of measurement	± 0.61 at 1×10^{-3} M & ± 0.32 at 1×10^{-2} M
S.D of slope (mV decade^{-1})	± 0.91
Response time (s)	≤ 5 s
Life time of the electrode	At least 14 weak

between −261.7 to −640.7, respectively. The tolerance ratio was calculated to be 160–500 for trivalent cations, expressed as $a_M^{1/3}/a_{Ag}$

3.3 *Effect of non-aqueous solvent*

The real samples may contain non-aqueous content, so the performance of the sensor must be investigated in partially non-aqueous media. In this regard, the characteristic

Table 4. Selectivity coefficients of the silver (I) ion coated-graphite electrode.

	$-\text{Log K}_{\text{Ag, M}}$			Log KAg, M	
Interfering ion	FIM	SSM	Interfering ion	FIM	SSM
Cu^{+2}	−3.04	−2.37	Tl^{+1}	−1.02	−2.25
Co^{+2}	−2.30	−2.08	Ca^{+2}	−2.30	−2.49
Zn^{+2}	−2.57	−2.77	K^{+}	−3.23	−3.42
Ni^{+2}	−2.41	−2.66	Mg^{2+}	−2.93	−3.06
			Hg^{2+}	−0.85	−1.23
Mn^{+2}	−2.13	−2.39			
Cr^{+3}	−2.86	−2.43			
Pb^{+2}	−2.61	−2.59	Na^{+}	−3.41	−3.24
Cd^{+2}	−2.59	−2.38			

Table 5. Effect of organic solvent on response of silver selective electrode.

ceton (%)	Slope (mV decade^{-1})	Linear range (M)
0	59.6	1×10^{-6} to 1×10^{-1}
5	59.0	$1 \times 10–{}^{6}$ to 1×10^{-1}
15	60.3	1×10^{-6} to 1×10^{-1}
25	61.5	1×10^{-6} to 1×10^{-1}
30	56.4	1×10^{-6} to 1×10^{-1}

performance of electrode including linear range and slope were evaluated in 10%, 20%, 25%, 30% and 35% (v/v) acetone-water mixtures. The results, which are summarised in Table 5, showed that the sensor did not show any appreciable change in working concentration range and slope in mixtures up to 25% (v/v) non-aqueous content. However, above 25% (v/v) non-aqueous content, the potentials showed drift with time slope which may be probably due to leaching of the ionophore and plasticiser at higher organic content.

3.4 *Effect of surfactant*

Ionic and non-ionic surfactants in solution could interact with the polymeric membrane ingredients so that an increase in the background potential and lower binding and solubility of the ionophore in the membrane [42] occurred. On the other hand, surfactants can also disturb the measurements because of their molecule adsorption on the membrane surface, which results in potential instability and prolonged time of electrode response.

Therefore, it leads to deterioration of detection limits, decreasing the response, slope of calibration curve and decrease the selectivity of membrane toward the primary ion. To investigate the effect of surfactant, response of a set of similar electrodes in solution containing various amounts of anionic surfactant (SDS), cationic surfactant (CTAB and DTAB) and non-ionic surfactant (Triton X-100 and Triton X-114) has been investigated.

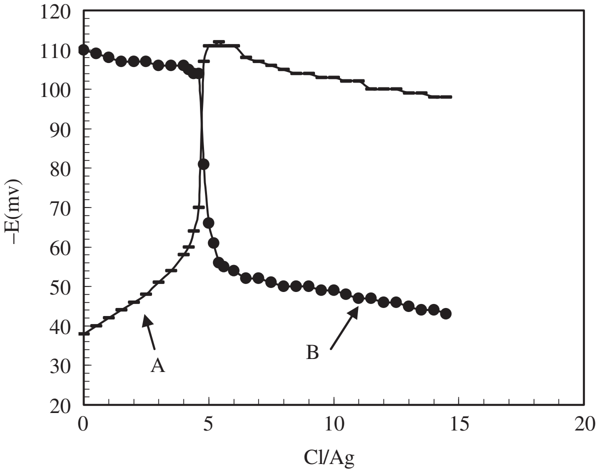


Figure 6. Potentiometric titration curve of (A) 50 mL of 0.01 mol L^{-1} of Ag^+ ion with 0.1 M Cl^- ion solution and (B) 50 mL of 0.01 mol L^{-1} of Cl^- ion with 0.1 M Ag^+ ion solution.

It was observed that the influence of the anion surfactant (sodium dodecyl sulfate, SDS) on electrode response is surprisingly large. The interference may be attributed to the interference of sodium ions or competition of SDS anion with ionophore with primary ion for complexation. The cation surfactant, due to the presence of bromide ion which precipitates with silver ion, seriously decreases the electrode response. Non-ionic surfactants (Triton X-100 and Triton X-114) do not respond potentiometrically. It was observed that the proposed sensor at optimum conditions can tolerate surfactant concentration up to 1.0% (v/w). These substances at high value undergo a division into membrane and enhance the extraction of interfering ions from the sample to membrane and lead to decrease membrane selectivity and cause errors in determination.

3.5 *Application*

The optimised coated-wire electrode was successfully applied as indicator electrodes in the potentiometric titration of silver nitrate with chloride. Typical results for the titration of a 50 mL of 0.01 M silver nitrate solution with 0.1 M chloride solution and vice versa and results are shown in Figure 6. A very good estimation of the end point can be obtained by extrapolation of the two linear portions of the titration plot. The observation of an unsymmetrical titration curve is due to the fact that, before the end point, the potential shows a usual logarithmic change with the volume of titrant added, while the potential response after the end point will remain almost constant, due to the low concentration of free silver in solution. The applicability of the electrode was also assessed for determination of Ag^+ ion concentration in radiographic waste solutions prepared as discussed in section 2 above by the standard addition method. The result obtained by proposed electrode in potentiometric method is in good agreement with those obtained by FAAS (Table 6). By performing the t-test, it was observed that no significant difference is observed between result of potentiometry and FAAS. The high recovery and precision

Table 6. Application of the electrode for the determination of silver ion in radiographic samples.

Sample	Proposed electrode	AAS
Radiographic	7.9 ± 0.3	8.1 ± 0.2
Dentist radiography	1.8 ± 0.2	1.9 ± 0.1

Note: All value are $\mu g\,mL^{-1}$ ($n = 3$).

and their agreements with result obtained by FAAS reflect the utility of the proposed sensors for evaluating Ag+ ion content in real samples.

4. Conclusion

A new silver-selective solid-contact membrane electrode was prepared using ANPIMMP complexes. On the basis of the results discussed in this paper, this ionophore is proposed as carrier for construction of PVC-based membrane coated-wire ISE for silver ions. These electrodes exhibited good stability and sensitivity and reasonable selectivity, and they are easy to prepare and use. Further, they presented satisfactory precision for the investigated silver concentration levels. Due to the high mechanical resistance and durability of the coated-wire electrodes and low solubility of the used carriers the proposed electrodes can be used in flowing streams. The electrodes were shown to have good operating characteristics (Nernstian response; reasonable detection limit; relatively high selectivity, especially with respect to the highly lipophilic cations wide dynamic range; fast response; applicability over a wide pH range). The characteristics and the typical applications presented in this paper make the electrodes suitable for measuring the silver ion content in a photographic and radiographic waste samples, without a significant interaction from concomitant cationic species. The results show that there was a coordination interaction between silver and the proposed carriers, which played an important role in the response characteristics and selectivity of the electrodes. Coated type electrodes are very easy to construct and handle, and offer much higher mechanical resistance, compared to their liquid membrane counterparts. As can be seen in Tables 2–6 in comparison to Table 1, the proposed electrodes are superior to reported silver ion selective electrodes in term of selectivity [1,12], linear range [5–7], detection limit [1,4,10,12], applicable pH range [3–5,8,11] and response time [2–12].

References

[1] A. González-Bellavista, S. Atrian, M. Muñoz, M. Capdevila, and E. Fàbregasa, Talanta **77**, 1528 (2009).

[2] V.K. Gupta, M.K. Pal, and A.K. Singh, Anal. Chim. Acta **631**, 161 (2009).

[3] H.A. Zamani, M.R. Ganjali, H. Behmadi, and M.A. Behnajady, Mater. Sci. Eng. C **29**, 1539 (2009).

[4] F. Bakhtiarzadeh and S.A. Ghani, J. Electroanal. Chem. **624**, 139 (2008).

[5] H.A. Zamani, M.T.H. Mosavian, E. Hamidfar, M.R. Ganjali, and P. Norouzi, Mater. Sci. Eng. C **28**, 1551 (2008).

[6] W. Ngeontae, W. Janrungroatsakula, N. Morakot, W. Aeungmaitrepirom, and T. Tuntulani, Sens. Actuators B **134**, 377 (2008).

[7] A.K. Singh, A.K. Jain, J. Singh, and S. Mehtab, Int. J. Environ. Anal. Chem. **89**, 1081 (2009).

[8] M.K. Amini, A. Rafi, and I. Mohammadpoor-Baltork, Anal. Lett. **35**, 1795 (2002).

[9] R.K. Mahajan and O. Parkash, Talanta **52**, 691 (2000).

[10] M.H. Mashhadizadeh and M. Shamsipur, Anal. Chim. Acta **381**, 111 (1999).

[11] D. Liu, J. Liu, D. Tiana, W. Honga, X. Zhoua, and J. C. Yub, Anal. Chim. Acta **416**, 139 (2000).

[12] L. Chena, H. Ju, X. Zeng, X. Hea, and Z. Zhang, Anal. Chim. Acta **437**, 191 (2001).

[13] J. Casabó, C. Perez-Jimenez, L. Escriche, S. Alegret, E. Martinez-Fabregas, and F. Teixidor, Chem. Lett. **19**, 1107 (1990).

[14] J. Casabó, L. Mestres, L. Escriche, F. Teixidor, and C. Pérez-Jiménez, J. Chem. Soc., Dalton Trans. **8**, 1969 (1991).

[15] F. Teixidor, M.A. Flores, L. Escriche, C. Viñas, and J. Casabó, J. Chem. Soc., Chem. Commun. **8**, 963 (1994).

[16] Z. Brzozka, P.L.H.M. Cobben, D.N. Reinhoudt, J.J.H. Edema, J. Buter, and R.M. Kellogg, Anal. Chim. Acta, **273**, 139 (1993).

[17] D. Siswanta, K. Nagatsuka, H. Yamada, K. Kumakura, H. Hisamoto, Y. Shichi, K. Toshima, and K. Suzuki, Anal. Chem. **68**, 41661 (1996).

[18] Y. Liu, B.T. Zhao, L.X. Chen, and X.W. He, J. Micromech. **65**, 75 (2000).

[19] (a) C.C. Su, M.C. Chang, and L.K. Liua, Anal. Chim. Acta **432**, 265 (2001); (b) D. Xu, and T. Katsu, Anal. Chim. Acta **443**, 235 (2001).

[20] X. Zeng, L. Weng, L. Chen, X. Leng, H. Ju, X. He, and Z.-Z. Zhang, J. Chem. Soc., Perkin Trans. **2**, 545 (2001).

[21] (a) R.K. Mahajan and O. Parkash, Talanta **52**, 691 (2000); (b) J.Q. Lu, D.W. Pang, X.S. Zeng, and X.W. He, J. Electroanal. Chem. **568**, 37 (2004).

[22] (a) L. Chen, X. He, B. Zhao, and Y. Liu, Anal. Chim. Acta **417**, 51 (2000); (b) M.K. Amini, A. Rafi, and I. Mohammadpoor-Baltork, Anal. Lett. **35**, 1795 (2002).

[23] L. Chen, X. Zeng, H. Ju, X. He, and Z. Zhang, Microchem. J. **65**, 129 (2000).

[24] K. Kimura, S. Yajima, K. Tatsumi, M. Yokoyama, and M. Oue, Anal. Chem. **72**, 5290 (2000).

[25] V.K. Gupta, Chimica **59**, 209 (2005).

[26] (a) V.K. Gupta, A.K. Sing, and M.K. Pal, Anal.Chim. Acta **631**, 161 (2009); (b) S.M. Lim, H.J. Chung, K.J. Paeng, C.H. Lee, H.N. Choi, and W.Y. Lee, Anal. Chim. Acta **453**, 81 (2002).

[27] P. Bühlmann, E. Pretsch, and E. Bakker, Chem. Rev. **98**, 1593 (1998).

[28] R.S. Hutchins and L.G. Bachas, Anal. Chem. **67**, 1645 (1995).

[29] J. Casabó, T. Flor, M.I. Romero, F. Teixidor, and C. Perez-Jimenez, Anal. Chim. Acta **294**, 207 (1994).

[30] X. Delaigue, J.M. Harrowfield, M.W. Hosseini, M. Mocerino, B.W. Skelton, and A.H. White, Aust. J. Chem. **51**, 111 (1998).

[31] (a) M. Ghaedi, A. Shokrollahi, M. Montazerzohori, and Sh.Gharaghani, Acta.Chim. Solv. **53**, 428 (2006); (b) A. Shokrollahi, M. Ghaedi, H. Ghaedi, and A. H. Kianfar, Inter. J. Environ. Anal. Chem. **88**, 841 (2008).

[32] (a) A. Shokrollahi, M. Ghaedi, M. Montazerozohori, O. Hosaini, and H. Ghaedi, Anal. Lett. **40**, 1738 (2007); (b) A. Shokrollahi, M. Ghaedi, H.R. Rajabi, and A. H. Kianfar, Chin. J. Chem. **27**, 258 (2009).

[33] K.C. Gupta and M.J. D'Arcy, Anal. Chim. Acta **437**, 199 (2001).

[34] K.C. Gupta and M.J. D'Arcy, Sens. Actuators, B **62**, 171 (2000).

[35] A. Rouhollahi, M.R. Ganjali, and M. Shamsipur, Talanta **46**, 1341 (1998).

[36] U. Schaller, E. Bakker, U.E. Spichiger, and E. Pretsch, Anal. Chem. **66**, 391 (1994).

[37] D. Amman, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, and E. Pungor, Anal. Chim. Acta **171**, 119 (1985).

[38] R. Eugster, P.M. Gehrig, W.E. Morf, U.E. Spichiger, and W. Simon, Anal. Chem. **63**, 2285 (1991).

[39] D. Ammon, W.E. Morf, P. Anker, P.C. Meier, E. Pretsch, and W. Simon, Ion-Sel. Electrode Rev. **5**, 3 (1983).

[40] P. Anker, E. Wieland, D. Ammann, R.E. Dohner, R. Asper, and W. Simon, Anal. Chem. **53**, 1970 (1981).

[41] Z. Szigeti, A. Malon, T. Vigassy, V. Csokai, A. Gr. un, K. Wygladacz, N. Ye, C. Xu, V.J. Chebny, I. Bitter, R. Rathore, E. Bakker, and E. Pretsch, Anal. Chim. Acta **572**, 1 (2006).

[42] L. Chen, J. Zhang, W. Zhao, X. He, and Yu Liu, J. Electroanal. Chem. **589**, 111 (2006).