

Full Paper

Novel PVC-membrane Potentiometric Sensors based on 2-Amino-N-(2-Mercapto phenyl) Benzamid for Silver Ion

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Abstract- A new highly selective silver (I) electrode was prepared with a PVC membrane using 2-amino-N-(2-Mercapto phenyl) Benzamid (L) as an electroactive material, 2-nitrophenyloctylether (*o*-NPOE) as a plasticizer and sodium tetraphenylborate (NaTPB) as an additive in the percentage ratio of 3:5:57:35 (NaTPB:L:*o*-NPOE:PVC, w:w). Potentiometric evaluation of the poly(vinyl chloride) (PVC) membranes containing L showed excellent affinity and selectivity to silver (I) ion over alkali, alkaline earth and other transition metal cations. These electrode works well over wide range of concentration (1.0×10^{-2} to 1.0×10^{-7} M) with a Nernstian slope 59.1 ± 0.2 mV/decade. The potentiometric responses are independent of the pH of the test solution in the pH range 2.9–10.3. The electrodes possess advantages of low resistance, fast response time and relatively long lifetimes. The electrodes were used, as indicator electrodes, in the potentiometric titration of silver ion and in the determination of Ag^+ in waste water.

Keywords- Silver Ion-Selective Electrode, PVC Membrane, 2-Amino-N-(2-Mercapto phenyl) Benzamid, Potentiometry, Sensors

1. INTRODUCTION

Silver is utilized for a wide range of applications, such as in medicine, electronics, optics, photography, and the production of jewelry, coins, batteries, photovoltaic cells, bearings, and catalysts. Because of their antibacterial properties, silver salts and silver nanoparticles are used for the disinfection of drinking water and the preparation of topical gels, specialty bandages, implantable prostheses, and catheters. As a result, about 2500 tons of silver are released into the environment annually, and approximately 80 tons end up in surface waters. [1] Silver is not as toxic to humans as many other heavy metals, but the US Environmental Protection Agency reported that a concentration higher than $0.17 \mu\text{M}$ is toxic to fish and microorganisms [2] and the maximum contaminant level for total silver in drinking water was set to $0.9 \mu\text{M}$ [3]. While other methods for the determination of silver are available, atomic absorption spectrometry and the use of an inductively coupled plasma in combination with atomic emission or mass spectrometry are recommended methods.[4,5] These and many other techniques often require quite expensive and time-consuming sample pretreatment, including preconcentration and matrix separation. In comparison, ion-selective electrodes (ISEs) require little sample preparation and manipulation while still permitting very wide ranges of linear response, low limits of detection, high selectivities, and the possibility to distinguish between the free metal ion and its complexes. [6-8] A number of silver selective sensors based mainly on Schiff bases, [9] podands, [10] cyclams, [11] calixarenes, [12] and polystyrene [13] have been developed. A typical ISE may have a response to ion activity changes in the aqueous phase [6] based on measurements of the phase boundary potential at the sample/membrane interface. The ionophore is an integral component of the polymeric membrane of an ion selective electrode. The ionophore selectivity over the interfering ion is the concerning issue in ionophore discovery. Good selectivity results from a stronger complex between the ionophore and detecting ion, rather than a weaker complex of the ionophore and interfering ions. [14] It is well known that sulfur and nitrogen-containing ligands prefer to bind with heavy metal ions such as Ag^+ . [15] The present study deals with the 2-amino-N - (2 Mercapto phenyl) Benzamid (L) based ISE for selective determination of silver.

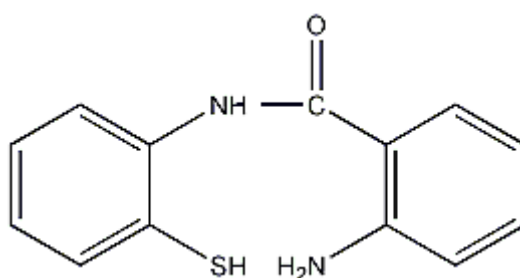


Fig. 1. Structure of the used selectophore (L)

This PVC membrane ion selective electrode shows a good response towards silver ions, and demonstrates an improved detection limit, response time and slope.

2. EXPERIMENTAL

2.1. Reagents

Reagent grade nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), Benzylacetat (BA), tetrahydrofuran (THF) and high relative molecular weight PVC call from Merck were used as received. Nitrate slats of all cations used call from Merck were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . 2 - amino-N-(2 Mercapto phenyl) Benzamid (L) was gifted from the Inorganic chem. laboratories, (Faculty of Chemistry, University of Tehran, Tehran, Iran). Triply distilled deionized water was used throughout.

2.2. Preparation of electrodes

Membrane solution were prepared by thoroughly dissolving 5 mg of L, 35 mg of powdered PVC, 3 mg of additive and 57 mg of plasticizer in 5 ml of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained.

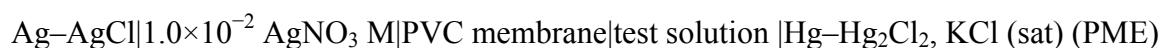
A Pyrex tube (3 mm o.d. on top) was dipped into the mixture for about 10 S so that a nontransparent membrane of about 0.3 mm thick was formed. The tube was then pulled out from the mixture and kept at room temperature for about 1h. The tube was then filled with an internal filling solution (1.0×10^{-3} M Ag^+ ion). The electrode was finally conditioned for 20 h by soaking in a 1.0×10^{-2} M Ag^+ . A Silver/Silver chloride electrode was used as the internal reference electrode.

2.3. Conductometric procedure

The complexation of L with a number of cations was conductometrically investigated in an acetonitrile solution, at 25 ± 0.05 °C, in order to obtain a clue about the stability and selectivity of the resulting complexes. Cation solutions 20mL of were titrated with a 0.01 M L solution in acetonitrile. The resulting molar conductance versus $[L]/[M^{n+}]$ molar ratio showed the formation of 2:1 complexes between L and metal ions tested. The complex formation constants, K_f , were evaluated by computer fitting of the molar conductance/molar ratio data with appropriate equations, and the results are summarized in Table 1 [16].

2.4. Emf measurements

All electromotive force (emf) measurements were carried out with the following cell assemblies:



The emf observations were made relative to a double – Junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solutions. A double-junctions Silver / Silver chloride electrode (Metrohm) containing a 3M solutions of KCl was used as the internal reference electrode. Activities were calculated according to the Debye – Hückel procedure. [17]

3. RESULTS AND DISCUSSION

3.1. Preliminary Studies

To examine ligand selectivity against various metal ions, the interaction of L with metal ions in an acetonitrile solution by conductometric method was investigated [18-25]. In all measurements, the cell should be thermo stated at the temperature of 25.0 °C, using a Phywe immersion thermostat. In this experiment, the ligand to cation mole ratio was equal to 2 in all cases. For evaluation of the stability constants from the conductivity versus $[L]/[M^{n+}]$ mole ratio data, a nonlinear least-squares curve-fitting program KINFIT was used. [26] The resulting K values, obtained from computer are summarized in Table 1. As seen, in the case of Ag^+ addition of the ligand to the cation solution caused a continuous increase in conductivity which begins to level off at molar ratios >2 , indicating the formation of relatively stable complexes with the ligand.

As it is obvious from table 1, in the case of other metal ions examined, the change in conductivity of the corresponding acetonitrile solutions upon addition of L is negligible, emphasizing the formation of very weak complexes between these cations and the ligand. The results thus obtained revealed the much higher selectivity of L for Silver ion over other cationic species studied.

Table 1. The formation constants of L - M^{n+} complexes at 25.0±0.1 °C

<i>Ion</i>	<i>Log K_f</i>	<i>Ion</i>	<i>Log K_f</i>	<i>Ion</i>	<i>Log K_f</i>
Ag^+	5.4±0.2	Hg^{2+}	3.9±0.5	La^{3+}	2.3±0.6
K^+	3.1±0.5	Co^{2+}	3.3±0.4	Na^+	2.7±0.2
Ni^{2+}	3.6±0.3	Rb^+	2.8±0.3	Al^{3+}	3.8±0.4
Be^{2+}	2.9±0.2	Cd^{2+}	2.4±0.3	Zn^{2+}	2.1±0.3
Cu^{2+}	2.6±0.1	Fe^{2+}	2.7±0.7	Mg^{2+}	2.4±0.2
Pb^{2+}	2.5±0.6	Ca^{2+}	3.0±0.5		

Lipophilic character the ligand was expected to act as a suitable ionophore for Ag^+ ion in a PVC membrane electrode. In preliminary experiments, it was found that, while the use of an ionophore-free PVC membrane resulted in no measurable response with respect to Ag^+ ,

the addition of L shows a Nernstian response for the cation in the range of 1.9×10^{-1} – 1.0×10^{-7} M (Fig. 2). Meanwhile, the ligand L was also used as a neutral carrier to prepare PVC membrane electrodes for a variety of metal ions other than Ag^+ . The potential responses of some of the most sensitive electrodes based on L are also shown in Fig. 2. As is obvious from Fig. 2, among different cations tested, Ag^+ with the most sensitive response seems to be suitably determined with the electrode. This is due to the selective behavior of the PVC membrane system against Ag^+ in comparison to the metal ions tested.

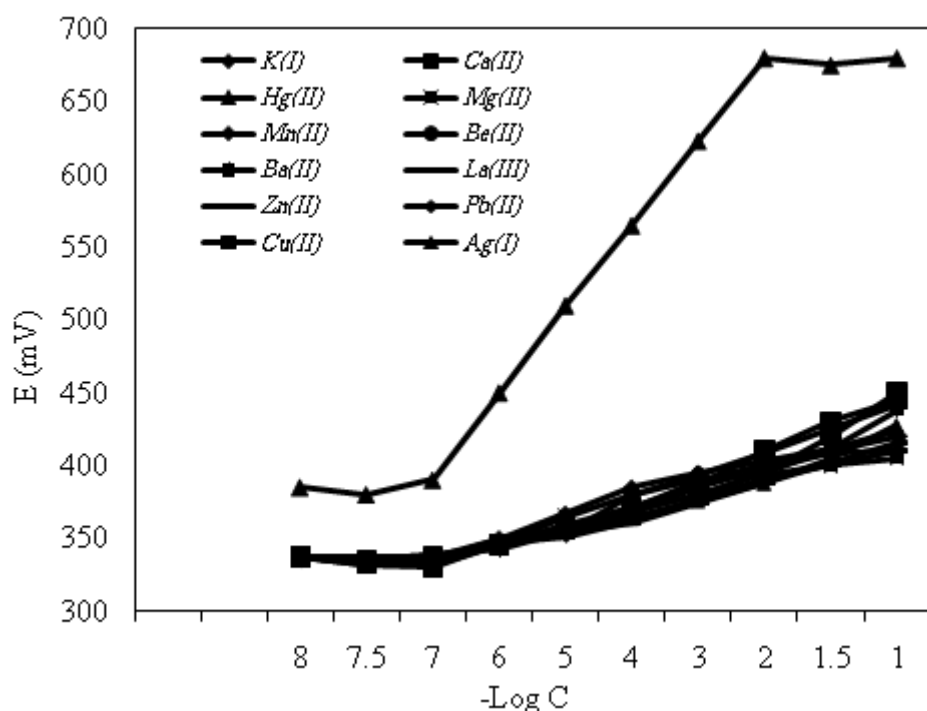


Fig. 2. Potential response of various ion-selective electrodes based on L

3.2. Membrane Composition

Besides of the critical role of the nature of the ionophore in preparing PVC membrane electrodes, it is well understood that the performance characteristics for the ionophore-incorporated PVC membrane may also be very dependent on electrode composition and the nature of the solution of which the electrodes are composed [27-38]. Thus, different aspects of the composition of membranes based on L for Ag^+ ion were optimized, and the results are summarized in Table 2.

As expected, the amount of ionophore was found to affect the PVC membrane sensitivity (nos. 1-4). The calibration slope increased with increasing L content until a value of 5% was reached. However, further addition of the ionophore resulted in a diminished response slope of the electrode, most probably due to some inhomogeneity and possible saturation of the membrane [39].

The potentiometric response of the membrane ion-selective electrodes based on neutral ionophore is greatly influenced by the polarity of the membrane medium, which is defined by the dielectric constants of the major membrane components [39-41]. The influence of the nature of plasticizer on the Ag^+ response was studied on electrodes containing three types of plasticizers having different dielectric constants, namely, DBP, DOP and NPOE. As shown in Table 2, NPOE with the highest dielectric constant in the series resulted in the best sensitivity of the potential responses.

It should be noted that the nature of the plasticizer affects not only the dielectric constant of membrane phase but also the mobility of ionophore molecules and the state of the ligands. [40,42]. Also amount of plasticizer in membrane was tested. The calibration slope increased with increasing NPOE content until a value of 57% was reached. However, further addition of the NPOE resulted in a diminished response slope of the electrode.

Table 2. Optimization of membrane ingredients during design of Ag(I) selective membrane sensor

No	Composition				Slope mV/decade	Concentration range M	D.L (M)
	PVC	Plasticizer	EANQ	Additive			
1	48	DOP,52	-	-	~0	-	-
2	45	DOP,52	3	-	30.5	8.0×10^{-5} - 9.5×10^{-2}	6.1×10^{-5}
3	43	DOP,52	5	-	37.2	1.9×10^{-5} - 2.5×10^{-2}	8.8×10^{-6}
4	41	DOP,52	7	-	35.1	4.5×10^{-5} - 3.7×10^{-2}	2.5×10^{-5}
6	43	DBP,52	5	-	26.3	8.8×10^{-6} - 9.4×10^{-1}	6.3×10^{-6}
7	43	NPOE,52	5	-	47.8	7.0×10^{-6} - 5.0×10^{-2}	4.6×10^{-6}
8	38	NPOE,57	5	-	50.9	3.5×10^{-6} - 1.7×10^{-2}	2.6×10^{-6}
9	33	NPOE,62	5	-	49.1	4.8×10^{-6} - 3.0×10^{-2}	3.7×10^{-6}
10	33	NPOE,57	5	OA,5	52.1	1.5×10^{-6} - 5.0×10^{-2}	9.9×10^{-7}
11	28	NPOE,57	5	OA,10	55.7	8.5×10^{-7} - 1.0×10^{-2}	6.0×10^{-7}
12	23	NPOE,57	5	OA,15	53.6	9.0×10^{-7} - 5.0×10^{-1}	7.5×10^{-7}
13	36	NPOE,57	5	NaTPB,2	57.3	5.4×10^{-7} - 2.3×10^{-2}	2.7×10^{-7}
14	35	NPOE,57	5	NaTPB,3	59.1	1.0×10^{-7} - 1.0×10^{-2}	9.1×10^{-8}
15	34	NPOE,57	5	NaTPB,4	57.9	3.5×10^{-7} - 3.7×10^{-2}	1.0×10^{-7}

It is well known that the incorporation of lipophilic additives can significantly influence the performance characteristics of a membrane sensor [43-46]. The presence of additives not only improves the response characteristics and selectivity [44] but also may catalyze the exchange kinetics at the sample-membrane interface [47]. In this work, we examined the influence of both OA and NaTPB, as suitable lipophilic additives, on the response

characteristics of the proposed PVC membrane, and the results are also included in Table 2. The data given in Table 2 indicate that, in the absence of a proper additive, the sensitivity of the PVC membrane based on *L* is quite low (nos. 1-9, with slopes of <50 mV decade⁻¹). However, the presence of 3% NaTPB (no. 14), as suitable lipophilic additive, will improve the sensitivity of the Ag⁺ sensor considerably (with a slope 59.1 mV decade⁻¹). It is interesting to note that, in membrane 14, the molar ratio of the ionophore to NaTPB is 1, which implies that NaTPB is not primarily a phase transfer catalyst but also contributes to the complexation mechanism, as described by Eugster et al. [48] Moreover, with a fraction of 3% wt, NaTPB is expected to contribute significantly to the dielectric constant of the membrane in addition to the plasticizer.

As it is obvious from Table 2, the membrane 14 having a PVC/NPOE/NaTPB/*L* composition of 35:57:3:5 shows Nernstian behavior over a wide concentration range.

3.3. Effect of Internal Solution

Based on the generally adopted ion-selective response formalism, [49] the internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable. Thus, the proposed sensor was examined at different concentrations of inner reference solution, as it is described in the Experimental Section. It was found that the variation of the concentration of the internal solution (in the range of 1.0×10^{-2} – 1.0×10^{-4} M Ag⁺) does not cause any significant difference in the corresponding potential response, except for an expected change in the intercept of the resulting Nernstian plots. (Fig. 3) A 1.0×10^{-3} M concentration of the reference solution is quite appropriate for smooth functioning of the electrode system.

3.4. Linear concentration range and detection limit

Under the optimized composition, the linear response to the activity of Ag⁺ ion was investigated for the prepared PME and the resulting plot is shown in Fig. 4. As is obvious from Fig. 4, Nernstian response are obtained in very broad concentration ranges of 1.0×10^{-7} to 1.0×10^{-2} M. The resulting limit of detection (LOD) for PME obtained from the intersection of the two linear parts of the calibration plot, were found to be 9.1×10^{-8} .

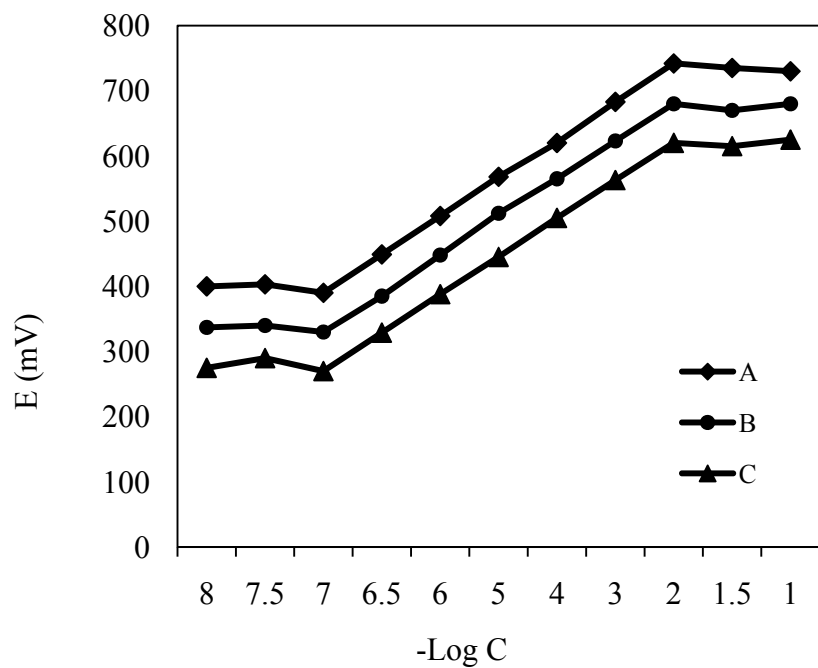


Fig. 3. The effect of different concentrations of the internal reference solution, A) $1.0 \times 10^{-4} \text{M}$, B) $1.0 \times 10^{-4} \text{M}$, C) $1.0 \times 10^{-4} \text{M}$ of the Ag^+ as internal solutions respectively

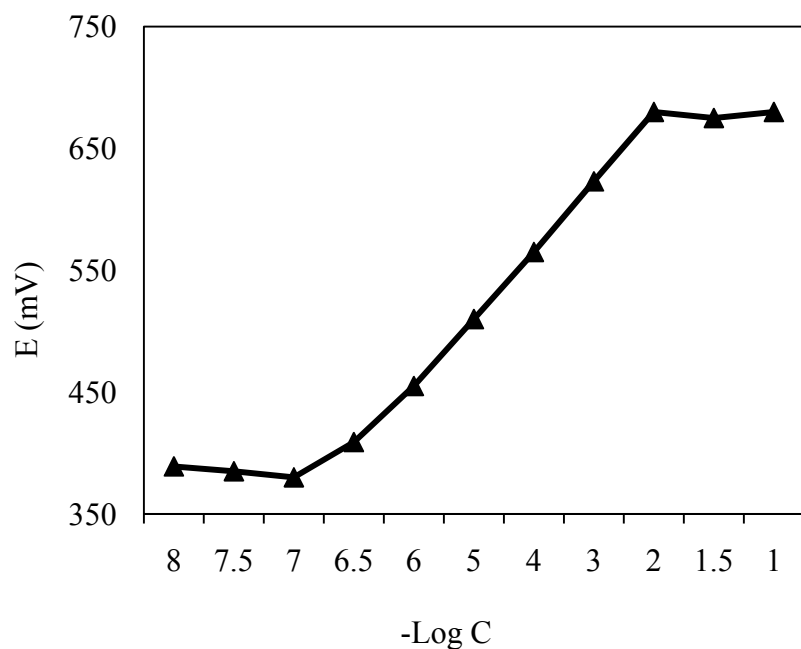


Fig. 4. Calibration curve of Ag^+ ion-selective electrode based on L

3.5. Response time

For analytical applications, the response time of a membrane sensor is an important factor. The static response time of the electrode tested by measuring the average time required to achieve a potential within ± 1 mV of the final steady state potential upon successive immersion of a series of Ag^+ ions, each having a tenfold difference in concentrations, was within $< 28\text{S}$ for Ag^+ concentrations $< 10 \times 10^{-3}\text{M}$. (Fig. 5)

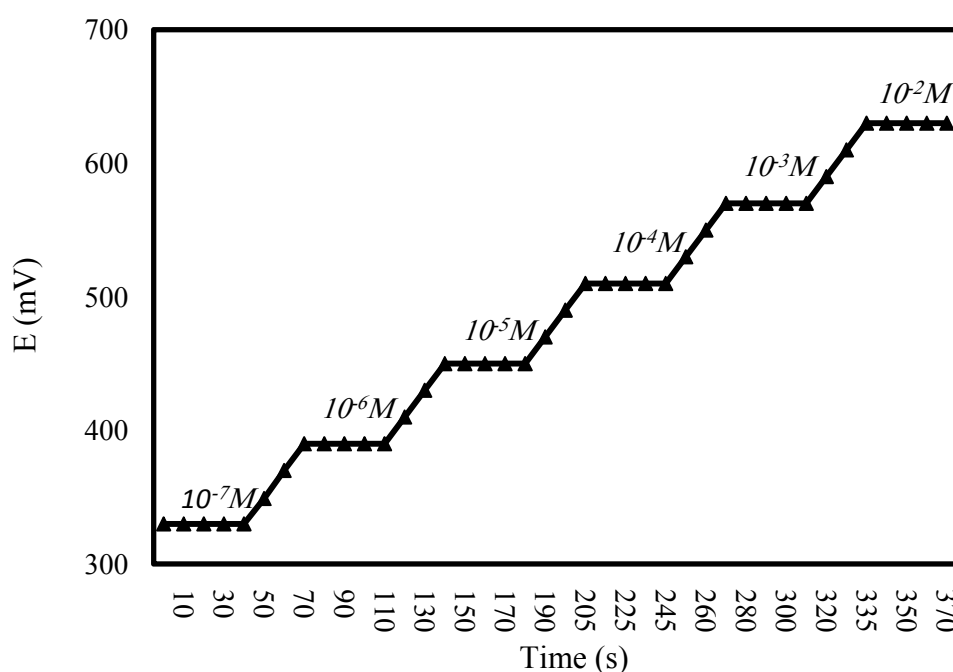


Fig. 5. Dynamic response time of the proposed sensor for step changes in the concentration of Ag^+

3.6. PH effect on the electrode response

The influence of pH of the test solution on the potential response of the membrane electrode was tested in the pH range of 1-13, and the results are shown in Fig. 6. As seen, the potential remained constant from pH 2.9 to 10.2, beyond which the potential changed considerably.

At low pH, the potential increased, indicating that the membrane sensor also responded to H^+ ions, by the protonation of the nitrogen and sulfur atoms of the ionophore, while the observed large decrease in potential at higher pH values could be due to the formation of some hydroxyl complexes of Ag^+ in solution.

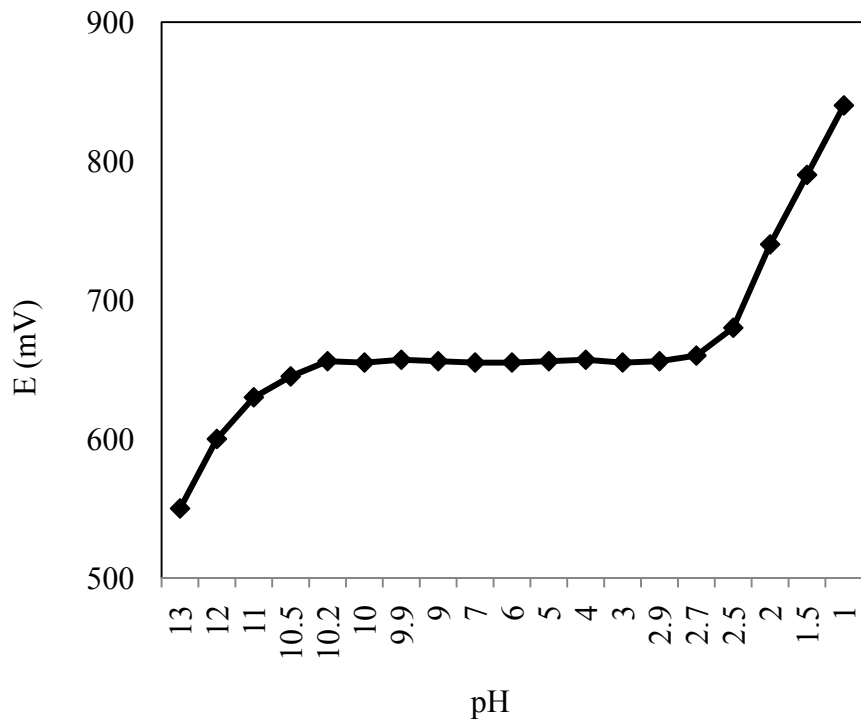


Fig. 6. Influences of pH of the test solution on the potential response of electrode in the presence of 1.0×10^{-4} M Ag^+

3.7. Potentiometric selectivity

The selectivity behavior is obviously one of the most important characteristics of a membrane sensor, determining whether a reliable measurement in the target sample is possible. In this work, the influence of several transition and heavy metal ions on the potential response of the Silver-selective electrode was tested by determining the potentiometric selectivity coefficients of the electrodes by the separate solution method (SSM) [53,54]. In this method, the potential of a cell comprising an ion selective electrode and a reference electrode is measured with two separate solutions.

One contains the ion of interest i at the activity a_i (but no j) and the other containing the interfering ion j at the same activity $a_j = a_i$ (but no i). In this method the values are the selectivity coefficient can be derived from the following equation:

$$K_{ij}^{pot} = \frac{(E_2 - E_1)}{2.303RT/Z_i F} + \left(1 - \frac{Z_i}{Z_j}\right) \log a_i$$

Where E_1 , E_2 and Z_i , Z_j are the respective measured potentials and charges on the ions i and j . The resulting $-\log K_{Ag,M_i}^{pot}$ values obtained are summarized in Table 3. It is seen that, in all cases, the log selectivity coefficients are in the order of 3.0 and upper, indicating negligible interference in the performance of the membrane sensor assemblies. [50–52,55].

Table 3. The selectivity coefficients of various interfering cations for the membrane sensor

M^{n+}	$-\text{Log } K_{Ag,M}^{pot}$	M^{n+}	$-\text{Log } K_{Ag,M}^{pot}$
Mg ²⁺	3.6	Rb ⁺	4.9
K ⁺	4.1	Cd ²⁺	3.8
Ni ²⁺	3.2	Fe ²⁺	<5.0
Be ²⁺	3.9	Ca ²⁺	4.2
Cu ²⁺	4.7	La ³⁺	<5.0
Pb ²⁺	3.1	Na ⁺	3.9
Hg ²⁺	3.0	Al ³⁺	<5.0
Co ²⁺	<5.0	Zn ²⁺	3.7

3.8. Stability and lifetime

Table 5. Lifetime of Ag(I) selective membrane sensor

Month	Slope (mV decade ⁻¹)	Detection Limit (M)
1	59.1±0.2	9.1±10 ⁻⁸
2	59.1±0.5	9.5±10 ⁻⁸
3	58.7±0.4	9.9±10 ⁻⁸
4	58.5±0.5	1.5±10 ⁻⁷
5	50.1±0.9	1.1±10 ⁻⁶

For the investigation of the stability and lifetime of the Ag(I) membrane sensor, two electrodes were tested over a period of 5 months and the results are in Table 5. The main factor limiting the lifetime of the ion-selective membrane in potentiometric measurements is the leakage of ionophore into the aqueous solutions. The proposed PVC-based membrane sensor could be used for at least 4 months (use of 1 h daily). After its utilization, it was washed and kept dry. During this certain time period, the membrane sensor could be used without any measurable divergence. After 4 months changes were observed in the slope and detection limit (from 58.5 to 50.1 mV decade⁻¹ and from 1.5×10⁻⁷ to 1.1×10⁻⁶ M, respectively) [56-59].

3.9. Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were 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 responses of the electrode was reversible; although the time needed to reach equilibrium values (28 s) were longer than that of low-to-high sample concentrations [7] (Fig. 7).

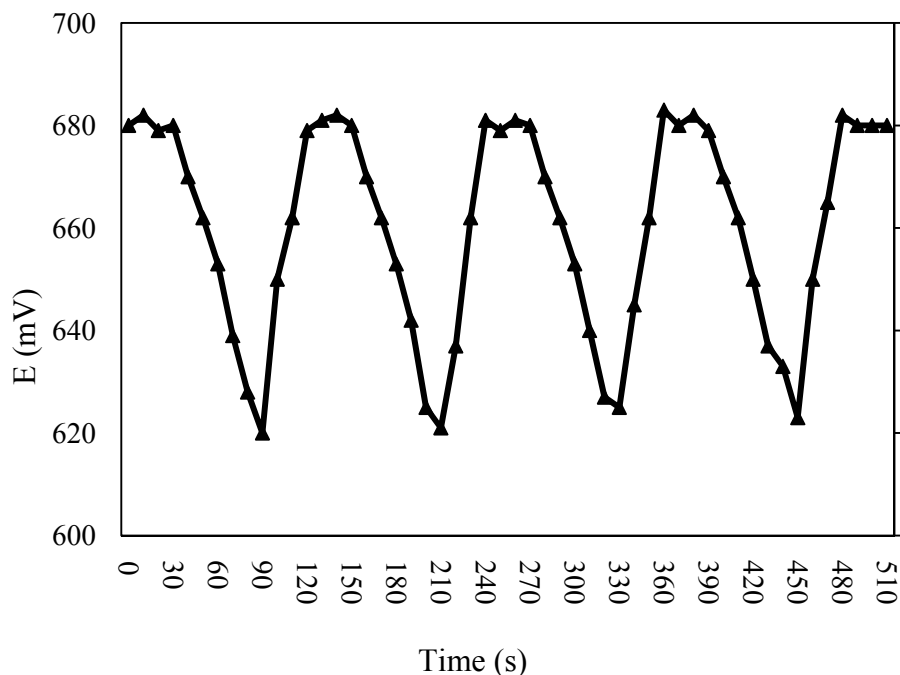


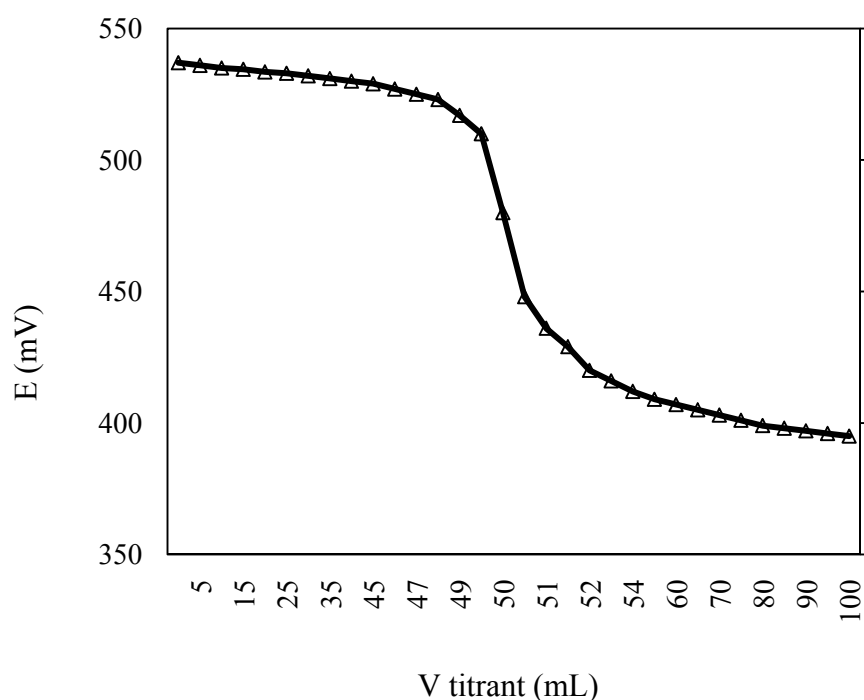
Fig. 7. Dynamic response characteristics of the Ag^+ membrane sensor for several high-to-low sample cycles

3.10. Analytical applications

The proposed membrane electrodes were found to work well under laboratory conditions. The PME based on L was used as indicator electrodes in the successful titration of Ag^+ with Cl^- ion. The resulting titration curve, shown in Fig. 8, indicates that the amount of silver ion can be accurately determined with the proposed electrode. The proposed electrodes were also applied to the recovery of silver from tap water samples (Table 5). The data given in Table 5 clearly revealed that the amount of silver in the tap water samples can be accurately determined by the proposed ion-selective electrodes, without any primary sample treatment.

Table 5. Recovery of Ag^+ from tap water samples

Sample	Added Ag^+ (M)	Recovered Ag^+ (M)	
		PME	AAS
1	5.0×10^{-6}	$(5.2 \pm 0.4) \times 10^{-6}$	$(5.1 \pm 0.3) \times 10^{-6}$
2	2.0×10^{-5}	$(2.1 \pm 0.2) \times 10^{-5}$	$(2.2 \pm 0.1) \times 10^{-5}$

**Fig. 8.** Potentiometric titration curve of 50.0 mL of a 1.0×10^{-3} M AgNO_3 solution with 1.0×10^{-3} M NaCl , using PME as an indicator electrode

4. CONCLUSION

Conductometric study in acetonitrile solution shows a selective interaction between 2 - amino-N - (2 Mercapto phenyl) Benzamid (L) and Silver cation in comparison with other inorganic metal ions. The ion-selective electrode constructed based on L showed a good performance in the linear concentration range, detection limit, and selectivity coefficients. The electrode exhibited a fast response time ($< 28\text{S}$), a detection limit of 9.1×10^{-8} M and pH independent potential responses across the range of 2.9-10.2. The proposed electrode can be employed as an indicator electrode in potentiometric titration and the determination of silver ions in the tap water samples.

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