

Novel Silver(I) Ion Selective PVC Membrane Electrode Based on the Schiff Base ($N^2E,N^2'E$)- N^2,N^2' -Bis(Thiophen-2-ylmethylene)-1,1'-Binaphthyl-2,2'-Diamine

Eunseon Jeong, Mohammad Shamsuddin Ahmed, Haesang Jeong, Eunhee Lee, and Seungwon Jeon*

Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea

*E-mail: swjeon@chonnam.ac.kr

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A potentiometric sensor based on the Schiff base ($N^2E,N^2'E$)- N^2,N^2' -bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine has been synthesized and explored as an ionophore PVC-based membrane sensor selective for the silver (Ag^+) ion. Potentiometric investigations indicate a high affinity of this receptor for the silver ion. Seven membranes have been fabricated with different compositions, with the best performance shown by the membrane with an ionophore composition (w/w) of: 1.0 mg, PVC: 33.0 mg, DOA: 66.0 mg in 1.0 mL THF. The sensor worked well within a wide concentration range of 1.0×10^{-2} to 1.0×10^{-7} M, at pH 5, at room temperature (slope 57.4 mV/dec.), and with a rapid response time of 9 s; the sensor also showed good selectivity towards the silver ion over a huge number of interfering cations, with the highest selectivity coefficient for Hg^{2+} at -3.7 . Thus far, the best lower detection limit was 4.0×10^{-8} M.

Key Words : Schiff base, Silver-ion selective electrode, Potentiometry, Ionophore, PVC membrane

Introduction

The adverse effects of chronic exposure to silver are a permanent bluish-gray discoloration of the skin (argyria) or eyes (argyrosis). Most studies discuss cases of argyria and argyrosis resulted primarily from exposure to soluble forms of silver. Besides argyria and argyrosis, exposure to soluble silver compounds may produce other toxic effects, including liver and kidney damage, irritation of the eyes, skin, respiratory, and intestinal tract, and changes in blood cells. Metallic silver, however, appears to pose a minimal risk to health.¹ Silver is used widely in different industries such as coins, jewelry, alloys, electrical devices, and mirrors. Furthermore, many silver based chemicals are used in photographic processes and research, as well as in the production of dental amalgams and burn creams due to its antibacterial properties.² Thus, there exists a high probability of surface and underground water contamination. Accordingly, there exist several techniques for silver metal ion determination, such as thermometric titration,³ flame atomic absorption spectroscopy (FAAS),⁴ inductively coupled plasma-atomic emission spectroscopy (ICP-AES),⁵ and inductively coupled mass spectroscopy (ICP-MS);⁶ nonetheless, all these methods are time consuming, involving sample manipulation, and are relatively expensive. Potentiometric sensors based on an ion-selective electrode (ISE) are a typical example of chemical sensors that use the principle of molecular recognition chemistry. They are readily prepared by immobilizing host molecules capable of recognizing a specific class of ionic species in an appropriate polymeric matrix system, which are then built upon an electrode body. In the last three decades, because of their ease of preparation and simplicity of use, ISEs have not only been practical solutions to a wide variety of analytical problems, but also useful tools for

probing host-guest chemistry.⁷ The ISE is an ion analysis technique that provides many unique characteristics, such as selectivity, sensitivity, (LODs of subnanomolar or subfemtomolar levels), good precision, simplicity, and low cost.⁸⁻¹² A number of silver selective sensors based mainly on Schiff bases,¹³ podands,¹⁴ cyclams,¹⁵ calixarenes,¹⁶ and polystyrene¹⁷ have been developed. A typical ISE may have a response to ion activity changes in the aqueous phase¹⁸ 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.¹⁹ It is well known that sulfur- and nitrogen-containing ligands prefer to bind with heavy metal ions such as Ag^+ .²⁰

The present study deals with the Schiff base ($N^2E,N^2'E$)- N^2,N^2' -bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine based ISE for selective determination of silver. This PVC membrane ion selective electrode shows a good response towards silver ions, and demonstrates an improved detection limit, response time and slope.

Experimental

Reagents. The Schiff base ($N^2E,N^2'E$)- N^2,N^2' -bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine tested as a carrier of silver ions was synthesized according to a similar procedure described previously.²¹ The precipitate was collected from ether by filtration. The product was recrystallized from ethanol and dried under reduced pressure at 40 °C; 90% yield, as shown in Figure 1. High molecular weight PVC, 2-

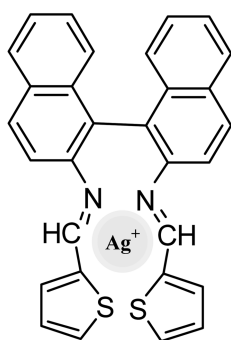


Figure 1. The proposed structure of (*N*²*E*,*N*²*E*)-*N*²,*N*²-bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine.

nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS), potassium tetrakis(*p*-chlorophenyl)borate (KTpCIPB), and tetrahydrofuran (THF), all obtained from Aldrich (City, State, Country), were used to prepare the PVC membranes. The nitrate salts of the cations (all from Merck, City, State, Country) were used without further purification, except for vacuum drying over P₂O₅. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions. High purity argon was used for deaeration. All experiments were carried out at room temperature. The potentials were measured by varying the concentration of AgNO₃ in the test solution in a range of 1.0 × 10⁻² to 1.0 × 10⁻⁷ M. The standard AgNO₃ solutions were obtained by gradual dilution of 0.1 M AgNO₃ and pH adjustment with Tris-HNO₃ buffer.

Instrumentation. Multichannel potentiometer (Model: KST101-1) was performed with a two-electrode system. An orion double-junction Ag/AgCl electrode supplied by BAS was used as the reference electrode. The Philips IS-561 electrode was used as the working electrode. An ISTEK (Model: 735p) pH meter was used after calibration with pH 4, 7, 10 solutions. All potentials were reported with respect to the Ag/AgCl electrode at room temperature and under an argon atmosphere.

Fabrication of Electrodes. It is known that the sensitivity and selectivity of the cation selective electrode depends upon the membrane composition and the nature of the plasticizer used.²² The plasticized PVC-based membranes and electrodes were prepared by a conventional procedure.^{23,24} This lab made several membranes as described in Table 1. The best responding membrane (m-2) was prepared with a

composition of (*N*²*E*,*N*²*E*)-*N*²,*N*²-bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine: 1.0 mg; PVC: 33.0 mg; DOA: 66.0 mg. The components were added in terms of weight. A homogeneous mixture was obtained after complete dissolution of all the components in THF, and then placed onto a smooth glass plate and concentrated by evaporation (THF) at room temperature. It is also known that the sensitivity, linearity, and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of plasticizer used.^{22,25} It is noteworthy that the lipophilicity of the plasticizer influences both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex,^{26,27} indicating that the DOA-plasticized membrane dissolves the ion association complexes and adjusts both permittivity and the ion exchanger sites mobility to give the highest possible selectivity and sensitivity. All electrodes were filled out with 0.1 mol L⁻¹ KCl as an internal filling solution.

Potentiometry. The potentiometric response measurements were carried out with a multi-channel potentiometer at room temperature. The electrochemical cell for the measurements can be represented as: Ag/AgCl | 0.1 M KNO₃ || 0.05 M Tris-HNO₃ (sample solution) || PVC membrane | Internal filling solution (0.1 M KCl) | AgCl/Ag. The steady-state potential (within 0.1 mV over a 1 min period) was recorded in all measurements. Conditioning of the membrane electrode was a fundamental step to achieve reliable results. The membranes were rinsed with distilled water and then conditioned for 24 h in 0.001 M AgNO₃, followed by 24 h in 0.1 M AgNO₃.

Results and Discussion

The Schiff base (*N*²*E*,*N*²*E*)-*N*²,*N*²-bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine was employed as a silver selective ionophore in the preparation of a silver ion selective electrode. The measurements were performed in a concentration range of 1.0 × 10⁻² to 1.0 × 10⁻⁷ M AgNO₃. The responses of the selective four electrodes (with different plasticizer) are shown in Figure 2. Most of the electrodes containing different plasticizers exhibited a wider linear response range. The linear range, limit of detection, and slope are summarized below (Table 2).

Membrane composition has a great effect over sensitivity, selectivity, and stability of the ion selective membrane electrodes. In this study, electrodes of four different

Table 1. Membrane composition

Membrane	Ionophore ^a	PVC ^a	<i>o</i> -NPOE ^a	DOA ^a	DOP ^a	DOS ^a	KTpCIPB ^b
m-1	1	33	66				0
m-2	1	33		66			0
m-3	1	33		66			20
m-4	1	33		66			50
m-5	1	33		66			100
m-6	1	33			66		0
m-7	1	33				66	0

^ain mg. ^bin mol % relative to the ionophore

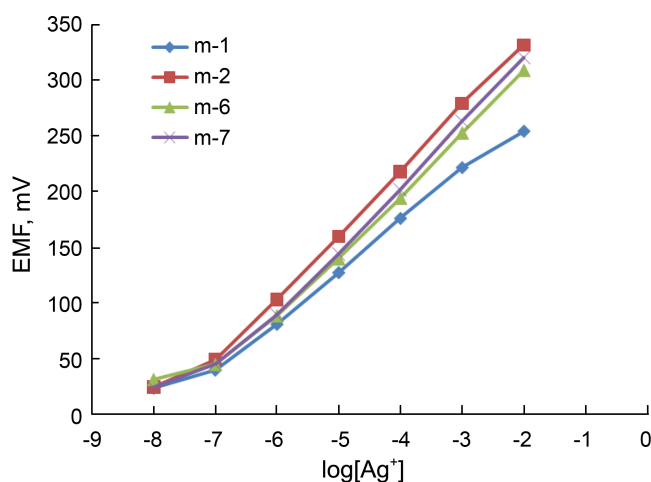


Figure 2. Potentiometric response of different membranes prepared from different plasticizers, with the ionophore towards Ag^+ at pH 5.

Table 2. Linear range, limit of detection, and slope of each membrane

Membrane	Linear range, M	LOD	Slope (mV/dec.)
m-1	1.0×10^{-3} to 1.0×10^{-7}	-7.30	45.9
m-2	1.0×10^{-2} to 1.0×10^{-7}	-7.40	57.4
m-3	1.0×10^{-2} to 1.0×10^{-6}	-6.78	55.2
m-4	1.0×10^{-2} to 1.0×10^{-6}	-6.75	51.0
m-5	1.0×10^{-2} to 1.0×10^{-6}	-6.14	62.8
m-6	1.0×10^{-2} to 1.0×10^{-7}	-7.12	53.4
m-7	1.0×10^{-2} to 1.0×10^{-7}	-7.23	55.9

compositions were prepared to identify their effects. The measurements were made in 100 mL of a 0.05 M Tris- HNO_3 solution in order to maintain the ionic strength of medium. The response of each electrode was measured after the addition of AgNO_3 solutions, such that the Ag^+ ion concentrations changed from 1.0×10^{-7} to 1.0×10^{-2} M. As shown in Figure 2, all membrane electrodes responded linearly. Membrane (m-2) containing DOA had the highest Nernstian slope of all tested membranes. Considering the detection limit and slope, the m-2 membrane provided the best results.

However, when membrane electrodes were prepared from different additive percentages, a dynamic response occurred (Figure 3). Here, m-5 (100%), m-4 (50%), and m-3 (20%) responded nearly in an identical manner, but m-2 (0%) responded with an improved potential response. Only m-2 responded to the lowest test concentration of silver ions. Therefore, at low concentrations and without any additives, m-2 was more sensitive than other membranes tested.

The proposed sensor (m-2) worked well under the same conditions and could be successfully employed in the potentiometric titration of 100 mL of 1.0×10^{-3} M Ag^+ solution with 0.01 M NaCl solution. The resulting titration curve is shown in Figure 4, indicating that the amount of Ag^+ ions in solution can be determined precisely from the titration curve, providing a sharp endpoint.

The pH of the test solution is a very important factor for

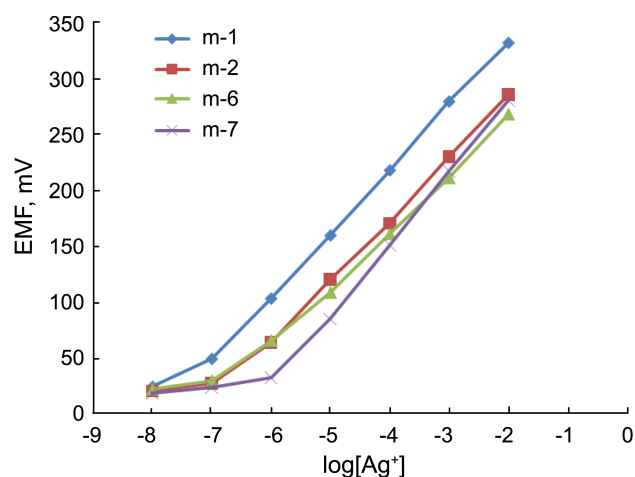


Figure 3. Potentiometric responses of membranes prepared from different amounts of additives, with the ionophore towards Ag^+ at pH 5.

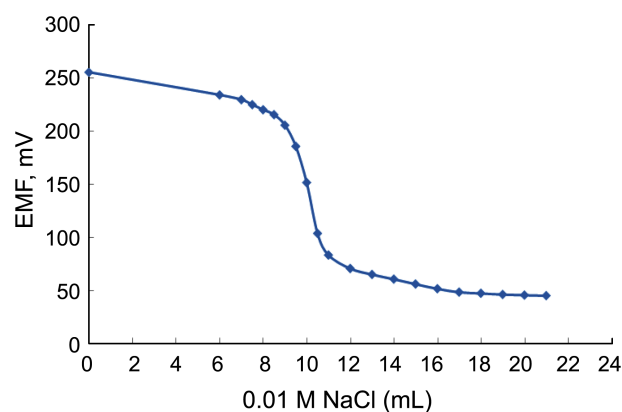


Figure 4. Plot showing the potentiometric titration of 100 mL of 1.0×10^{-3} AgNO_3 with the successive addition of 1.0×10^{-2} M NaCl solution for m-2.

ion selective electrodes. The pH response profile for the m-2 electrode was examined using 1.0×10^{-3} M AgNO_3 in the Tris- HNO_3 buffer solution. The pH was adjusted by introducing small drops of 0.1 M nitric acid. The influence of the pH response upon the PVC membrane electrode is shown in Figure 5. As it proves, potentials were found to remain constant from pH 2 to 6, beyond which the potential changed considerably. After pH 6, the potential decreased radically (250 to 30 mV) with a low concentration of the proton ion. The observed drift at high pH values might have been due to protonation of the chelating ionophore, making complexation with silver(I) impossible. Furthermore, the sensor could also be exhibiting an interference effect due to hydrogen ions. Therefore, the best performance for m-2 was found at pH 5.

Selectivity is perhaps the most important characteristic of any sensor, which defines the nature of the device and the extent to which it may be employed in the determination of a particular ion in the presence of other interfering ions. It is measured in terms of potentiometric selectivity coefficients, which have been evaluated using a fixed interference

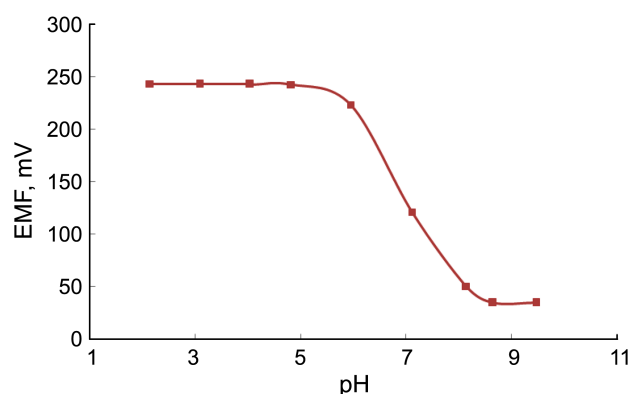


Figure 5. Effect of pH of the test solution (1.0×10^{-3} M of Ag^+) on the potential response of the Ag^+ ion-selective electrode (m-2).

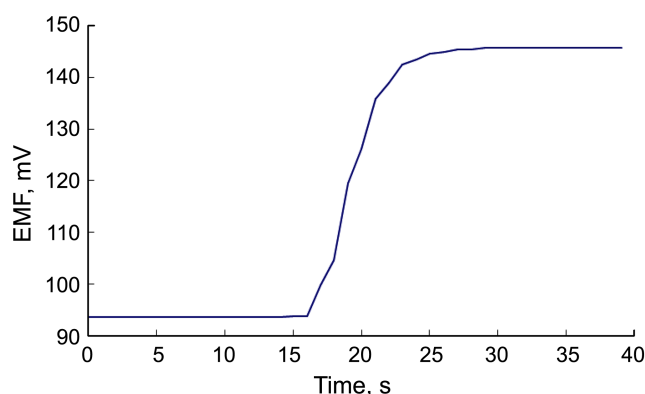


Figure 6. The static response time of m-2 towards 1.0×10^{-6} to 1.0×10^{-5} M Ag^+ .

method at a 1.0×10^{-3} M concentration of interfering ions. The potentiometric selectivity coefficients measure the response of the electrode for the primary ion in the presence of foreign ions.²⁸ The results for the Schiff base (m-2) are shown in Table 3. A perusal of the coefficients reveals that the sensor was selective to silver ions over the other cations. The common ions of alkali, alkaline earth metals, and transition metals would not cause any significant interference unless present at high concentrations. This Schiff-base ($N^2E, N^2'E$)- N^2, N^2' -bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine performed primarily as a Ag^+ selective ionophore and avoided interference from at least 17 cited cations, a key advantage for analyzing various industrial wastewater samples. The response characteristics of the proposed PVC membrane electrode are compared with those of the best Ag^+ ion-selective electrodes reported earlier (Table 4).

This proposed membrane was highly selective to silver ion over a huge number of metal ion interferences and the value of selectivity coefficients were so high. For instance some comparisons have been given, ten cations were tested for interference and Na^+ and K^+ are very low.¹³ Thirteen cations were tested for interference and Na^+ and Hg^{2+} are very low.²⁸

Twenty cations were tested for interference but the value of selectivity coefficients are not close to our reporting.²⁹ According to these comparisons our proposed m-2 has shown a significant selectivity with high sensitivity.

As the concentration of silver changed from 1.0×10^{-6} to 1.0×10^{-5} M, the potential changed dynamically (Figure 6). The static response time thus obtained was less than 9 s; however, at a concentration lower than 1.0×10^{-6} M, the potential was constant. The sensing behavior of the membrane electrode remained unchanged when the potentials were recorded either from low to high concentration, or vice versa.

Conclusion

A novel Schiff-base ($N^2E, N^2'E$)- N^2, N^2' -bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine has been synthesized and finally used as PVC-based membrane sensors for potentiometric determination of silver ions. The membrane electrode (m-2), plasticized with DOA, showed better selectivity coefficients than others membrane without any additives. This proposed PVC membrane ion selective electrode exhibited a good response towards silver ions over a large concentration range of 1.0×10^{-2} to 1.0×10^{-7} M, with a

Table 3. Selectivity coefficients of various interfering ions for the membrane electrode (m-2)

Membrane	LOD	Slope	$\text{Log}K_{\text{Ag}^+, j}^{\text{Pot}}$																	
			Ag^+	Hg^{2+}	Rb^+	K^+	Li^+	Cs^+	Cu^{2+}	Mg^{2+}	Ni^{2+}	Sr^{2+}	Pb^{2+}	Mn^{2+}	Cd^{2+}	Zn^{2+}	Ba^{2+}	Cr^{3+}	Al^{3+}	Na^+
m-2	-7.85	57.4	0	-3.7	-4.9	-4.9	-4.9	-5	-5.4	-6.5	-6.3	-6.5	-6.4	-6.5	-6.4	-6.3	-6.5	-5.6	-5.9	-5

Table 4. Comparative analysis of proposed electrode with reported electrodes

Ionophore	LOD	Slope	pH range	Response time (s)	Ref. no.
Derivative of 4,13-diaza-18-crown-6	4.4×10^{-8}	59.3	3.0-8.0	12	13
Schiff-base- <i>p-tert</i> butylcalix[4]arene	6.3×10^{-6}	58.9	1.0-6.0	30	28
Azathioether crown	8.0×10^{-7}	57.1	3.0-7.0	–	29
Hexa-thia-18-crown-6	4.0×10^{-6}	59.0	2.0-7.5	< 10	30
Calix[4]arene	–	56.0	> 2	–	31
Calix[2]furano[2]pyrrole	6.0×10^{-7}	57.1	–	–	32
Schiff-base ($N^2E, N^2'E$)- N^2, N^2' -bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine	4.0×10^{-8}	57.4	2.0-6.0	9	This work

Nernstian slope of 57.4 mV/dec. at pH 5, with selectivity over 17 interfering cations. The presented electrode demonstrates an improved detection limit, response time and slope over those reported in the literature. The response time was very fast (9 s), with an optimal lower detection limit of 4.0×10^{-8} M. This lab has shown that the fabricated electrode (m-2) can be employed for both residual silver and total Ag^+ content determination, employing only a simple procedure.

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