

A potentiometric sensor of silver ions based on the Schiff base of diphenol

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Abstract A potentiometric sensor based on the Schiff base 2,2'-(1E,1'E)-(1,1'-binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol was synthesized and tested as an ionophore PVC-based membrane sensor selective towards silver ions (Ag^+). Potentiometric testing demonstrated the high affinity of this receptor to silver ions. Seven membranes were fabricated with different compositions, with best performance shown by that with an ionophore composition (*w/w*) of 1.0 mg, PVC 33.0 mg, 2-nitrophenyl octyl ether 66 mg, and potassium tetrakis(*p*-chlorophenyl)borate 50 mol% in 1.0 mL tetrahydrofuran. The sensor worked well over a wide range of concentrations (1.0×10^{-2} to 1.0×10^{-6} M Ag^+) at pH 6, showing a slope of 60.99 mV/dec with rapid response times of less than 3 s. The sensor also showed good selectivity towards Ag^+ in the presence of interfering cations, with the highest selectivity coefficient observed for Hg^{2+} (2.7). A low detection limit of 3.4×10^{-7} M Ag^+ was established.

Keywords Schiff base · Silver-ion-selective electrode · Potentiometry · Ionophore · PVC membrane

Introduction

There is great interest in the development and application of potentiometric sensors for monitoring the concentrations of various species in biological, environmental, and industrial fields. They have shown advantages such as fast responses,

easy preparation, low cost, compatibility with complex and colored media, wide linear dynamic ranges, and relatively low detection limits. Chronic exposure to silver has adverse effects such as permanent bluish-gray discoloration of the skin (argyria) or eyes (argyrosis). Most reported cases of argyria and argyrosis have been due to exposure to soluble forms of silver. Exposure to soluble silver compounds may also produce other toxic effects, including liver and kidney damage, irritation of the eyes, skin, respiratory system, and intestinal tract, and changes in blood cells [1]. Silver is used widely in various industries and items such as coins, jewelry, alloys, electrical devices, and mirrors. Silver-based chemicals are used in photographic processes and research, as well as in dental amalgams and burn creams due to their antibacterial properties [2]. Therefore there is a high risk of surface and ground water contamination by silver and several techniques for silver metal ion determination have been developed, such as thermometric titration [3], flame atomic absorption spectroscopy [4], inductively coupled plasma atomic emission spectroscopy [5], and inductively coupled mass spectroscopy [6]. These methods are time-consuming, involve sample manipulation, and are relatively expensive. Potentiometric sensors based on ion-selective electrodes (ISEs) employ molecular recognition chemistry. The ISE dynamic response is generated by selective complexation of the target ion with neutral carrier ionophores dispersed in a poly(vinyl chloride) (PVC) matrix. Polymeric membrane ISEs provide one of the most powerful sensing methods because it is possible to select various sensory elements according to the shape and size of the target ion. Many of these ISEs exhibit excellent selectivity for metal cations as guests. They are prepared by immobilizing host molecules capable of recognizing a specific class of ionic species in an appropriate polymeric matrix, which is then built on an electrode body. In the last three decades, because of their

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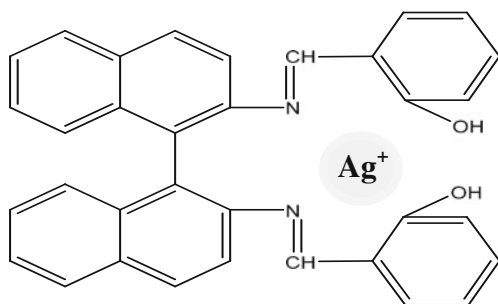


Fig. 1 Proposed structure of BDBD

ease of preparation and simplicity of use, ISEs have been applied to many analytical problems. They have also been used in probing host–guest chemistry [7]. ISEs have many advantages, such as selectivity, sensitivity, precision, simplicity, and low cost [8–12]. Silver selective sensors, based mainly on Schiff bases [13], podands [14], cyclams [15], calixarenes [16], and polystyrene [17], have been developed. Typical ISEs respond to ion activity changes in the aqueous phase [18] based on measurements of the phase boundary potential at the sample/membrane interface. Ionophores are important components of polymeric membrane ISEs. The selectivity towards the target over interfering ions is of great concern in ionophore development. Good selectivity results from strong complexation between the ionophore and the target ion, rather than weak complexation of the ionophore with interfering ions [19]. Sulfur- and nitrogen-containing ligands have been reported to bind preferentially with heavy metal ions such as Ag^+ [20].

This work reports the Schiff base ionophore 2,2'-(1*E*,1'*E*)-(1,1'-binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (BDBD), developed and tested as an ISE for the selective determination of Ag^+ . The best performing membrane (m-3) was prepared from ionophore (*w/w*) 1.0 mg, PVC 33.0 mg, 2-nitrophenyl octyl ether (*o*-NPOE) 66 mg, and potassium tetrakis(*p*-chlorophenyl)borate (*KTpCIPB*) 50 mol%. This PVC-based membrane ISE showed good responses towards Ag^+ , with improved detection limit, rapid response times, and good slope. The linear concentration range of the m-3 membrane was 1.0×10^{-2} to 1.0×10^{-7} M Ag^+ at ca. pH 6, with a slope of 60.99 mV/dec.

Experimental

Reagents

The Schiff base BDBD Ag^+ carrier was synthesized by a previously described method [21]. The precipitate was collected from ethanol by filtration. The product was recrystallized from ethanol and dried under reduced pressure at 40 °C with 97% yield. A possible structure is shown in Fig. 1. High molecular weight PVC, *o*-NPOE, dioctyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS), *KTpCIPB*, and tetrahydrofuran (THF) were obtained from Aldrich (Gwangju, Korea) and used without further purification. Nitrate salts of the cations (from Merck) were used without further purification. Doubly distilled water was used to prepare all aqueous electrolyte solutions. High-purity argon was used for deaeration. All experiments were carried out at room temperature (RT). Potentials were measured at various concentrations of AgNO_3 between 1.0×10^{-2} and 1.0×10^{-7} M. Standard AgNO_3 solutions were obtained by dilution of 0.1 M AgNO_3 ; pH was adjusted with Tris– HNO_3 buffer.

Instruments

A multichannel potentiometer (model KST101-1) was used with a two-electrode system. An orion double-junction Ag/AgCl (3 M NaCl) electrode (BAS) was used as the reference electrode. A Philips IS-561 electrode was used as the working electrode. An ISTEK 735p pH meter was used for pH confirmation and calibrated with pH 4, 7, and 10 solutions. All potentials were reported with respect to the Ag/AgCl electrode at RT in argon.

Electrode fabrication

The sensitivity and selectivity of a cation-selective electrode depend on the membrane composition and the nature of the plasticizer [22]. Plasticized PVC-based membranes and electrodes were prepared by a conventional procedure [23, 24]. Several membranes were fabricated (Table 1). The best responding membrane (m-3) was prepared from BDBD

Table 1 Membranes' compositions

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

^aIn milligrams

^bIn moles percent relative to the ionophore

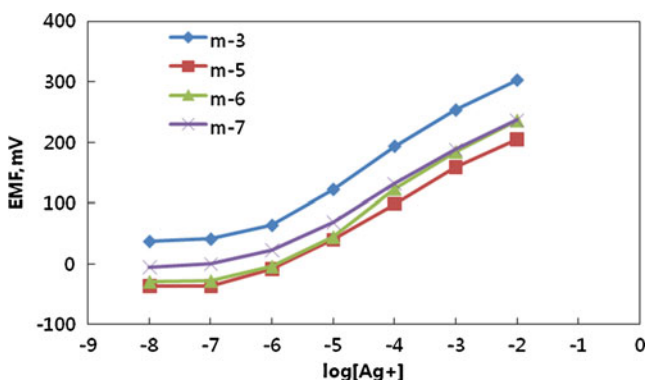


Fig. 2 Potentiometric responses of membranes prepared with different plasticizers towards Ag^+ at pH 6

1.0 mg, PVC 33.0 mg, NPOE 66.0 mg, and KTPCIPB 50 mol%. The components were portioned by weight. A homogeneous mixture resulted from the complete dissolution of the components in THF. It was placed onto a smooth glass plate and concentrated through evaporation of the THF at room temperature. The sensitivity, linearity, and selectivity of ionophores depend significantly on the membrane composition and the nature of the plasticizer [22, 25]. The lipophilicity of the plasticizer can influence both the dielectric constant of the polymeric membrane and the mobility of the ionophore and its metal complexes [26, 27], indicating that the *o*-NPOE-plasticized membrane dissolved the ion association complexes and affected both permittivity and the mobility of the ion exchanger sites, giving highest selectivity and sensitivity. All electrodes were used with 0.1 M KCl as an internal filling solution.

Potentiometry

Potentiometric response measurements were carried out with a multichannel potentiometer at room temperature. An electrochemical cell of $\text{Ag}/\text{AgCl}|0.1 \text{ M KNO}_3||0.05 \text{ M Tris-HNO}_3 \text{ (sample solution)}||\text{PVC membrane}| \text{internal filling solution (0.1 M KCl)}|\text{AgCl}/\text{Ag}$ was used. Steady-state potentials (within 0.1 mV over a 1-min period) were recorded in all measurements. Conditioning

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

Membrane	Linear range (M)	LOD ($\log \text{Ag}^+$)	Slope (mV/dec)
m-1	1.0×10^{-2} to 1.0×10^{-4}	-4.33	19.55
m-2	1.0×10^{-2} to 1.0×10^{-6}	-6.13	64.47
m-3	1.0×10^{-2} to 1.0×10^{-6}	-6.46	60.99
m-4	1.0×10^{-2} to 1.0×10^{-6}	-6.24	68.54
m-5	1.0×10^{-2} to 1.0×10^{-6}	-6.48	54.62
m-6	1.0×10^{-2} to 1.0×10^{-6}	-6.35	62.01
m-7	1.0×10^{-2} to 1.0×10^{-6}	-6.47	54.70

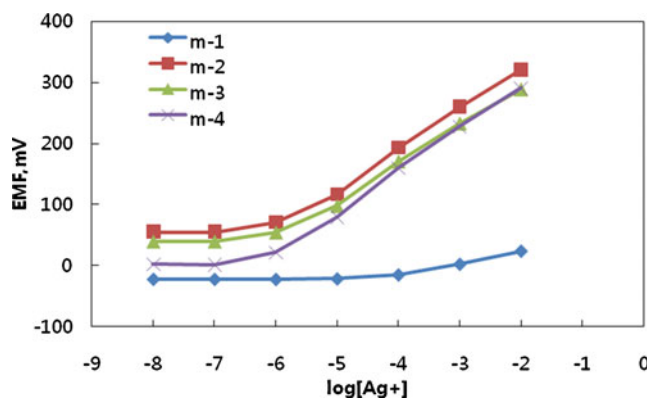


Fig. 3 Potentiometric responses of membranes prepared with different amounts of additive towards Ag^+ at pH 6

of the membrane electrode was required to achieve reliable results. The membranes were rinsed with distilled water and then conditioned for 24 h in 0.001 M AgNO_3 , followed by 24 h in 0.1 M AgNO_3 .

The selectivity coefficients ($\log K_{\text{Ag}^+}^{\text{pot}}$) were determined by the separate solution method using nitrate salts of the cations involved. Detection limits were estimated at the intersection of two linear lines, the one extrapolated from a high concentration range and the other parallel to the *X* axis drawn through the mean potential value of the lowest metal ion concentration used in the plot of the potential change and the concentration of Ag^+ .

Results and discussion

The Schiff base BDBD was employed as a silver selective ionophore in the preparation of a silver ISE. Measurements were taken at AgNO_3 concentrations of 1.0×10^{-2} – 1.0×10^{-7} M. Electrodes were tested with four different membrane compositions; they exhibited wide linear response ranges (Fig. 2). The electrodes were also characterized through their limits of detection and slopes (Table 2).

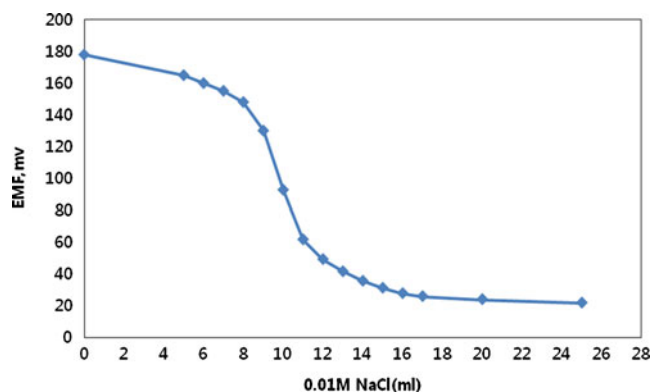


Fig. 4 The potentiometric titration of 100 mL 1.0×10^{-3} AgNO_3 with 1.0×10^{-2} M NaCl using m-3

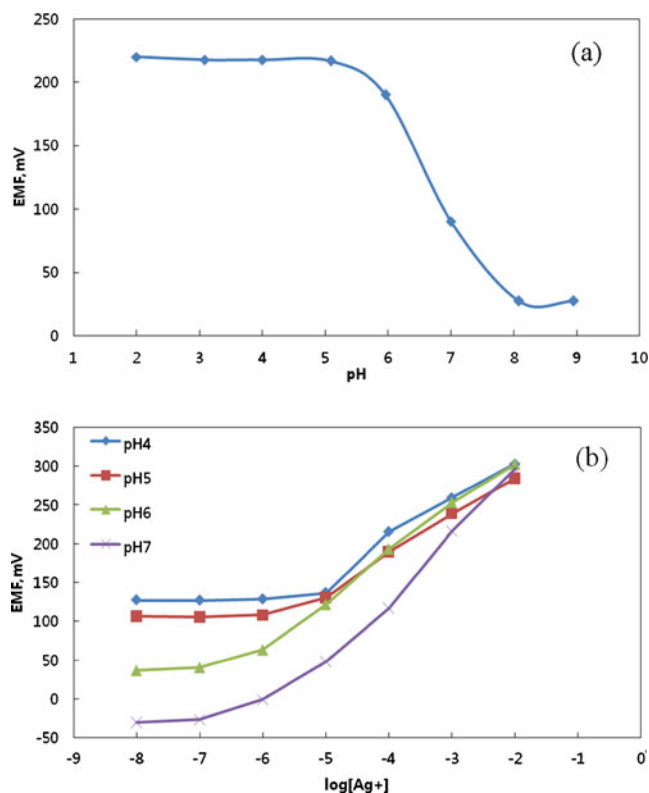


Fig. 5 **a** Effect of pH on m-3 in 1.0×10^{-3} M Ag^+ solution and **b** potentiometric responses of m-3 in different pH solutions

The membrane's composition determined the sensitivity, selectivity, and stability of the resulting ion-selective electrode. Four different compositions were compared here. Measurements were taken in 100 mL 0.05 M Tris– HNO_3 in order to maintain the ionic strength of the medium. The electrodes' responses were measured after additions of AgNO_3 over an Ag^+ concentration range of 1.0×10^{-2} – 1.0×10^{-7} M. Each tested membrane composition resulted in an electrode with linear responses (Fig. 2). Membrane m-3, containing *o*-NPOE and KTpClPB 50 mol%, showed the greatest Nernstian slope; it was the best performing composition in terms of detection limit and slope.

When this membrane composition was used in electrodes with different percentages of additive, dynamic responses were observed (Fig. 3). Additive present at 0%, 50%, and 100% (m-1, m-3, and m-4, respectively) resulted in similar electrode responses. Electrode m-2 (with 20% additive) showed improved potential responses. However, m-3 was more sensitive at low concentrations, with a slope closest to the standard.

The proposed sensor (m-3) was employed in the potentiometric titration of 100 mL 1.0×10^{-3} M Ag^+ with 1.0×10^{-2} M NaCl. A sharp end point was observed at the expected 10 mL NaCl (Fig. 4). The sharp end point indicates that Ag^+ in solution can be determined precisely from titration curves.

The pH of the test solution is important in ISE experiments. The pH response profile of the m-3 electrode was examined using 1.0×10^{-3} M AgNO_3 in Tris– HNO_3 buffer (Fig. 5a). pH was adjusted by dropping 0.1 M nitric acid. Potential was constant from pH 2 to 6, but it decreased from 220 to 28 mV above pH 6 as the concentration of protons dropped. The observed drift at high pH may have been due to the deprotonation of the chelating ionophore. Therefore, the best performance of m-3 was found at pH 6, according to slope (Fig. 5b).

Selectivity is important for ISE sensors. It defines the nature of the device and the interference environments in which it operates. Selectivity, in terms of potentiometric selectivity coefficients, was evaluated for m-3 using interference ions at 1.0×10^{-3} M (Table 3). The potentiometric selectivity coefficients describe the response of the electrode to the target ion when in the presence of foreign ions [28]. The sensor was shown to be selective to Ag^+ over the other cations, with common ions of alkali, alkaline earth, and transition metals not causing significant interference unless present at high concentrations. The Schiff base BDBD performed primarily as an Ag^+ selective ionophore and avoided interference from at least 17 cations, an important property for the analysis of industrial wastewater samples. The response characteristics of the proposed PVC membrane electrode are compared with those of other reported Ag^+ ISEs (Table 4).

Table 3 Selectivity coefficients ($\log K_{\text{Ag}^+}^{\text{pot},j}$) for various different silver ion-selective electrode

Electrode	Al^{3+}	Cr^{3+}	Mg^{2+}	Zn^{2+}	Cu^{2+}	Ca^{2+}	Hg^{2+}	Pb^{2+}	Cd^{2+}	K^+	Na^+
5,11,17,23-Tetra- <i>tert</i> -butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4 [29]			-3.87	-3.60	-3.73	-3.71	-0.28	-2.98	-3.72	-3.95	-3.69
Schiff base- <i>p</i> - <i>tert</i> butylcalix[4]arene [28]			-4.57	-3.82	-3.80	-3.42	-2.00	-3.54	-3.42	-2.65	-2.35
Derivative of octahydroxycalix[4]arene [30]	-3.89	-3.33	-3.43	-5	-3.37	-4.05		-3.08	-4.00	-1.17	-2.07
5,10,15-Tris(pentafluorophenyl)corrole [31]	-3.98		-4.20	-4.51	-3.42	-4.67	-2.60	-4		-3.23	-3.71
Bis-oxime derivative of diaza-18-crown-6 [32]					-2.68		-2.38	-2.68	-3.18		
Derivative of 4,13-diaza-18-crown-6 [13]		-2.11		-1.95	-1.67			-1.47	-2.01	-3.14	-3.79
Schiff base BDBD (this work)	-4.10	-4.00	-5.10	-5.50	-3.50	-5.00	-2.70	-4.40	-4.80	-3.50	-3.60

Table 4 Comparative analysis of the proposed electrode with other reported electrodes

Ionophore	LOD	Slope	pH range	Response time (s)	Ref. no.
Schiff base- <i>p-tert</i> butylcalix[4]arene	6.3×10^{-6}	58.9	1–6	30	[28]
5,10,15-Tris(pentafluorophenyl)corrole	–	54.8	4–8	<30	[31]
Azathioether crown	8.0×10^{-7}	57.1	3–7	–	[33]
Benzothiazole calix[4]arene	5×10^{-7}	59.7	2–8	<5	[19]
Bis-oxime derivative of diaza-18-crown-6	1×10^{-5}	59.5	30–90	6.2–6.3	[32]
Calix[2]furano[2]pyrrole	6.0×10^{-7}	57.1	–	–	[34]
Derivative of octahydroxycalix[4]arene	2.1×10^{-6}	58	1.5–6.5	<20	[30]
Calix[4]arene	–	56.0	>2	–	[35]
5,11,17,23-Tetra- <i>tert</i> -butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4	8×10^{-7}	53.8	2–6	5–10	[29]
Hexa-thia-18-crown-6	4.0×10^{-6}	59.0	2–7.5	<10	[36]
O,O"-bis[2-(methylthio)ethyl]- <i>tert</i> butylcalix[4]arene (Ag ⁺ ionophore IV)	4×10^{-6}	56.7	2.5–6	<10	[37]
Bis(thiothiazole)	–	60.3	2–7.5	60	[38]
Derivative of 4,13-diaza-18-crown-6	4.4×10^{-8}	59.3	3–8	12	[13]
Schiff base BDBD	3.4×10^{-7}	60.99	2–6	3	This work

The proposed membrane was highly selective to silver ions, showing high selectivity coefficients when in the presence of several metal ion interferences. The proposed m-3 electrode showed significant selectivity with high sensitivity.

As the concentration of Ag⁺ was increased from 1.0×10^{-4} to 1.0×10^{-3} M, the potential changed quickly and significantly (Fig. 6) with a static response time of less than 3 s. However, the potential was constant at concentrations below 1.0×10^{-6} M. The potential response behavior of the membrane electrode was consistent with both increases and decreases of concentration.

Determination of Ag⁺ in tap water

The Ag⁺ concentration in spiked tap water samples were determined by multichannel potentiometer. The results are shown in Table 5. It can be seen that the recoveries vary

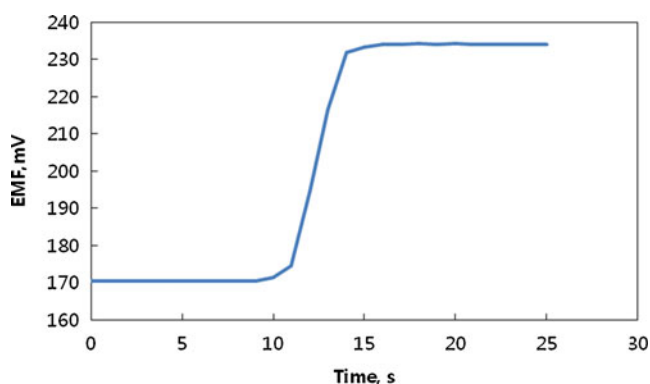


Fig. 6 Static response profile of m-3 upon addition 1.0×10^{-4} to 1.0×10^{-3} M Ag⁺

between 95% and 103%, thus indicating that the potential application of this proposed electrode could show high accuracy for real water sample analysis.

Conclusions

A novel Schiff base, BDBD, was synthesized and explored as a PVC-based membrane sensor for the potentiometric determination of Ag⁺. The m-3 membrane electrode plasticized with *o*-NPOE and with 50 mol% KTpCIPB additive showed better selectivity than other tested membranes. This proposed PVC-based ISE exhibited good responses to Ag⁺ over a wide range of concentrations (1.0×10^{-2} to 1.0×10^{-7} M), with a Nernstian slope of 60.99 mV/dec. Seventeen potentially interfering cations were shown to have little effect on the electrode at pH 6, demonstrating its selectivity to Ag⁺. The proposed electrode had improved detection limit, response time, and slope over previously reported electrodes. It showed fast responses (3 s) and a low detection limit (3.4×10^{-8} M). The electrode sensor demonstrated applicability as a simple determination method for both residual silver and total Ag⁺ content.

Table 5 The determination of Ag⁺ in spiked tap water

Added (μM)	Found (μM)	Recovery (%)
10	9.5	95
20	19.8	99
50	51.3	102.6
100	103.2	103.2

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