

## Polymeric Membrane Silver-ion Selective Electrodes Based on Schiff Base *N,N'*-Bis(pyridin-2-ylmethylene)benzene-1,2-diamine

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The Schiff base *N,N'*-bis(pyridin-2-ylmethylene)benzene-1,2-diamine [BPBD] has been synthesized and explored as ionophore for preparing PVC-based membrane sensors selective to the silver ( $\text{Ag}^+$ ) ion. Potentiometric investigations indicate high affinity of this receptor for silver ion. The best performance was shown by the membrane of composition (w/w) of ionophore: 1 mg, PVC: 33 mg, *o*-NPOE: 66 mg and additive were added 50 mol % relative to the ionophore in 1 mL THF. The sensor works well over a wide concentration range  $1 \times 10^{-3}$  to  $1.0 \times 10^{-7}$  M by pH 6 at room temperature (slope 58.6 mV/dec.) with a response time of 10 seconds and showed good selectivity to silver ion over a number of cations. It could be used successfully for the determination of silver ion content in environmental and waste water samples.

**Key Words:** Schiff base, Silver-ion selective electrode, Potentiometry, Ionophore, *N,N'*-Bis(pyridin-2-ylmethylene)benzene-1,2-diamine

### 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 that have resulted primarily from exposure to the 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 appears to pose minimal risk to health.<sup>1</sup> So that it is necessary to determine the silver ion concentration in natural drinking water and imported food. In the mean time we feel interest to introduce an effective and fast working Schiff base electrode. ISEs permit the potentiometric measurement of the activity of a given ion in the presence of other ions. Synthesis and then application of an ion selective electrode as a potentiometric sensor offers interesting advantages<sup>2</sup> over the traditional methods of analysis such as easy to preparation and procedures, simple instrumentation, relatively fast response,<sup>3</sup> wide dynamic range,<sup>4</sup> reasonable selectivity and low cost. Moreover they provide accurate, reproducible,<sup>5</sup> fast and often selective determination of various ionic species. Not only this, ISEs allow non-destructive, on line monitoring of particular ion in small volume of sample without any pretreatment. Because of these merits, the use of ISEs are increasing day by day in different fields. For instance electroconducting polymers are widely used in the solid-state ion selective electrodes.<sup>6,7</sup> Loads of metal chelators are based on crown-type ligands which usually are full of O, N, or S donor atoms, and they are often employed as ionophore in ion-selective electrodes.<sup>8</sup> Poly(vinyl chloride) [PVC]-based film ion selective electrodes are now well established analytical tools routinely used for chemical, biological and environmental analysis of a wide variety of different ions.<sup>9-12</sup> It is well known that the important components of PVC membrane are

the carrier that determines the selectivity of the electrodes. By reason of their electrical neutrality, lipophilic character, and capability to selectively and reversibly bind with metal ions. Macrocyclic compounds have considerable attention for the development of carrier-based PVC membrane sensors sensitive toward cationic species.<sup>9-15</sup> Different number of the macrocyclic ring or replacing atoms by nitrogen atoms in the macrocyclic ring, the affinity will be expected to be toward heavy or transition metal cations.<sup>16</sup> On the other hand, by using aza-macro compounds as neutral carriers in PVC membranes, highly selective electrodes for heavy<sup>17</sup> and transition metal<sup>18</sup> cations and silver ions<sup>19-22</sup> have been developed. Many Schiff bases have been studied as carriers for various metal ion-selective electrodes.

In our study, deals with Schiff base BPBD-based ISE for selective determination of silver. The silver ion selectivity may be due to electrostatic interaction between the metal ion and aza cavity composed of two highly pre-organized units. This silver ion selective electrode exhibit a good response to silver ion over small concentration range of  $1 \times 10^{-3}$  to  $1.0 \times 10^{-7}$  M with a Nernstian slope of 58.57 mV/decade. Under pH 6, it performed well over a number of interfering cations within 10 seconds. The proposed ion selective electrode incorporates PVC as supporting material, Potassium tetrakis(4-chlorophenyl) borate as additive and 2-nitrophenyl octyl ether (*o*-NPOE) as plasticizing agent. The presentation of this electrode which involves linear range, detection limit, response time, slope etc is in synchronization and in many respects better than those reported in literature.<sup>22</sup>

### Experimental

**Reagents.** The Schiff base *N,N'*-bis(pyridin-2-ylmethylene)benzene-1,2-diamine [BPBD] tested as a carrier of silver ion was synthesized according to the similar procedure described

previously.<sup>23</sup> A solution of 0.1 mol 1,2-diaminobenzene was slowly added to 0.2 mol 2-pyridinecarboxaldehyde in ethanol under nitrogen atmosphere. After 3 h at room temperature, the precipitate was collected by filtration. The product was recrystallized from ethanol and dried under reduced pressure at 50 °C; 97% yield, <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.8–7.4 (ArH), 8.6 (CH N), 13.0 (C OH). BPBD is shown in Fig. 1. High molecular weight PVC, 2-nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS), potassium tetrakis(*p*-chlorophenyl)borate (KTpCIPB) and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare the PVC membranes. The nitrate salts of cations (all from Merck) were used without any further purification except for vacuum drying over P<sub>2</sub>O<sub>5</sub>. 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 membranes were equilibrated for 24 hours in 1.0 M AgNO<sub>3</sub> solution. The potentials have been measured by varying the concentration of AgNO<sub>3</sub> in test solution in the range  $1 \times 10^{-3}$  to  $1.0 \times 10^{-7}$  M. The standard AgNO<sub>3</sub> solutions of metal salt have been obtained by gradual dilution of 0.1 M AgNO<sub>3</sub> solution and pH adjusted by using Tris-HNO<sub>3</sub> buffer.

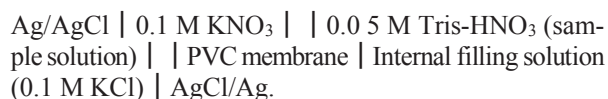
**Instrumentation.** Multichannel potentiometer (Model: KST 101-1) was performed with two-electrode. An Orion double-junction Ag/AgCl electrode supplied by BAS was used as the reference electrode. The Philips IS-561 electrode was used as the working electrode. ISTEK (Model: 735p) pH meter was used after calibration by pH 4, pH 7, pH 10 solution. All potentials were reported with respect to the Ag/AgCl electrode at room temperature under argon atmosphere.

**Preparation of electrode.** It is familiar that the sensitivity and selectivity of cation selective electrode confirmly depend on the membrane composition and the nature of the plasticizer

used.<sup>32</sup> The plasticized PVC based membranes and electrodes were prepared by a conventional procedure.<sup>24,25</sup> We made several membranes as shown in Table 1. The best responding composition for the membrane was of *N,N'*-bis(pyridin-2-yl-methylene)benzene-1,2-diamine: 1 mg, PVC: 33 mg, *o*-NPOE: 66 mg and additive was added 50 mol % relative to the ionophore. The components were added in terms of weight. The homogeneous mixture was obtained after complete dissolution of all the components in THF, and then it has been placed on a smooth glass plate and concentrated by evaporating THF at ambient temperature. It is known that the sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of plasticizer used.<sup>26,32</sup> It is noteworthy that the lipophilicity of plasticizer influences both dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex.<sup>27,31</sup> This indicates that *o*-NPOE plasticized the membrane, dissolves the ion association complexes and adjusts both permittivity and ion exchanger sites mobility to give highest possible selectivity and sensitivity.<sup>28,30</sup>

The electrodes were filled with 0.1 mol L<sup>-1</sup> KCl as an internal filling solution. The solvent was allowed to evaporate at room temperature.

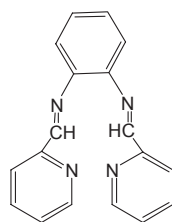
**Potentiometry.** The potentiometric response measurements were carried out with Multi channel potentiometer at room temperature. The electrochemical cell for measurements can be represented as follows:



The steady-state potential (within 0.1 mV over a 1 min period) was recorded in all measurements.

## Results and Discussion

It is well known that the O, N and S atoms in ionophores can play the role of an electron donor. The co-ordination interaction between electron donors and acceptors causes the electrode respond to metal ions.<sup>29</sup> The Schiff base *N,N'*-bis(pyridin-2-yl-methylene)benzene-1,2-diamine was employed as silver selective ionophore in the preparation of silver ion selective electrode. The measurements were performed in the concentration range of  $1.0 \times 10^{-3}$  to  $1.0 \times 10^{-7}$  M AgNO<sub>3</sub>. The electrode shows

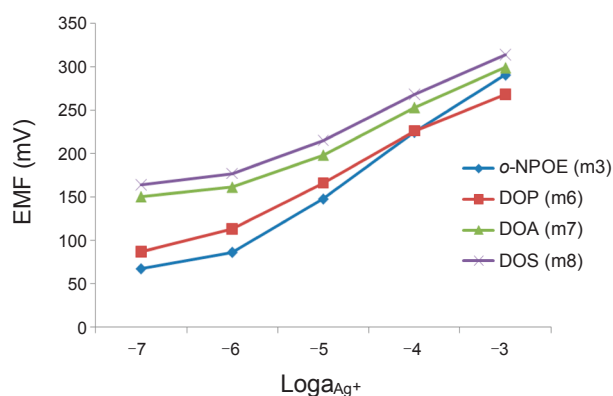


**Figure 1.** Ionophore *N,N'*-bis(pyridin-2-ylmethylene)benzene-1,2-diamine.

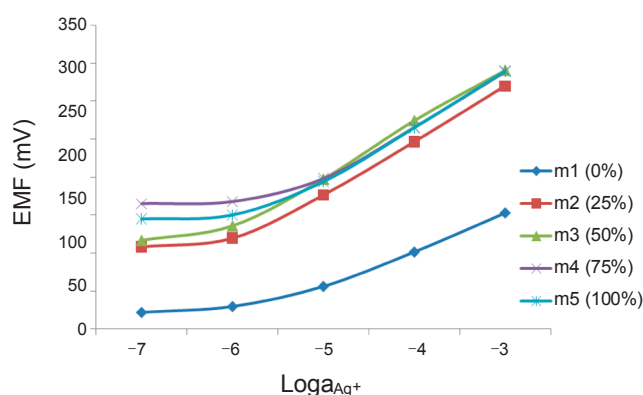
**Table 1.** Compositions of PVC-based silver ion selective membranes

Membrane	Ionophore <sup>a</sup>	PVC <sup>a</sup>	<i>o</i> -NPOE <sup>a</sup>	DOP <sup>a</sup>	DOA <sup>a</sup>	DOS <sup>a</sup>	KTpCIPB <sup>b</sup>
m1	1	33	66				0
m2	1	33	66				25
m3	1	33	66				50
m4	1	33	66				75
m5	1	33	66				100
m6	1	33		66			50
m7	1	33			66		50
m8	1	33				66	50

<sup>a</sup>In mg. <sup>b</sup>in mol % relative to the ionophore.



**Figure 2.** Potentiometric responses of membranes prepared from different plasticizer towards silver ion.



**Figure 3.** The potentiometric responses of the membranes prepared with several additive mol % towards silver ion in pH 6.0 buffer solutions.

**Table 2.** Linear range, LOD, and slope of each membrane

Membrane	Linear range (M)	LOD	Slope (mV/dec)
m1	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.51	33.3
m2	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.54	55.0
m3	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.64	58.6
m4	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.39	44.6
m5	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.46	50.3
m6	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.79	47.5
m7	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.59	39.0
m8	$1 \times 10^{-3}$ to $1.0 \times 10^{-7}$	-6.63	39.1

**Table 3.** Linear comparison between our study and others reported literature

Comparative area	Our study	Others study	References
Concentration range	$1.0 \times 10^{-3}$ to $1.0 \times 10^{-7}$ M	$1.0 \times 10^{-2}$ to $5.0 \times 10^{-7}$ M	4
		$1.0 \times 10^{-1}$ to $1.0 \times 10^{-5}$ M	20
		$1.0 \times 10^{-1}$ to $1.0 \times 10^{-6}$ M	21
		$1.0 \times 10^{-1}$ to $1.0 \times 10^{-5}$ M	22
Response time	10 s	12 s	4
		Less than 20 s	20
		$\leq 17$ s	21
		30 s	22
Nernstian slope	58.6 mV/dec.	$52 \pm 7$ mV	4
		52 mV/dec.	20

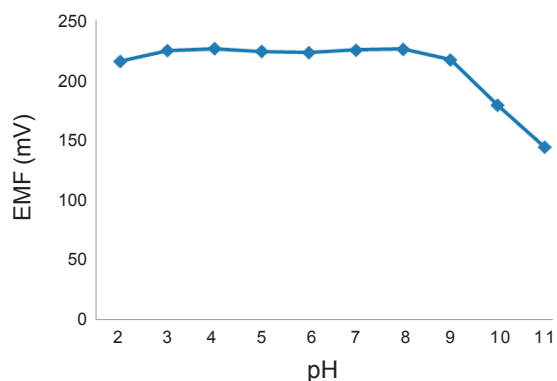
linear response in the concentration range from  $1.0 \times 10^{-3}$  to  $1.0 \times 10^{-7}$  M. The responses of the four electrodes (with different plasticizer) at pH 6 are shown in Fig. 2. The electrodes containing *o*-NPOE (m3) exhibits wider linear response range than that with DOP (m6), DOA (m7) and DOS (m8). The linear range, limit of detection (LOD), and slope were summarized in Table 2.

It was also investigated that the potentiometric response to silver ion with different amount of additive at pH 6 as shown in Fig. 3. It shows highest performance of selectivity when we filled with 50 mol % of additive. The measured potentials were within  $-0.3$  mV over a 5 h period when the electrode was repeatedly dipped in a  $10^{-3}$  mol L $^{-1}$  Ag $^{+}$  solution. The sensor shows nearly Nernstian slope 58.6 mV/dec. The response time of the sensor is 10 seconds which is enough short. In the terms of lifetime of the PVC membrane electrodes, their response stability was observed for over more than two months. We are trying to improve its existence. Here we present a comparative study with others reported literature which was summarized in Table 3.

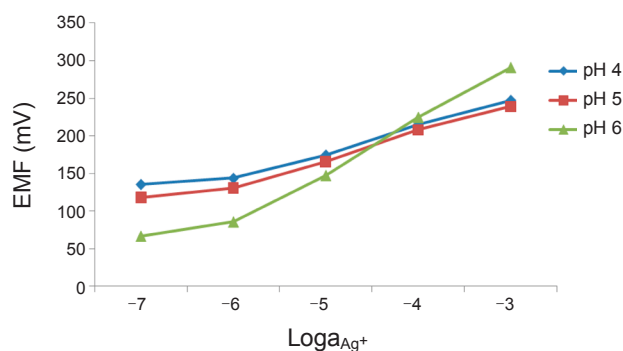
The pH adjustment is very important for ion selective membrane. So, the influence of pH on electrode response was investigated by measuring the potential of *o*-NPOE (m3) electrode in  $10^{-3}$  mol L $^{-1}$  Ag $^{+}$  solution over a pH range of 1 - 11. As shown in Fig. 4, the response of the electrode would remain constant at between pH 3 and 8. This means that the *o*-NPOE (m3) electrode can be used to measure a wide range of environmental and industrial water samples without pH adjustment.

We found another pH responding result for m3. As shown in Fig. 5, the best performing pH is 6. Our proposed membrane (m3) can perform in the range of pH 3 - 8, but pH 6 is the best for Schiff base BPBD.

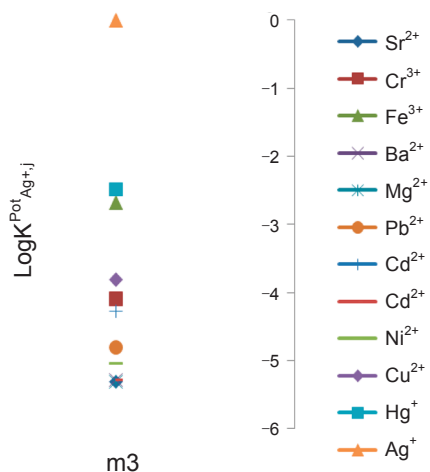
The selectivity is perhaps the single most important characteristic of any sensor which defines the nature of device and the extent to which it may be employed in the determination of a particular ion in the presence of other interfering ions. This is measured in terms of potentiometric selectivity coefficients which have been evaluated using fixed interference method at  $1.0 \times 10^{-3}$  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.<sup>22</sup> The selectivity coefficients of the electrodes were determined by a method developed by Bakker.<sup>27</sup> The result for Schiff base BPBD (m3) is shown in Fig. 6. A perusal of the coefficients reveals that all the sensors are selective to silver ion over the



**Figure 4.** The pH dependence of the novel electrode (m3) on the potentiometric responses under the constant concentration ( $10^{-3}$  M) of silver ion.



**Figure 5.** The potentiometric responses of the membrane m3 towards silver ion in different pH solutions.



**Figure 6.** The selectivity coefficients towards the silver ion with respect to the interfering ion (m3).

other cations. The common ions of alkaline earth metals and transition metals would not cause any significant interference unless present in high concentrations.

This Schiff-base *N,N'*-bis(pyridin-2-ylmethylene)benzene-1,2-diamine (m3) performed primarily as a Ag<sup>+</sup> selective ionophore and avoided interference from other cations. This is very important advantage for analysis of various industrial waste water samples.

## Conclusion

As a final point, we present here the synthesis and characterization of new Schiff-base, finally used them as PVC-based membrane sensors for potentiometric determination of silver ion. The substituents (m1-m8) of the Schiff base structure were found a significant effect on the sensitivity and selectivity for silver ion over several interfering cations. The best results were obtained from Schiff base BPBD, the polymeric membrane electrode (m-3) with *o*-NPOE used as plasticizer, involved 50 mol % additive, exhibited near-nernstian response (58.6 mV/dec.), a detection limit of  $\log [\text{Ag}^+] = -6.64$  in pH range 3 - 8. Among them we didn't find suitable result as like as m3 in any other membrane due to change the percentage of plasticizers and additive.

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