

Sensor for Silver(I) Ion Based on Schiff-base-p-tert-butylcalix[4]arene

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Abstract: The preparation of polymer membrane selective to silver ion and its application to ion-selective electrode is reported here. PVC membrane contain silver-selective calix[4]arene derivative as ionophore. The membrane electrode is highly selective to silver ion and exhibit good linear response over a wide concentration range of 1.0×10^{-1} to 1.0×10^{-5} M AgNO₃ with Nernstian slope of 58.9 mV per decade. The detection limit of electrode is 6.31×10^{-6} M. The calix[4]arene based membrane electrode exhibit enhanced selectivities for silver ion over other cations; $\log K^{\text{Pot}}_{\text{Ag,Na}} = -2.35$, $\log K^{\text{Pot}}_{\text{Ag,K}} = -2.65$, $\log K^{\text{Pot}}_{\text{Ag,Mg}} = -4.57$, $\log K^{\text{Pot}}_{\text{Ag,Ba}} = -4.10$, $\log K^{\text{Pot}}_{\text{Ag,Cd}} = -3.42$, $\log K^{\text{Pot}}_{\text{Ag,Pb}} = -3.45$. Even the strongest interferent Hg²⁺ do not interfere to great extent, $\log K^{\text{Pot}}_{\text{Ag,Hg}} = -2.0$. The electrode response is stable over wide pH range of 1.0-6.0. The response time of the sensor is 30 seconds and the membrane can be used for more than 6 months without observing any divergence. The sensor can also be applied as an indicator electrode for potentiometric titration of Ag⁺ ions with Cl⁻. It is possible to determine Ag(I) in the natural water spiked with silver with this electrode assembly.

Keywords: Sensor, Silver(I), Potentiometry

Introduction

Amongst the various analytical techniques available, the use of ion-selective membrane electrodes is well establish routine analytical technique. Good ion-selective electrodes (ISEs) possess many advantages over the traditional methods of analysis as they provide accurate, reproducible, fast and often selective determination of various ionic species. Not only this, the ion-selective electrodes (ISEs) allow non-destructive, on line monitoring of particular ion in small volume of sample without any

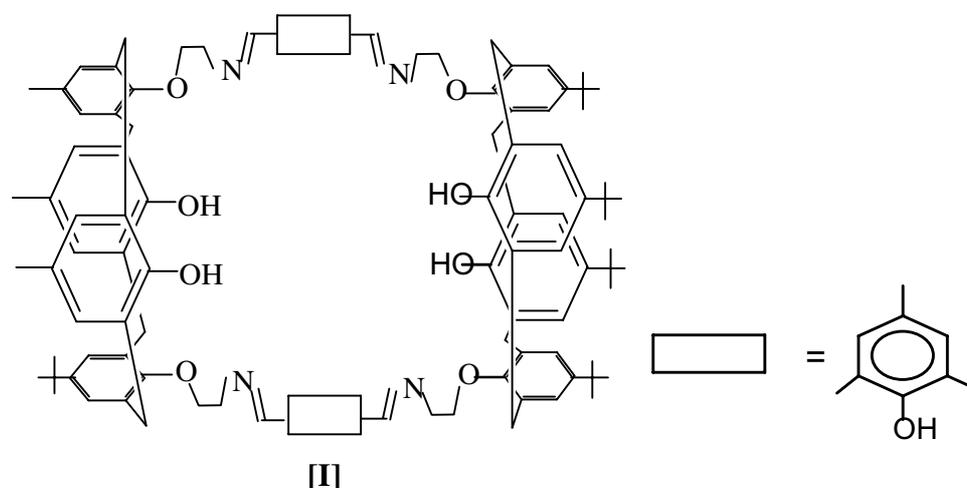
pretreatment. Because of these merits, the use of ISEs is increasing day by day in medicinal, environmental, agricultural and industrial field. During last three decades, a number of ion-selective electrodes with polymeric membranes have been reported[1-10]. Among the various ligands available for ion-selective electrodes such as crowns, podands, cryptands and spherands, the calixarenes met many of the requirements that an ionophore should satisfy for the use in ion-selective electrodes[11]. A number of calixarene derivatives containing pendant ether, amide, ketonic and ester groups have been incorporated as neutral carriers into ion-selective electrodes sensitive to sodium, potassium and cesium ions[12-15]. Recently, we reported silver(I) and cesium ion-selective PVC membrane electrode based on bis(pyridine tetramide) macrocycle and calix crown ether ester, respectively[2,3,10]. The present paper deals with Schiff-base-p-tert-butylcalix[4]arene derivative [I] based ISE for selective determination of silver. The silver ion selectivity may be due to electrostatic interaction between the metal ion and aza crown cavity composed of four highly preorganized soft binding units (imine units).

The silver(I) ion selective electrode exhibit a good response for silver ion over wide concentration range of 1.0×10^{-5} - 1.0×10^{-1} M with a Nernstian slope of 58.9 mV per decade. The proposed ion selective electrode incorporates PVC as supporting material to give a pseudo-solid sensing membrane and bis(2-ethylhexyl)sebacate as plasticizing agent. The performance of this electrode which involves linear range, detection limit, response time, slope etc is in agreement and in many respects better than those reported in literature [8, 9].

Experimental

Reagents

Schiff-base-p-tert butylcalix[4]arene derivative was prepared as reported earlier[2]. High molecular weight poly(vinylchloride) PVC and bis(2-ethylhexyl)sebacate were obtained from Fluka. All other reagents used were of Analytical - Reagent grade.



Electrode Preparation

The PVC based ion selective electrode membrane is prepared by dissolving 100.0 mg of PVC, 211.0 mg of bis(2-ethylhexyl) sebacate as plasticizer and 5.6 mg of calix[4]arene as ionophore in 5 ml

tetrahydrofuran(THF). The mixture so obtained was shaken vigorously and poured into 50 mm petridish after removing air bubbles. The solvent was allowed to evaporate at room temperature and the resulting membrane was cut to size, attached to pyrex tube with PVC glue and conditioned with AgNO_3 solution of $1.0 \times 10^{-1} \text{M}$ for two days.

Potentiometric measurements

The potentiometric measurements were carried at room temperature with the following cell set up:

$\text{Ag}/\text{AgCl} / 1.0 \times 10^{-1} \text{M AgNO}_3 / \text{PVC membrane} / \text{test solution} / \text{Ag}/\text{AgCl}$

All the measurements were made with Elico LI Model-120 pH meter. Standard AgNO_3 solutions for calibration were obtained by gradual dilution of 0.1M AgNO_3 solution.

Results and Discussion

Schiff-base-p-tert-butylcalix[4]arene derivative[I] was employed as silver selective ionophore in the preparation of silver ion- selective electrode. The potentiometric response of the electrode is shown in Fig 1. The measurements were performed in the concentration range of 1.0×10^{-8} - $1.0 \times 10^{-1} \text{M AgNO}_3$. The electrode shows linear response in the concentration range from 1.0×10^{-5} to $1.0 \times 10^{-1} \text{M}$. The detection limit obtained from the intersection of the extrapolated linear regions in the plot, is $6.31 \times 10^{-6} \text{M}$. The sensor shows nearly Nerntian slope 58.7mV per decade. The response time of the sensor is 30 seconds which is quite short. In terms of lifetime of the PVC membrane electrodes, their response stability was observed for over more than six months.

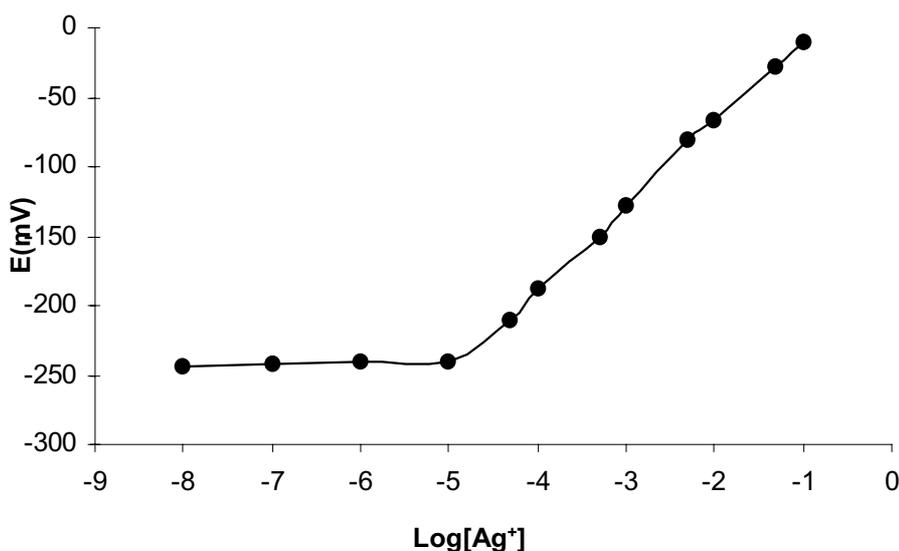


Figure 1. Potential responses of silver ion sensors based on ionophore[I].

The pH dependence of the membrane potential was also examined at $1.0 \times 10^{-2} \text{ M}$ silver(I) concentration. As shown in Fig. 2, the membrane electrode shows good stability in relation to pH changes over wide pH range i.e 1.0 -6.0, which may be taken as the functional pH range of the sensor. In this plot, the high variation of the potentiometric response corresponds to pH limit. This points towards the applicability of the developed electrode in the moderately acidic media. As the pH of silver nitrate solutions lies in the functional range of the sensor, do not need any pH adjustment.

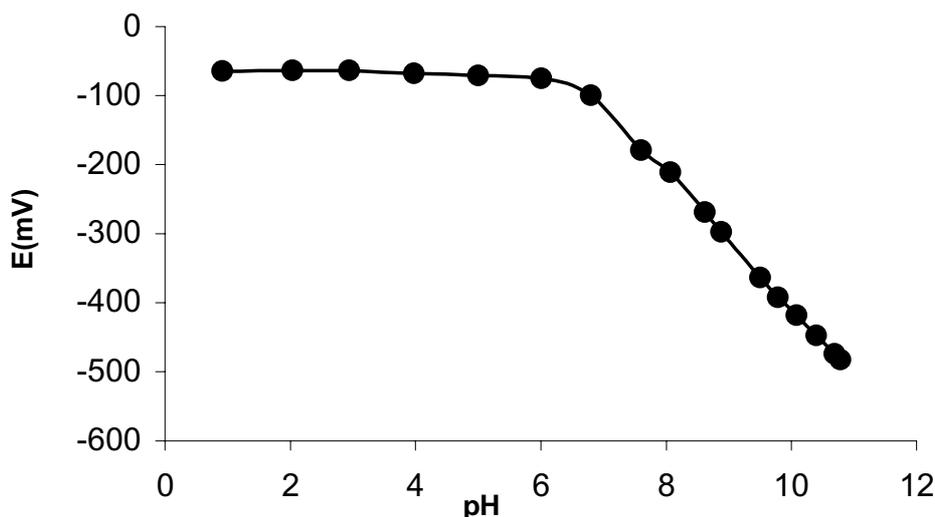


Figure 2. Plot showing the variation of membrane potential with pH at $1.0 \times 10^{-2} \text{ M}$ Ag^+ ions.

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 ($\log K_{\text{Ag,M}}^{\text{Pot}}$) which has been evaluated using fixed interference method at $1.0 \times 10^{-2} \text{ M}$ concentration of interfering ions. The potentiometric selectivity coefficients ($\log K_{\text{Ag,M}}^{\text{Pot}}$) measures the response of the electrode for the primary ion in the presence of foreign ions. Table 1 shows potentiometric selectivity coefficient data of Schiff-base-p-tert-butyl calix[4]arene based silver ion-selective electrode for interfering cations relative to Ag^+ . The selectivity coefficients data indicate that $K_{\text{Ag,M}}^{\text{Pot}}$ values are of the order of 10^{-3} for monovalent and for divalent metal ions (except for the mercury(II) ions) the values are of the order of 10^{-4} and 10^{-5} . Therefore, the electrode can be used for the determination of silver ions in the presence of interfering ions.

These results demonstrated that Schiff-base-p-tert-butylcalix[4]arene[I] acted primarily as a Ag^+ selective ionophore and avoided interference from other cations when present at high concentration of $1.0 \times 10^{-2} \text{ M}$. Even the strongest interferent Hg^{2+} does not disturb the performance of sensor when present at the concentration less than $1.0 \times 10^{-5} \text{ M}$ (Fig. 3).

In a comparison with PVC based Ag^+ ion sensor having calix[4]arene derivatives with functional heterocyclic group such as pyridyl[9] as ionophore, it is interesting to note that the interference from Hg^{2+} is much prominent in normal performance of the sensor, $\text{Log } K_{\text{Ag,Hg}}^{\text{Pot}} = -1.80$. Further, the slope

and linear range, detection limit of the proposed sensor are comparable and better in many respects than that sensor. From another comparison with Ag^+ ion selective electrode incorporating bis(3-pyridinecarboxylate)calix[4]arene as an ionophore[8] in which the Hg^{2+} act as an strongest interferent with $\text{Log } K^{\text{Pot}}_{\text{Ag,Hg}} > +1.0$., we find the sensitivity and selectivity of the Ag^+ selective electrode develops in this study are better than those of previous electrodes.

Table 1. The selectivity coefficients of diverse ions.

Diverse ions	$K^{\text{Pot}}_{\text{Ag,M}}$	$\text{Log } K^{\text{Pot}}_{\text{Ag,M}}$
K^+	2.24×10^{-3}	-2.65
Na^+	4.47×10^{-3}	-2.35
NH_4^+	4.47×10^{-3}	-2.35
Mg^{2+}	2.69×10^{-5}	-4.57
Ca^{2+}	3.80×10^{-4}	-3.42
Ba^{2+}	7.94×10^{-5}	-4.10
Ni^{2+}	5.01×10^{-5}	-4.30
Co^{2+}	2.51×10^{-4}	-3.60
Cu^{2+}	1.59×10^{-4}	-3.80
Pb^{2+}	3.55×10^{-4}	-3.54
Hg^{2+}	1.0×10^{-2}	-2.00
Zn^{2+}	1.51×10^{-4}	-3.82
Cd^{2+}	3.80×10^{-4}	-3.42

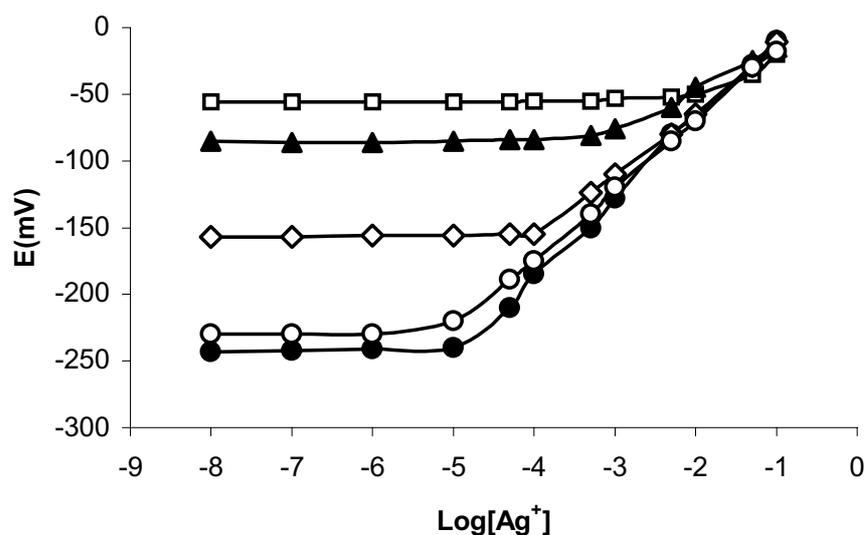


Figure 3. Plots showing E vs Log $[\text{Ag}^+]$ in the presence of Hg^{2+} ions at varying level of interference (\square) 1.0×10^{-2} , (\triangle) 1.0×10^{-3} , (\circ) 1.0×10^{-4} (\diamond) 1.0×10^{-5} and (\bullet) 0.0 M.

The proposed sensor works well under laboratory conditions and can be successfully employed in the potentiometric titrations of Ag^+ solutions with sodium chloride and the resulting titration curve is shown in Fig. 4. The electrode assembly can also be used to determine chloride ion concentration in the tap water by potentiometric titration.

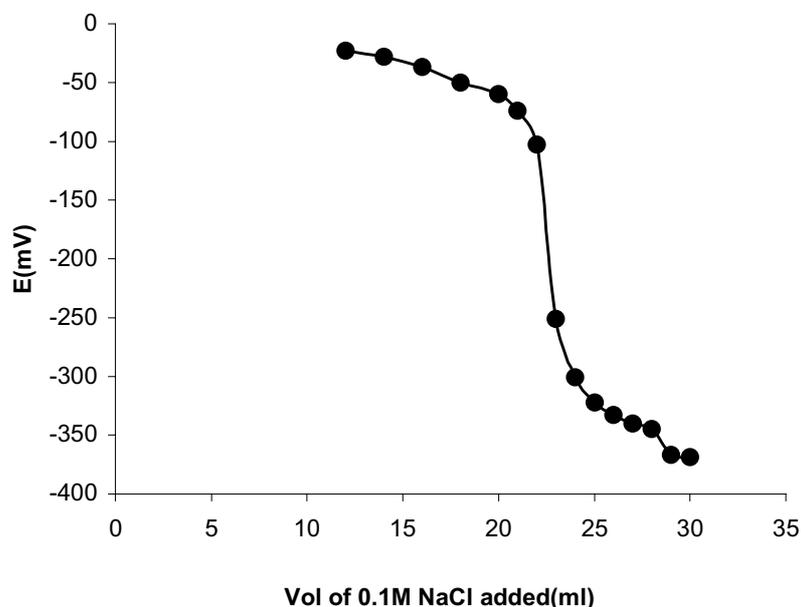


Figure 4. Plot showing the potentiometric titration of $1.0 \times 10^{-1} \text{M}$ of AgNO_3 with $1.0 \times 10^{-1} \text{M}$ NaCl solution.

Table 2. Analysis of water sample spiked with silver(I).

Sample No.	$[\text{Ag}^+]\text{AAS}(\text{ppm})/\text{SD}(\text{n}=4)$	$[\text{Ag}^+]\text{ISE}(\text{ppm})/\text{SD}(\text{n}=4)$
1	40/ 0.3	39.5/ 0.2
2	29/ 0.4	29.1/ 0.3
3	19.5/ 0.3	19.3/ 0.3

The applicability of the sensor is illustrated by measuring the silver(I) ion potentiometrically in Doubly distilled deionised water (DDW) spiked with 40, 30 and 20ppm silver(I). The results obtained were compared with those obtained from atomic absorption spectrometric (AAS) analysis and were found in good agreement (Table 2).

Conclusion

The silver ion selective electrode based on Schiff-base-p-tert-butylcalix[4]arene is comparable and superior in many respects than those reported in literature. The proposed Ag^+ ion selective electrode possess better linear range (1.0×10^{-5} - $1.0 \times 10^{-1} \text{M}$) and detection limit $6.31 \times 10^{-6} \text{M}$ and short response

time. The Ag^+ - ion selective electrode based on Schiff-base-p-tert-butylcalix[4]arene shows good selectivity for Ag^+ ion over other alkali metal ions.

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Sample Availability: Available from the authors.

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