

Polystyrene Based Silver Selective Electrodes

Vinod Kumar Gupta^{1,*}, Milan M. Antonijevic², Sudeshna Chandra¹ and Shiva Agarwal¹

¹ Department of Chemistry, Indian Institute of Technology Roorkee (formerly University of Roorkee), Roorkee- 247667 (India). Tel: 0091-1332-85801. Fax: 0091-1332-73650.

² Department of Chemistry and Chemical Technology, Technical Faculty Bor, University of Belgrade, P.O.Box 50, 19210 Bor, Serbia, Yugoslavia

* Author to whom correspondence should be addressed. E-mail: vinodfcy@iitr.ernet.in

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Abstract: Silver(I) selective sensors have been fabricated from polystyrene matrix membranes containing macrocycle, Me₆(14) diene.2HClO₄ as ionophore. Best performance was exhibited by the membrane having a composition macrocycle : Polystyrene in the ratio 15:1. This membrane worked well over a wide concentration range 5.0×10^{-6} – 1.0×10^{-1} M of Ag⁺ with a near-Nernstian slope of 53.0 ± 1.0 mV per decade of Ag⁺ activity. The response time of the sensor is <15 s and the membrane can be used over a period of four months with good reproducibility. The proposed electrode works well in a wide pH range 2.5-9.0 and demonstrates good discriminating power over a number of mono-, di-, and trivalent cations. The sensor has also been used as an indicator electrode in the potentiometric titration of silver(II) ions against NaCl solution. The sensor can also be used in non-aqueous medium with no significant change in the value of slope or working concentration range for the estimation of Ag⁺ in solution having up to 25% (v/v) non-aqueous fraction.

Keywords: Ion-selective electrodes, Sensors, Ag⁺-selective electrode, Me₆(14) diene.2HClO₄

Introduction

The determination of heavy metal ions in water, soil, and effluents is important in view of their toxic nature above certain concentration level. Elevated environmental level of heavy metals come from a variety of sources. The average crustal abundance of silver has been estimated at 0.07 mg/kg,

ranking it 69th amongst the element. Silver is thus less common than metals such as cadmium and mercury but more abundant than selenium, gold or platinum. Bulk of silver produced in the world is used in photographic materials. Other major uses of silver are in the manufacture of sterling and plated ware, jewellery, coins, medallions, electrical and electronic products such as batteries, contacts and conductors, brazing alloys and solders, catalysts, mirrors and dental and medical supplies. Whereas silver has a relatively low toxicity to humans and other highest life forms, to primitive life forms such as bacteria and viruses, silver is as toxic as the most powerful chemical disinfectant. This gives the metal great potential as disinfectant. Silver nitrate taken orally caused necrosis of the gastrointestinal tract. In the body silver is precipitated by chloride ion or protein. Generalized argyria, localized argyria and argyrosis (argyria of the eye, unless otherwise stated) are the most common effects of chronic exposure to silver. Argyria occurred almost exclusively among silver nitrate makers and in some workers involved in mirror plating, silver mixing, photographic plate making and glass bead silvering, but it can also occur as a result of medicinal applications of silver.

Chemical sensors are increasingly used in the field of environmental analysis as they enjoy a number of advantages over other methods of analysis. The most attractive features of this technique are the speed with which samples can be analyzed, portability of the device, sample non-destruction, cost effectiveness and also large measuring range, often spanning across as many as six decades of ion concentration. Moreover, their fabrication in the laboratory is quite easy and may become commercially available soon after their development. During the last few decades efforts have been made by many researchers in the field of ISEs to develop sufficiently selective sensors for silver.

Unlike many other sulfide-based solid-state electrodes, the Ag₂S electrode has a very high primary ion selectivity and only weakly responds to most transition metal ions. Only Hg²⁺ gives a serious interference [1]. This may be one reason the interest in developing liquid membrane ISEs for Ag⁺ has for a long time been fairly small. However, there have recently been an increasing number of reports on carrier-based Ag⁺ selective electrodes [2]. These include membranes of crown ethers, viz., 1,4-dithia-15-crown-5 and 1,4-dithia-12-crown-4 [3], dodecyl-16-crown-5 [4] and dibenzo-15-crown-4 [5]; calixarene based viz., thioether functionalized calix[4]arene [6]. Recently, Chen et al. [7] reported polymeric membranes based on two calix[4]arene derivatives functionalized by two hydroxy and two benzothiazoly-1-thioethoxy groups. These electrodes gave a Nernstian response in the activity range 5 μM to 100 mM, a detection limit of 0.8 μM and high selectivity towards alkali, alkaline earth and some transition metal ions. A loss in selectivity towards various metal ions is observed when an aromatic carbon in 2-position of benzene-1,3-bis(thioic) acid bis(S-propyl) ester is replaced by nitrogen atom [8]. Chung et al. [9] used sulfur containing podants with diisodecyl adipate in PVC matrix to develop Ag⁺ selective sensor. Katsu and Xu [10] reported organoselenide as a noble ionophore for a silver selective membrane electrode. It gave a near-Nernstian response from 0.1 μM to 0.01 M with a slope of 52 mV per decade of activity. Higher activities of silver ions are obtained with the selenides compounds than with the corresponding sulfides.

Taking into consideration all the above facts, Me₆(14) diene.2HClO₄ has been studied as an electroactive phase in polystyrene matrix for the fabrication of Ag⁺-selective electrode and the results are presented in this paper. The present electrode shows good selectivity over other cations and is superior to the existing electrodes in some aspects.

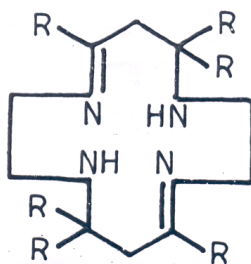
Experimental

Reagents

All reagents used in the investigations were of analytical reagent grade (BDH, UK). Doubly distilled water was used for preparing all aqueous solutions.

Preparation of Me₆(14) diene.2HClO₄

20g of ethylenediamine was added to 500ml of anhydrous acetone followed by drop wise addition of 55.7g of 60% perchloric acid from a dropping funnel with constant stirring of the solution. After addition of the acid, the solution was vigorously stirred and allowed to cool to room temperature. The fine crystalline compound was filtered and washed thoroughly with acetone and dried in vacuum. The ligand was a white crystalline material that can be recrystallised from hot aqueous methanol. This compound shows a strong broad band at 3050 cm⁻¹ in the infrared spectra due to the N-H vibration, and another weaker but broad band at 1530 cm⁻¹ due to NH₂⁺ vibration. The C=N stretching mode occurs as a strong sharp band at 1650 cm⁻¹. The melting point of the ligand is 110°C.



Apparatus

The potential measurements were carried out at $25 \pm 0.1^\circ\text{C}$ on a PH 5652 digital pH meter/millivoltmeter (ECIL, Hyderabad, India) and CVM 301 Century microvoltmeter (Century Instruments, Chandigarh, India). pH measurements were made on a digital pH meter (model PH 5652, ECIL, Hyderabad, India; Glass electrodes as pH electrode and calomel as reference electrode).

Membrane preparation

Heterogeneous membranes were prepared by taking different compositions of the ionophore and polystyrene and the mixture was heated to 80°C under pressure (6500 to 7000 psi) in a die kept in a metallurgical specimen mount press. Membranes were fabricated under optimum conditions of temperature and pressure which were fixed up after a great deal of preliminary investigations. Membranes prepared in this way were quite stable and did not show any dispersion in water or in other electrolyte solutions.

The membranes were subjected to microscopic and electrochemical examination for cracks and homogeneity of the surface and only those which had smooth surface and generated reproducible potentials were chosen for subsequent investigations. Membrane to membrane (and batch to batch) reproducibility was assured by carefully controlling the conditions of fabrication.

Determination of Functional Properties of Polystyrene based Membranes

The prerequisite for understanding the performance of a membrane is its complete physico-chemical characterization which involves the determination of all such parameters which affects its electrochemical properties. These parameters are porosity, electrolyte absorption, water content and swelling. A survey of literature reveals that this particular aspect of membrane phenomena has received less importance.

The first major attempt to establish standard methods for membrane characterization was reported on dried colloidal membrane by Michaelis [11]. Hale et.al. [12] investigated the effect of resin content and the degree of cross linking of the resin on the physical and electrochemical properties of membranes. Gregor [13] and Kawabe [14] studied the characterization of ion-exchange membrane in a number of different exchange states and correlated this information with their structure. Wyllie and Kannan [15] reported that if a rigid plastic such as polystyrene is used the properties of the ion-exchange membrane may be modified. Lakshminarayaniah and Subhramaniyam [16] gave a direct method of measuring the membrane resistance which gives better results as compared to the methods followed by earlier workers. Another important parameter which plays an important role in the functioning of a membrane electrode is the surface study. A detailed methodology of surface study and its effect on the membrane was reported by Marco [17] in 1990.

Porosity

The stability, response time and selectivity of an electrode is influenced by the diameter and the multiplicity of the membrane pores. Mizutani and Nishimura [18] gave the method for the estimation of porosity of the membrane which is calculated from water content data by using the following formula:

$$\Sigma = \text{water content} / A.L.\rho_w$$

Where, A = area of the membrane, L =thickness and ρ_w = Density of water

Electrolyte Absorption

The membrane after attaining equilibrium in 1.0 M NaCl solution was wiped free of adhering electrolyte and then dipped in 20 mL distilled water. It was shaken intermittently and left as such for few hours. The solution was then transferred to a 100 mL measuring flask, The whole process was repeated 3-4 times and the entire solution was collected in a measuring flask. It was finally made up to the mark by distilled water and the strength was measured conductometrically.

Water Content

Membrane was kept immersed in a solution of 1.0 M concentration of electrolyte. It was then washed several times with distilled water and the adhering liquid was wiped off with blotting paper. Then the membrane was weighed and dried to a constant weight in a vacuum desiccator. The

difference in the two weighings divided by the weight of the wet membrane was taken as the water content.

Swelling

After measuring the thickness of the dried membrane it was immersed into 1.0 M solution of NaCl for 24 hours and again the thickness was measured after wiping with blotting paper. Difference between the thickness of dry and swollen membrane was taken as a measurement of swelling.

Potential Measurements

The membranes were equilibrated for 3 days in 1.0 M Ag^+ solution to generate noiseless and reproducible potentials. The conditions necessary for equilibration i.e., the contact time and concentration of salt solutions of the cation were decided by observing the performance of electrode systems equilibrated for different period of time with solutions of varying concentrations.

The membranes were fixed to one end of a “Pyrex” glass tube with araldite and equilibrated with silver nitrate solution. The glass tube containing 0.1M silver nitrate solution, as the internal solution, was placed in test solutions of different concentrations. Potentials were measured by direct potentiometry at $25 \pm 0.1^\circ\text{C}$ with the help of ceramic junction calomel electrodes and the cell setup was the same as reported earlier [19]. 1.0×10^{-1} M silver nitrate was taken as inner reference solution and saturated calomel electrodes (SCE) were used as reference electrode. All pH adjustments were made with appropriate acid or base.

Results and Discussion

Membrane Characteristics

Functional properties of polystyrene based membrane no.3 of macrocycle $\text{Me}_6(14)\text{diene} \cdot 2\text{HClO}_4$ are given in Table 1. Potential studies on the membrane sensors were carried out with the varying Ag^+ concentration (1.0×10^{-6} to 1.0×10^{-1} M). Table 2 depicts the results of the working concentration range, slope, and response time of each membrane. The membranes with macrocycle and polystyrene in the ratio 8:1 showed a large response time with less Nernstian potential response and a narrow working concentration range. Though the membranes having macrocycle and polystyrene in the ratio 20:1 and 30:1 (w/w) showed a fast response time (20s) and near- Nernstian slope (40 mV/decade) each, respectively but they exhibited a narrow working concentration range. The membranes with macrocycle and polystyrene in the ratio 12:1 and 15:1 (w/w) showed a near- Nernstian slope with a response time of 20 and 15 s respectively. Membrane sensor no.3 exhibited a rectilinear potential response in the concentration range of $5.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M with a near-Nernstian slope of 53 mV/decade of $[\text{Ag}^+]$. Potentials generated with dummy membranes were insignificant (5-10 mV). As such, the potentials generated in the proposed sensor are ascribed to the uptake of silver ions on the macrocycle. Thus, it can be seen that the membrane no. 3 (**Fig.1a**) gave the best performance with regard to working concentration range, slope and response time. The sensing behavior of the

membranes did not change when the potentials were recorded from lower to higher concentrations or vice versa.

Table 1. Functional properties of polystyrene based membrane of macrocycle Me₆ (14) diene.2 HClO₄.

Membrane No.3	Water content per gram of wet membrane g(H ₂ O)/g(w.mem.);g/g	Porosity	Swelling	Amount of electrolyte absorbed per gram of wet membrane (moles)
Me ₆ (14)diene. 2HClO ₄	0.0254	0.0320	0.204	4.6×10^{-2}

Table 2. Composition of polystyrene based membranes of Me₆(14)diene. 2 HClO₄ and performance characteristics of Ag⁺- selective electrodes based on them.

Membrane No.	Composition in ratio (w/w)		Working concentration range, M	Slope, mV/decade[Ag ⁺]	Response time, s
	Me ₆ (14)diene. 2HClO ₄ (ionophore)	Polystyrene (Binder)			
1	8	1	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	48	30
2	12	1	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	53	20
3	15	1	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	53	15
4	20	1	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	40	20
5	30	1	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	40	20

Reference Solution

In order to observe the effect of reference solution concentration on the functioning of the membrane sensor, measurements with varying concentrations with reference solutions (5.0×10^{-2} and 1.0×10^{-2} M Ag⁺ solutions) were also observed (**Fig 1b**). It was found that the membrane sensor exhibited optimum performance at 1.0×10^{-1} M concentration of Ag⁺ ions as internal solution while at other concentration the magnitude of potential falls and the working concentration range also decreased with decreasing concentration of reference solution. Therefore all subsequent investigations were performed with 1.0×10^{-1} M concentration of Ag⁺ as reference solution.

Response and Lifetime

The static response time (time in which the membrane sensor generates constant potential) of the membrane sensor is observed at various determinand ion concentrations and the same is found to be <15 s at all dilutions. Besides this, the potentials stayed constant for more than 3 min, after which a slow divergence is recorded. Potentials were repeatedly monitored at a fixed concentrations and the standard deviation of twenty identical potential measurements is 0.2 mV. The membrane sensor could be used for four months, at a stretch, without observing any change in response time or slope,

thereafter a slight change in slope and response time is observed and this could be corrected by equilibrating the membrane again with 1.0 M Ag^+ solution for 10 h (lesser time is required in comparison to the initial equilibration). With this treatment the assembly could again be used for two months time and then it was replaced by a fresh membrane.

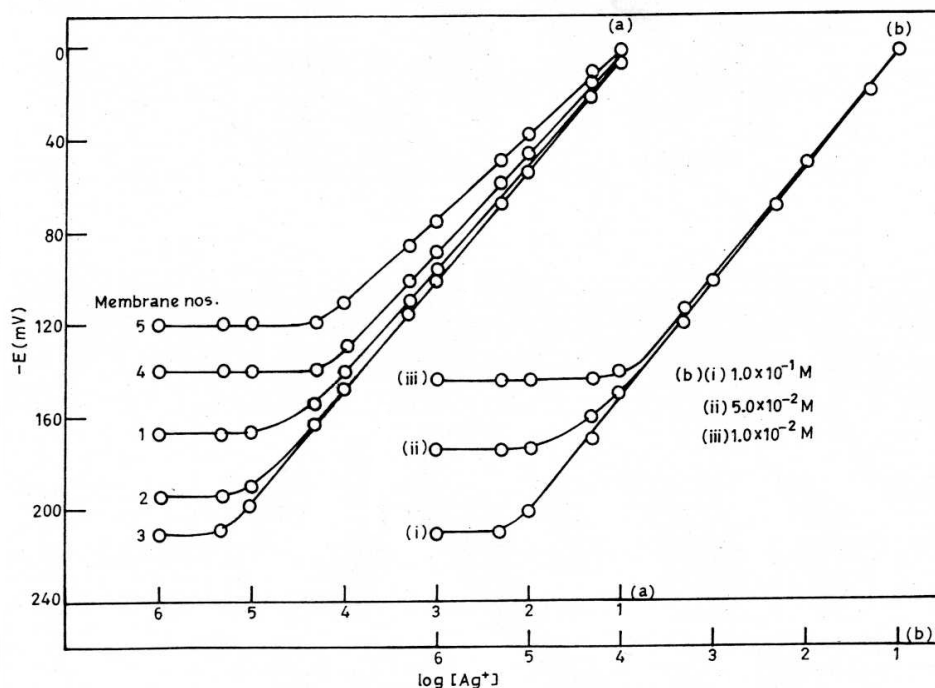


Figure 1. (a) Potential vs $-\log[\text{Ag}^+]$ plots of different compositions. (b) Potential vs $-\log[\text{Ag}^+]$ plots of varying compositions of internal reference solutions.

pH and Solvent Effect

The potentiometric response of the silver electrode was found to be sensitive to pH changes. Thus, the pH dependence of the electrodes was tested by measuring the potential response of solutions containing 1.0×10^{-3} and 1.0×10^{-2} M of silver ions in the pH range 1.0 -11.0. The pH was adjusted using nitric acid or ammonium hydroxide. As seen from **Fig.2**, the potential remained constant from 2.5 to 9.0, which can be taken as the working pH range of the assembly. Beyond this pH range a drift in potentials was observed. The observed drift at higher pH values could be due to the formation of some hydroxy complexes of Ag^+ in solution. At low pH, there could be protonation of the macrocycle in the membrane, which results in loss of their complexing ability with the metal ion.

The performance of the membrane (no. 3) was also investigated in partially non-aqueous medium using methanol-water, ethanol-water, and acetone-water mixtures. The membrane worked satisfactorily in solutions having maximum of 25% (v/v) non-aqueous content as in these mixtures the working concentration range and slope remained unaffected (**Fig.3**). However, above 25% non-aqueous content, slope, and working concentration range was reduced and potentials showed drift. It is worth mentioning that the lifetime of the membranes did not alter in non-aqueous solutions.

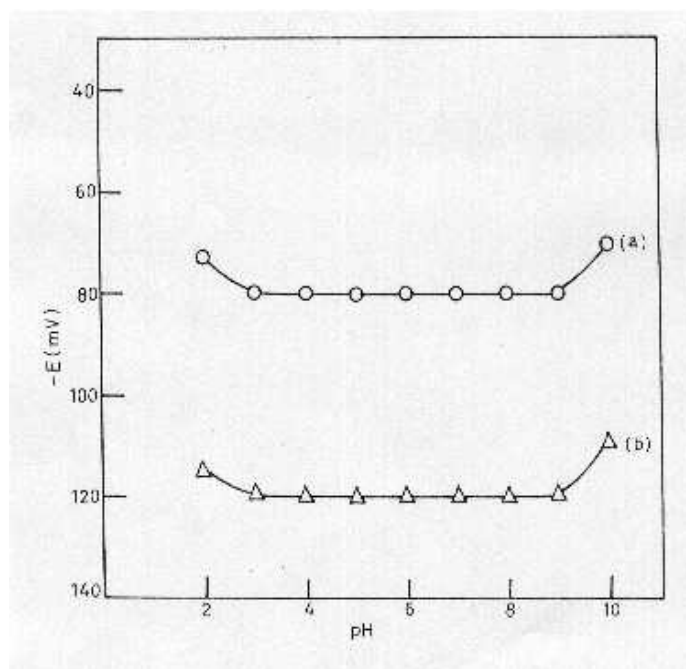


Figure 2. Effect of pH on cell potential; $[Ag^+] = 1.0 \times 10^{-2}$ M (a) and 1.0×10^{-3} M (b).

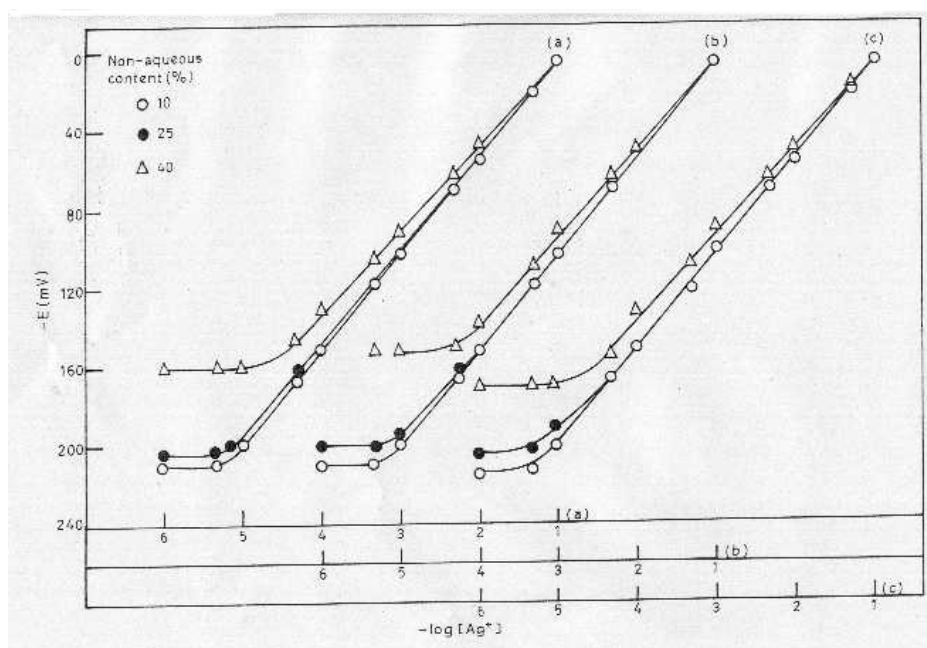


Figure 3. Variation of cell potential with Ag^+ concentration in (a) ethanol-water (b) methanol-water and (c) acetone-water mixtures.

Potentiometric Selectivity

The selectivity coefficients ($K_{A,B}^{Pot}$) were evaluated by modified form of the fixed interference method [16] as suggested by Sa'ez de Viteri and Diamond at 1.0×10^{-2} M interfering ion concentration and varying concentration of Ag^+ solution (Table 3). The selectivity pattern indicates sufficiently low ($\sim 10^{-3}$) values for monovalent cations and quite low ($\sim 10^{-4}$) for bivalent and trivalent ions. As such,

these cations are not expected to interfere even at this higher concentration level (1.0×10^{-2} M) of the interfering ions. Heavy metals such as Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+} (normal interferents) also do not disturb the functioning of the membrane sensor at all.

Table 3. The selectivity coefficient values ($K_{\text{Ag}^+, \text{B}}^{\text{Pot}}$) for Ag^+ selective sensor as calculated by fixed interference method

Interfering ion (B)	Selectivity coefficients by Fixed interference method
NH_4^+	4.46×10^{-3}
Na^+	3.16×10^{-3}
K^+	4.46×10^{-3}
Li^+	5.0×10^{-3}
Mg^{2+}	5.0×10^{-4}
Ca^{2+}	3.54×10^{-4}
Sr^{2+}	3.54×10^{-4}
Ba^{2+}	5.0×10^{-4}
Cu^{2+}	3.54×10^{-4}
Cd^{2+}	2.52×10^{-4}
Co^{2+}	3.54×10^{-4}
Pb^{2+}	3.16×10^{-4}
Hg^{2+}	4.46×10^{-4}
Ni^{2+}	3.54×10^{-4}
Al^{3+}	1.16×10^{-4}
Cr^{3+}	2.32×10^{-4}
Fe^{3+}	1.32×10^{-4}

Analytical Application

The practical applicability of the electrode was tested by using it as an indicator electrode to determine the end point in the potentiometric titration of Ag^+ with NaCl solution. 20 mL of 1.0×10^{-3} Ag^+ solution was titrated against 4.0 mL of 1.0×10^{-3} M NaCl solution. The potential data are plotted against the volume of NaCl (**Fig. 4**). Although the changes observed in potentials are not large, the end point is quite sharp and a perfect stoichiometry is observed. The removal of silver ions results in a decrease in membrane potentials and beyond the end point the potentials almost stay constant and the change is also nominal.

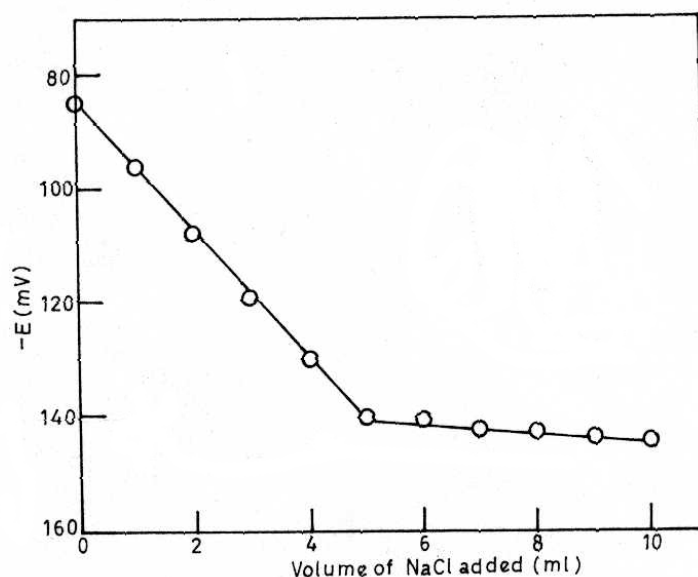


Figure 4. Plot of potentiometric titration of 20 mL of 1.0×10^{-3} M Ag^+ against 4.0×10^{-3} M NaCl solution.

Conclusion

The polystyrene based membrane incorporating $\text{Me}_6(14)$ diene. 2HClO_4 as an ionophore, could be used to determine Ag^+ in the concentration range 5.0×10^{-6} - 1.0×10^{-1} M with a slope of 53.0 mV/decade of activity. The sensor works in a wide pH range 2.5-9.0 with a response time of 15 s. The selectivity of the electrode towards Ag^+ is quite good over other cations and the lifetime of the assembly is 4 months in aqueous and non-aqueous medium also. In addition, the membrane sensor can be used as an indicator electrode in potentiometric titration involving silver(I) ions against NaCl.

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References

1. Umezawa, Y. *CRC Handbook of Ion Selective Electrodes: Selectivity Coefficients*. CRC Press: Boca Raton, Ann Arbor, Boston, (1990).
2. Casabo, J.; Teixidor, F.; Escriche, L.; Vinas, C.; Perez- Jimenez, C. *Adv. Mater.* **1995**, *7*, 238 .
3. Lai, M. T.; Shia, J. S. *Analyst.* **1986**, *111*, 891.
4. Oue, M.; Kimura, K.; Akama, K.; Tanaka, M.; Shono, T. *Chem. Lett.* **1988**, *3*, 409.
5. Xi, Z.; Li, J.; Yu, L.; Zhang, D.; Yang, J.; Luo, S.; Wu, B.; Cun, L. *Huaxue Xuebao* **1986**, *44*, 951.

6. Malinowska, E.; Brazozka, Z.; Kasiura, K.; Egberink, R.J.M.; Reinhoudt, D.N. *Anal. Chi. Acta.* **1994**, *298*, 245.
7. Chen, L.X.; Zeng, X.S.; He, X.M.; Zhang, Z.Z. *Frensenius' J. Anal. Chem.* **2000**, *367*, 535.
8. Bates, M.; Cardwell, T.J.; Cattrall, R.W.; Deady, L.W.; Gregorio, C. G. *Talanta* **1995**, *42*, 999.
9. Chung, S.; Kim, W.; Park, S. B.; Kim, O.Y.; Lee, S. S. *Talanta* **1997**, *44*, 1087.
10. Katsu, T.; Xu, D. H. *Anal. Lett.* **1998**, *31*, 1979.
11. Michaelis, L. *Proc. Intern. Congr. Plant Sci. Iltaco* **1929**, *2*, 1139.
12. Hale, D.K.; McCanley, M.J. *Trans. Faraday. Soc.* **1961**, *57*, 135.
13. Gregor, H.P.; Jacobson, H.; Shir, R. C. *J. Phy. Chem.* **1957**, *61*, 141.
14. Kawabe, M.; Tanagita, M.; Shinohara, M.; Takamatsu, T. *Bull. Chem. Soc. Jpn.* **1962**, *21*, 157.
15. Wyllie, M. R. J.; Kannan, S. L. *J. Phy. Chem.* **1954**, *58*, 73.
16. Lakshminarayanan, N.; Subrahmanayam, V. *J. Phy. Chem.* **1968**, *72*, 4314.
17. Marco, R.D.; Cattrall, R.W.; Leisengang, J. *Anal. Chem.* **1990**, *62*, 2339.
18. Mizutani, V.; Nishimura, M. *J. Appl. Polymer Sci.* **1970**, *14*, 1847.
19. Srivastava, S. K.; Gupta, V. K.; Dwivedi, M. K.; Jain, S. *Anal. Proc.* **1995**, *32*, 21.

Sample Availability: Available from the authors.

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