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Notes

Methacryloyloxycalix[4]arene based ion imprinted polymer as Ag(I) potentiometric sensor

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A new potentiometric sensor for the rapid, easy and cheap determination of Ag(I) ions is proposed. This sensor has been prepared via suspension polymerization using ethylene glycol dimethacrylic acid (EDMA) as cross-linker, 2, 2-azobisisobutyronitrile (AIBN) as initiator and methacryloyloxycalix[4]arene as the monomer. The ion imprinted polymer-based Ag(I) memory sensor has been prepared by dispersing Ag(I) imprinted polymer throughout the DBP plasticizer and embedding in PVC. The sensor responds to Ag(I) in the pH range of 2.0–8.0 with a working range of 1.0×10^{-3} – 1.0×10^{-7} M and detection limit of 1.53×10^{-8} M.

Keywords: Sensors, Potentiometric sensors, Ion-selective electrodes, Ion imprinted polymers, Silver imprinted polymers

The rapid determination of Ag^+ ions is critically important due to its importance in the photographic and imaging industry, dental and medical products, electrical and electronic equipment and products such as jewelry, coins, and mirrors[1,2]. Potentiometric detection via potentiometric sensor is a simple method, with advantages such as rapid response, easy preparation, applicability to colored and turbid solutions and low cost[3,4]. However, the detection limit of potentiometric sensors based on PVC is usually close to 10^{-6} M and is limited by the leakage of primary ions from the polymeric membrane[5-9]. Decreasing the detection limits of a potentiometric sensor was reported to decrease the selectivity as well[10]. Molecular imprinted polymer (MIP)-based ion-selective electrodes are new approaches which are intended to have improved performance[11-18].

Molecular imprinting is a method of introducing molecular recognition sites into a polymeric material. In other words, molecular memory, which involves both capturing the shape of a target molecule and aligning the functional moieties that interact with it, is incorporated into a polymeric material during its formation for the recognition or separation of the target[19-28].

Imprinted polymers are biomimetic materials that sensitively and selectively detect an analyte. They are inexpensive to produce and can be stored for long periods of time in dry conditions and at room temperature. Ion-imprinted polymers (IIPs) are similar to MIPs, but they recognize metal ions after imprinting.

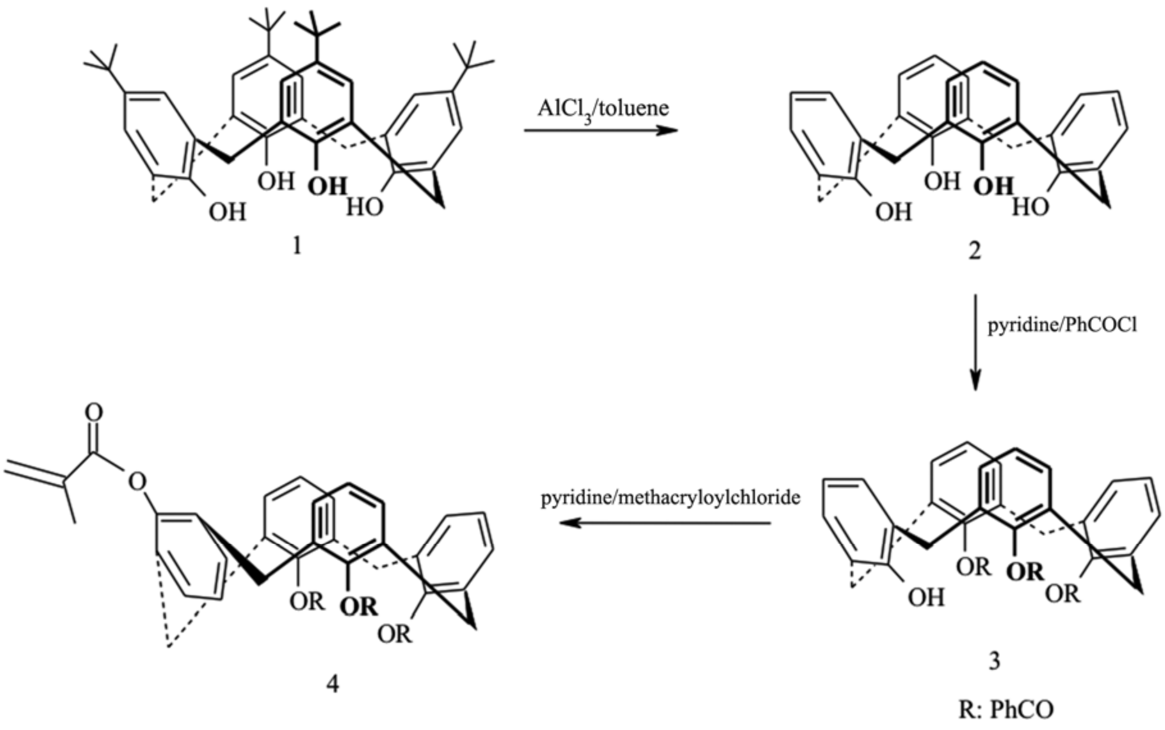
Calixarenes, cyclic oligomers of phenol-formaldehyde condensates, have been taken as receptors to recognize a wide variety of ions and guest molecules. Derivatives containing a wide range of functional groups have been synthesized and shown to exhibit different degrees of receptor ionophoric activity[29]. Only a few studies have reported that calixarene derivatives have been used for silver selective electrodes[30–32].

Herein, the IIP-based Ag(I) potentiometric simple sensor was prepared for the determination of Ag(I) ions in aqueous solution. In this study, it has been used for both the molecular memory of molecular imprinting technique and molecular-binding properties of calixarenes. This sensor was synthesized using methacryloyloxycalix[4]arene functional monomer cross-linked with EDMA and Ag(I) as the template. The silver ion memories having sensing materials were dispersed in a PVC matrix plasticized with DBP and the sensor performance was evaluated in the steady state.

Experimental

DBP, high relative molecular weight PVC, 2,2-azo-bisisobutyronitrile (AIBN) and EDMA were obtained from Aldrich Chemical (USA). HNO_3, NaOH and $AgNO_3$ were purchased from Merck (Darmstadt, Germany). A Mettler Toledo Seven Multi pH-ion meter was used at 25.0 ± 0.1 °C to measure the pH values and ion concentrations. FTIR spectroscopy (FTIR 100 series, Perkin Elmer, USA) over the range from 4000–400 cm^{-1} was used for the characterization of sorbent.

25,26,27-Tribenzoyloxy-28-methacryloyloxycalix[4]-arene (**4**) was synthesized as given in Scheme 1. Compound **3** (1.472 g, 2.0 mmol) was dissolved in



Synthesis of 25,26,27-tribenzoyloxy-28-methacryloylcalix[4]arene

Scheme 1

100 mL of dry pyridine and cooled to 0 °C. Then, methacryloylchloride (0.209 g, 2.0 mmol) was added to the above solution dropwise over 4 h at room temperature with magnetic stirring and the solution was poured into ice water. The resultant solid was filtered, washed with cold water and dried. It was then recrystallized in chloroform-methanol solution (Yield of **4**: 72%, m.pt.: decomp. 265 °C). IR (KBr) υ (cm^{-1}): 3028 cm^{-1} (aromatic C-H), 2978 cm^{-1} (aliphatic C-H), 1722 cm^{-1}, 1620 cm^{-1} (C=O), 1095 cm^{-1} (C-O). ^{1}H-NMR ($CDCl_3$-d_6, 25 °C) δ (ppm): 2.90 (3H, s, vinyl-CH_3), 3.40–3.55 and 3.87–3.92 (8H, d, Ar-CH_2-Ar), 5.2 and 5.5 (2H, s, =CH_2) 7.30–8.16 (27H, m, Ar-H).

Compounds **1**, **2**, and **3** were synthesized according to previously published methods[33-35] and compound **4** was synthesized according to Scheme 1.

The Ag(I)-imprinted polymer was prepared via a dispersion polymerization technique. Methacryloylcalix[4]arene (1.0 mmol) was dissolved in ethyl alcohol (15 mL). $AgNO_3$·(1.0 mmol) was added slowly to the mixture. The solvent was then removed using a rotovap to yield a solid. The polymerization of the poly(EDMA-methacryloyl-calix[4]arene/Ag(I)) microbeads was as follows: The methacryloylcalix[4]arene/Ag(I) was dissolved in ethyl alcohol (4.0 mL). The above solution was added to EDMA/toluene mixture (8.0 mL/12.0 mL) and then 0.06 g AIBN was added. The polymerization was performed at 90 °C over 3 h in a thermostatic water bath. After polymerizing, the poly(EDMA– methacryloylcalix[4]arene/Ag(I)) beads were filtered. The resultant microbeads were cleaned with a 60/40 *v/v* mixture of methanol/water. The polymers were treated with EDTA at pH 12 to remove the Ag(I) ions. IR (KBr) υ (cm^{-1}): 3163 cm^{-1} (aromatic C-H), 2935-2868 cm^{-1} (aliphatic C-H), 1199 cm^{-1}, (C=O), 1095 cm^{-1} (C-O), 752 cm^{-1} (Ag-O) .

Non-imprinted microbeads (NIP) were prepared in the same way using methacryloylcalix[4]arene and EDMA. The sensor was modified according to the general procedure[36]. For the preparation of ion imprinting-based potentiometric sensor, PVC, THF, DBP and IIP were used. The mixture was homogenized and then poured into a glass tube. The tube was then filled with a 10^{-3} M Ag(I) internal filling solution. A blank membrane was also prepared in a similar manner but without the IIP or NIP particles.

The potentiometric sensors were conditioned in 10^{-3} M Ag(I) solution for 3 days. Then, the membrane was reacted with EDTA at pH 12 to remove excess Ag(I) ions. The measurements were performed using a saturated Ag/AgCl electrode.

The potentials of the test solutions were measured at Ag(I) concentrations ranging from 1.0×10^{-9} to 1×10^{-2} M. The sensor via IIP response was investigated by measuring the EMF of the cell: Cu wire|1 mM KCl+1 mM Ag(I) (internal solution)|(MIP) membrane||test solution|Ag–AgCl, KCl (salt). The EMF was plotted as a function of logarithm of Ag(I) concentration.

The IIP beads (approximately 0.1 g) were thoroughly mixed with KBr (0.1 g, IR grade, Merck, Germany) and pressed into pellets for FTIR characterization.

Results and discussion

As shown in Fig. 1, the sensing potential of potentiometric sensor increased with increasing Ag(I) concentration. Ag(I) imprinted microbeads that used ligands, i.e., IIPs, were prepared via Ag (I) imprinting through metal-ion coordination interactions and have attractive binding sites and high surface area[36] which provides greater access to the active sites that have size and shape memories for Ag(I) ions . The sensing potential of the IIP sensors was higher than that of the NIP and control sensors. These results clearly indicate an 'imprinting effect'.

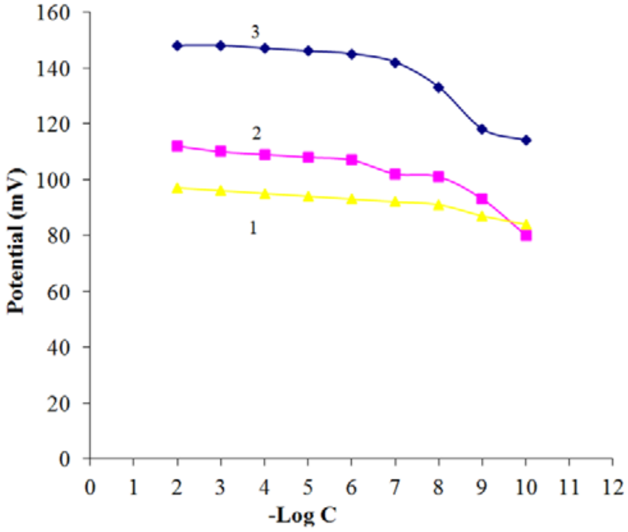


Fig. 1 — The effect of imprinting on a potentiometric sensor. [1, Control; 2, Non-Imprinted sensor; 3, Ag(I)-Imprinted sensor. pH: 6.0; temp.: 25 °C].

The effect of the test solution pH on the IIP-based Ag(I) sensor performance was investigated by varying the pH from 2.0–8.0. As seen in Fig. 2, the maximum response was obtained at pH 6.0, above which there was a decrease in the potential.

It is well known that response time is one of the most important factors for evaluating a modified electrode. The response time of a sensor is defined as the time required for a limiting potential to be reached after adding an analyte to the sample solution. In practice, the response time was recorded by increasing the Ag(I) ion concentration of the solution from 1.0×10^{-6} M to 1.0×10^{-4} M and measuring the corresponding stabilized potentials. The results, depicted in Fig. 3, clearly indicated that equilibrium was rapidly reached (3 min). The potentiometric sensor reached equilibrium in 3 minutes without being affected by the concentration difference (1.0×10^{-6} M to 1.0×10^{-4} M).

Storing and conditioning the sensors in 1×10^{-3} M Ag(I) solution provided detection limits, response times, linear ranges and calibration slopes that were reproducible to within ±3% of their original values over at least a 5-month period. This is because the high molecular weight of the polymeric sensing materials increases its lipophilicity.

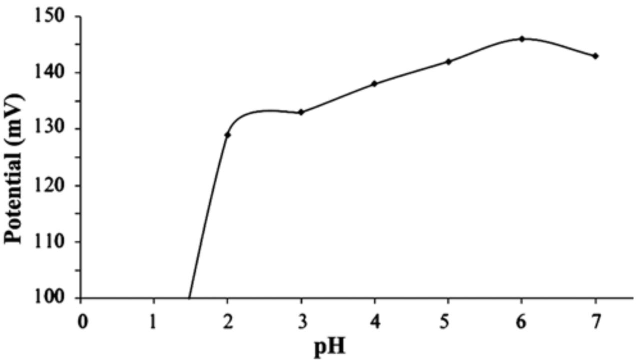


Fig. 2 — The effect of pH on the MIP-based Ag(I) sensors. [Conc.: 10^{-5} M; temp.: 25 °C]

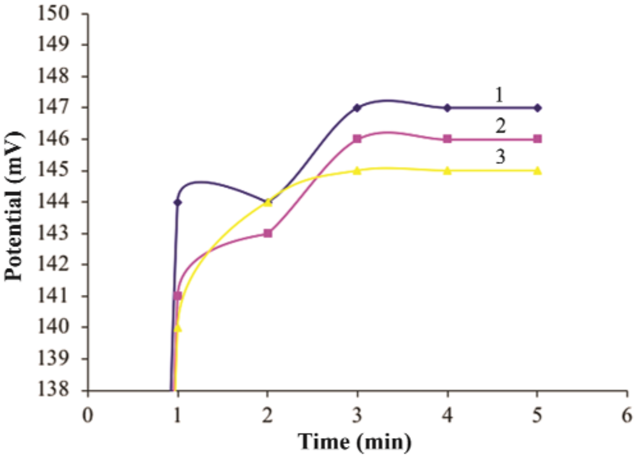


Fig. 3 — Response time for the MIP-based Ag(I) potentiometric sensor. [Ag(I): 1, 10^{-6} M ; 2, 10^{-5} M; 3, 10^{-4} M. pH: 6.0; temp.: 25 °C].

Sensitivity and detection limit for the sensor was investigated with Ag(I) solutions of different concentration. After attainment of equilibrium, IIP based Ag(I) potentiometric sensor was recovered by sequential washes with 10^{-1} M EDTA solution and deionized water until the potential of the sensor reached a steady value. The results showed that the potential responses of IIP based Ag(I) potentiometric sensor increased with increasing Ag(I) concentration, over a linear working range of 1.0×10^{-7} to 1.0×10^{-3} M. The limit of detection in the present study was 1.53×10^{-8} M, which is lower than that reported in earlier studies[30-32] (Supplementary data, Table S1).

Susheel *et al.*[37] studied the potentiometric performance of 2-aminothiophenol-based dipodal ionophore as a silver sensing material and reported a detection limit of 6×10^{-5} M. Kumar *et al.*[38] investigated a highly selective transport using ion-selective electrodes for Ag(I) ions under two different conditions and found that the detection limit of these electrodes was 1×10^{-6} M.

The selectivity coefficients for Ag(I) ions were studied by the matched potential method (MPM) recommended by IUPAC[39]. According to MPM, the selectivity coefficient is given by the ratio of the concentration of resulting primary ion to the concentration of the interfering ion . The results of the matched potential method (MPM) study are summarized in Table 1. The selectivity coefficient obtained for the IIP-based Ag(I) potentiometric sensor was compared to previously reported values (see Table 1). The selectivity of the proposed IIP-based Ag(I) potentiometric sensor was excellent according to recent studies, which can be attributed to the size and shape of the silver ion imprinted polymer binding sites being specific to Ag(I).

Table 1 — Comparison of the selectivity coefficients for the MIP-based Ag(I) potentiometric sensor. [pH: 6.0; temp.: 25 °C]

Ion	Selectivity coefficient ($-\log K^{pot}_{Ag+,B}$)		
	This work	Ref. 38	Ref. 37
K^+	1.65	-	2.1
NH_4^+	1.05	-	-
Na^+	0.51	0.6	2.1
Ca^{2+}	1.58	2	2.3
Mg^{2+}	0.31	1.2	2.1
Cu^{2+}	1.73	2	1.7
Zn^{2+}	1.1	1.2	2.6

Two important criteria beyond sensitivity and selectivity for any sensing device are the stability and reusability. The reproducibility of the Ag(I)-imprinted sensor was studied by continuously measuring the response signal of a single sensor (14 times). The IIP-based Ag(I) potentiometric sensor was recovered after reaching equilibrium following each Ag(I) treatment by sequentially washing with a 10^{-1} M EDTA solution at pH 12 and deionized water until the sensor potential stabilized. The IIP-based Ag(I) potentiometric sensor could be used repeatedly without a significant decrease in the response. The IIP-based Ag(I) potentiometric sensor developed above was stable for 5 months and could be reused over 110 times without loss of its sensing ability.

The present work demonstrates the fabrication of the IIP-based Ag(I) potentiometric sensor. This strategy involves embedding Ag(I)-imprinted particles dispersed in DBP into a PVC and then casting it as a membrane after dissolving in THF. These sensors possessed a detection limit of 1.53×10^{-8} M, linear response across the range of 1.0×10^{-3} L^{-1} – 1.0×10^{-7} M, rapid response time (3 min) and long operational lifetime. The selectivity and detection limit of the proposed IIP-based Ag(I) potentiometric sensor was superior to several recent sensors. Overall, this technique is simple, precise and accurate while being inexpensive with regards to the reagents consumed and equipment required.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(03)444-448_SupplData.pdf.

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