

A New PVC-Membrane Electrode Based on a Thia-Substituted Macrocylic Diamide for Selective Potentiometric Determination of Silver Ion

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A new PVC-membrane electrode for Ag⁺ ion based on a thia-substituted macrocylic diamide has been prepared. The electrode exhibited a Nernstian response for Ag⁺ over a wide concentration range (1.7×10^{-6} - 1.0×10^{-1} M). It has a response time <15 s and can be used for at least 3 months without divergence. The proposed membrane sensor revealed good selectivities for Ag⁺ over a variety of metal ions and can be used in a pH range 3.0-7.5. It has been used successfully for direct determination of Ag⁺ in different real samples and, as an indicator electrode, in the titration of silver ion.

Keywords : Ag⁺-selective electrode, PVC-membrane, Macrocylic diamide, Potentiometry.

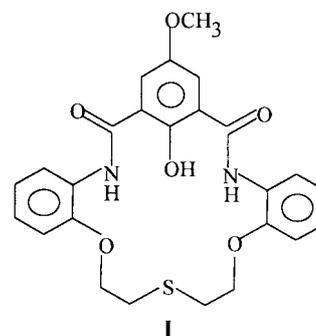
Introduction

The toxicity, bio-availability and accumulation to particulate matter and sediment of heavy metal ions are well known to be strongly dependent on their activity rather than their total concentration.^{1,2} Thus, the activity measurements of these cations in aqueous systems is of vital importance from an environmental point of view. Ionophore-based PVC-membrane electrodes are well-established analytical tools routinely used for the measurement of the activity of a wide variety of different ions selectively and directly in complex biological and environmental samples.¹⁻⁶ The key ingredient of such plasticized PVC membranes is the incorporated ionophore, which defines the selectivity of the electrodes via selective complex formation with the cation of interest.

Due to their specific selectivity and extraction efficiency, crown ethers have been widely used as suitable neutral ionophores for constructing membrane-selective electrodes for alkali and alkaline earth cations.^{1,4-7} The substitution of some oxygen atoms of crown ethers by nitrogen and/or sulfur atoms will make them ideal candidates for use as ion carriers in the preparation of transition and heavy metal ion-selective electrodes,⁷⁻¹³ where facile complexation and de-complexation of the ionophore is of vital importance.

During the past decade, increasing interest has been directed toward the design and synthesis of new functionalized macrocylic ligands for specific analytical applications, including the construction of ion-selective electrodes.¹⁴⁻¹⁶ The in-built configuration rigidity induced by *N*-substituted amides in the periphery of benzomacrocycles invokes a preorganization leading to ionophoric selectivity.¹⁷⁻²¹ A number of macrocylic diamides, prepared from salicylaldehyde derivatives and some appropriate diamine compounds, have been shown to possess wide applications in selective metal ion extraction.²²⁻²⁵ Moreover, the use of some benzo-substituted macrocycles as ion carrier in preparation of PVC-based Li⁺ and Pb²⁺ ion-selective electrodes has already been reported in the literature.^{26,27}

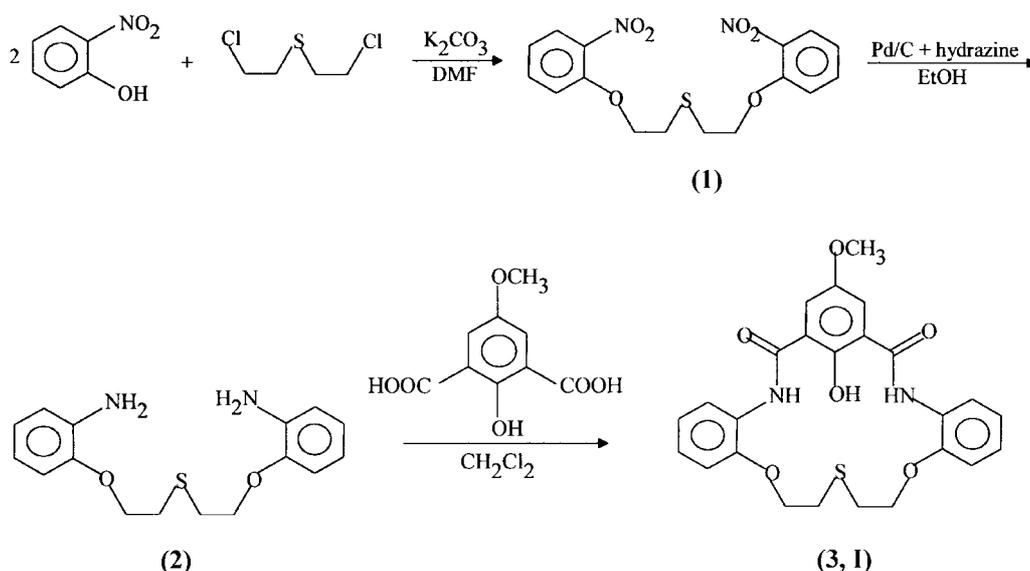
Recently, we have used some new macrocylic diamide derivatives, synthesized in our laboratories, as suitable neutral ionophores in the construction of PVC-membrane electrodes for Sr²⁺,²⁸ Zn²⁺,²⁹ Cu²⁺³⁰ and Hg²⁺ ions.³¹ In the present paper, we report the first synthesis of 3,5-diaza-4,5;13,14-dibenzo-21-hydroxy-19-methoxy-9-thia-6,12-dioxabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (**I**) and its successful use as an excellent neutral ionophore for the preparation of a highly selective and stable plasticized PVC-membrane electrodes for the potentiometric determination of Ag⁺ ion over a wide concentration range.



Experimental Section

Reagents. Reagent grade dibutyl sebacate (DBS), dioctyl phthalate (DOP), benzyl acetate (BA), *o*-nitrophenyl octyl ether (NPOE), potassium tetrakis(4-chlorophenyl) borate (KTCPB), tetrahydrofuran (THF) and high relative molecular weight PVC (all from Fluka) were used as received. The nitrate salts of all cations used (all from Merck) were of the highest purity available and used without further purification except for vacuum drying over P₂O₅. All other chemicals used were obtained from either Fluka or Merck and were used as received. Doubly distilled deionized water was used throughout.

Synthesis of Ionophore. 3,5-Diaza-4,5;13,14-dibenzo-



21-hydroxy-19-methoxy-9-thia-6,12-dioxabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (**I, 3**) was synthesized in three steps as follows.

1,5-Bis(o-nitrophenoxy)-3-thiapentane (1): *o*-Nitrophenol (0.1 mol) and potassium carbonate (14 g) were mixed and stirred in DMF (100 mL) for 2 h. Thiodiethylene glycol dichloride (0.05 mol) was added dropwise during 4 h, and the mixture was refluxed for 3 days. After cooling, the mixture was poured into ice, and the resulting precipitate was filtered off. The precipitate was washed with distilled water, and the crude product was purified by column chromatography, using petroleum ether (bp = 60-80 °C)/ethyl acetate as eluent to give compound (**1**) as a pale yellow solid with 63% yield, mp = 24.25 °C. The structure of compound (**1**) was confirmed by ¹H NMR and IR spectroscopy.

1,5-Bis(o-aminophenoxy)-3-thiapentane (2): In a two-necked round-bottomed flask (250 mL) equipped with a reflux condenser and a dropping funnel, a suspension of compound (**1**) (0.012 mol), palladium on carbon 5% (0.4 g) and absolute ethanol was prepared. The mixture was warmed and, while being stirred magnetically, hydrazine hydrate 80% (10 mL) was added dropwise over 1.5 h through the dropping funnel, while maintaining the temperature at about 50 °C. The reaction mixture was refluxed for 2 h and filtered while hot. On cooling, the filtrate gave the diamino compound (**2**), after vacuum drying, as white crystals (mp = 28-29 °C) with 89% yield. The structure of compound (**2**) was confirmed by ¹H NMR and IR spectroscopy.

3,5-Diaza-4,5;13,14-dibenzo-21-hydroxy-19-methoxy-9-thia-6,12-dioxabicyclo [15.3.1]heneicosa-1(21),17,19-triene-2,16-dione (I, 3): A solution of compound (**2**) (2 mmol) in dry CH₂Cl₂ (50 mL) was added quickly to a vigorously stirring solution of 4-methoxyphenol-2,6-dicarboxylic acid dichloride (2 mmol) in dry CH₂Cl₂ (50 mL) at room temperature. The reaction mixture was stirred for a further 20 min and washed with bicarbonate solution (2 × 50 mL) and water (2 × 50 mL). The organic layer was dried over magnesium sulfate, and the solvent was evaporated to give an oily

product. The crude was purified by column chromatography, using petroleum ether (bp = 60-80 °C)/ethyl acetate as eluent. The pure product was obtained as a red solid; mp = 154-156 °C; yield 66%, IR (KBr, cm⁻¹): 749.2 (s), 1051.5 (m), 1253.0 (s), 1454.5 (m), 1535.1 (m), 1602.2 (s), 1662.7 (s), 2918.7 (s), 3301.5 (s); ¹H NMR (CDCl₃, ppm): 3.31 (t, 4H, *J* = 6.30 Hz), 3.86 (s, 3H), 4.37 (t, 4H, *J* = 6.30 Hz), 7.03-7.06 (m, 6H), 8.08 (s, 2H), 8.65 (m, 4H), 11.70 (s, 1H); MS (*m/z*, %): 466 (*M*⁺ + 1 - NH, 4.1), 465 (*M*⁺ - NH, 30.9), 464 (*M*⁺ + 1 - OH, base peak), 357 (11.3), 356 (91.8), 328 (4.1), 296 (26.8), 270 (60.8), 268 (32.0), 241 (16.5), 226 (39.2), 179 (21.6), 178 (17.5), 163 (50.5), 152 (27.8), 135 (4.1), 120 (32.0), 109 (17.5), 93 (11.3), 87 (88.7), 77 (15.5); UV, (CHCl₃, nm): 249.5, 378.0, 510.5; Elemental Analysis, Calculated for C₂₅H₂₄N₂O₆S: C, 62.49; H, 5.03; N, 5.83; S, 6.67. Found: C, 62.17; H, 5.38; N, 5.52; S, 6.92.

Electrode Preparation. The PVC-membranes were prepared by thorough mixing of 56.2 mg plasticizer NPOE, 32 mg powdered PVC, 2 mg ionophore I and 0.8 mg additive KTCPB in 3 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm o.d. on top) was dipped into the mixture for about 10 s so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 1 h, after which the tube was filled with internal filling solution (1.0 × 10⁻³ M silver nitrate). The electrode was finally conditioned for 20 h by soaking in a 1.0 × 10⁻² M AgNO₃. A silver/silver chloride electrode was used as an internal reference electrode.

Emf Measurements and Apparatus. All emf measurements were carried out by the following assembly:

Ag/AgCl 3M, KCl/internal solution, 1.0 × 10⁻³ M AgNO₃/PVC membrane/test solution/Ag/AgCl, KCl (satd.)

A Metrohm ion analyzer pH/mV meter was used for potential measurements at 25.0 ± 0.1 °C. Activities were calcu-

lated according to the Debye-Hückel procedure.³²

NMR spectra were recorded using a Bruker Advance DPX-250 in pure deuterated solvents with tetramethylsilane as internal standard. IR spectra were obtained on an Impact 400 D Nicolet FTIR spectrometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument at 70 eV. UV-Vis spectra were recorded on a PUB 700 spectrometer.

Determination of Silver from a Developed Radiological Film. A 69-cm² sheet of the film was left in a furnace for 2 h at 700 °C. The residue was dissolved in hot 1 : 1 nitric acid-water and the pH of the resulting solution was adjusted to about 5 by a NaOH solution. Finally, the solution was completely transferred into a 250-mL volumetric flask and diluted to the mark with water. The silver content of the solution as determined by AAS was found to be 5.0×10^{-5} M (equivalent to 196 mg silver per square meter of the film).

Determination of Silver from a Silver-Solder Sample. A 0.324 g of a sample of the silver solder was dissolved in 5 mL of concentrated nitric acid, and the solution was heated until fumes were observed. 5 mL of water was added to the solution after it had been cooled to room temperature, and the solution was again heated until fumes were observed. This treatment was repeated three times to ensure complete dissolution of the sample. The resulting solution was completely transferred into a 100-mL volumetric flask and diluted to the mark with water. Finally, 2 mL of this solution was diluted to 500 mL in a volumetric flask with water. The concentration of Ag⁺, Cu²⁺ and Zn²⁺ ions in the diluted solution was determined with AAS and found to be 6.2×10^{-5} M, 5.5×10^{-5} M and 3.0×10^{-5} M, respectively.

Results and Discussion

Due to the vital importance of silver ion concentration measurements in industrial, pharmaceutical and environmental samples,³³⁻³⁵ there have been recently an increasing number of reports on carrier-based Ag⁺-selective electrodes in the literature.^{7,36-40} Ligands for use as ionophore in an Ag⁺ ion-selective electrode should fulfill the following conditions. They should be selective for Ag⁺ over metal ions, they should have rapid exchange kinetics and should be sufficiently lipophilic to prevent leaching of the ligand into the solutions surrounding the membrane electrode. Our preliminary conductometric studies in DMSO solution revealed that carrier **I** possesses a tendency to form a relatively stable and highly selective complex with Ag⁺ ion, compared with other transition and heavy metal ions. Thus, based on this information and the water insolubility of the ionophore, we decided to use the ligand **I** as a potential ionophore in the preparation of a new PVC-membrane electrode for silver ion.

Optimum membrane ingredients were tested by changing the plasticizer/PVC ratio from 0.5 to 2.5, while keeping the amount of ionophore constant (*i.e.* 2%). The most sensitive, reproducible and stable results were obtained at a plasticizer/PVC ratio of about 2. It is reported that the response

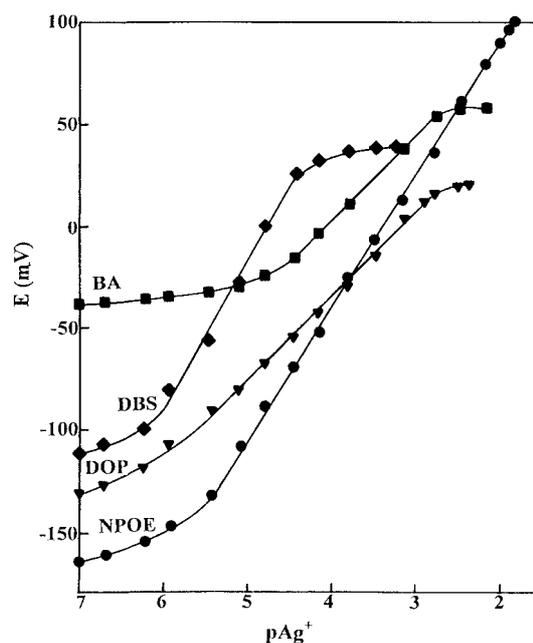


Figure 1. Effect of different plasticizers on the potential response of the Ag⁺ ion-selective electrode.

characteristics of ion-selective electrodes are largely affected by the nature of the plasticizer used.⁴¹⁻⁴⁴ This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ligands.¹⁰ Thus, in the present work we examined DBS, DDP, BA and NPOE as plasticizer and the resulting emf-pAg plots are shown in Figure 1. As is quite obvious from Fig. 1, the use of NPOE results in a Nernstian linear plot over a wide concentration range, whereas in the case of other solvent mediators, the slope of the potentiometric response is much different from the expected Nernstian value of 59.5 mV decade, although at a limited concentration range.

The optimization of the permselectivity of the PVC-membrane electrodes is known to be highly dependent on the incorporation of additional membrane components.⁴⁴ In fact, it has been clearly demonstrated that the presence of the lipophilic negatively charged additives improves the potentiometric behavior of certain cation-selective electrodes not only by reducing the ohmic resistance^{45,46} and improving the response behavior and selectivity,^{47,48} but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane sensor.⁴⁹ Moreover, lipophilic additives may catalyze the exchange kinetics at the sample-membrane interface.⁵⁰ In the present work, we found that the use of 0.8% KTCBP resulted in a Nernstian behavior and improved linearity, selectivity and stability of the electrodes response. Thus, membranes with an optimized PVC : NPOE : I : KTCBP percent ratio of 32:65.2:0.8 were prepared for further studies.

The influence of the concentration of the internal solution on the potential response of the Ag⁺-selective electrode was studied. The Ag⁺ concentration was changed from 1.0×10^{-2}

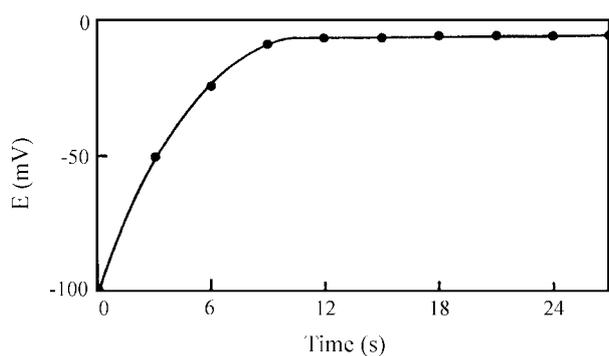


Figure 2. Response-time profile of the Ag^+ ion-selective electrode.

to 1.0×10^{-4} M and an emf vs. $-\log [\text{Ag}^+]$ plot was obtained. It was found that the variation in the concentration of the internal solution did not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting plots. A 1.0×10^{-3} M concentration of silver nitrate was quite appropriate for smooth functioning of the system.

The static response time of the electrode was found to be <15 s over the entire concentration range. A sample emf vs. time plot is shown in Figure 2. This is actually the average time required for the electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of Ag^+ ions, each having a tenfold difference in concentration. The optimum conditioning time for the membrane electrode in a 1.0×10^{-2} M AgNO_3 solution was 20 h, after which it generated stable potentials ion contact with Ag^+ ion solutions. The membrane electrode was used practically for 3 months, at a stretch, without any significant

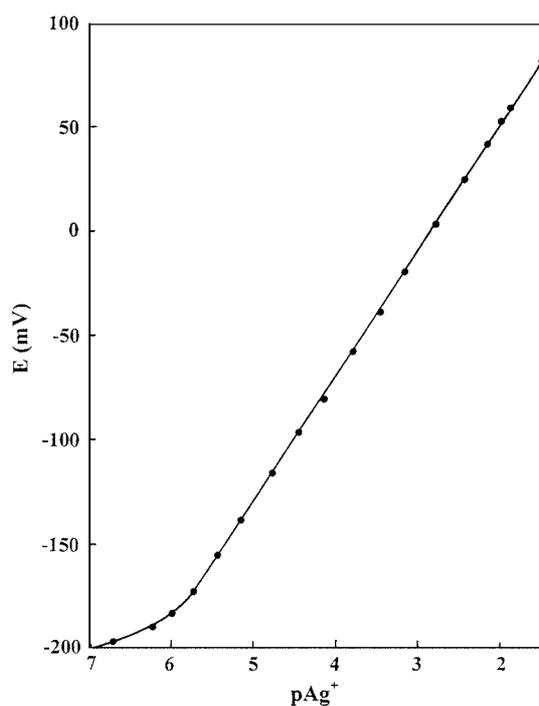


Figure 3. Calibration graph for the proposed Ag^+ ion-selective electrode.

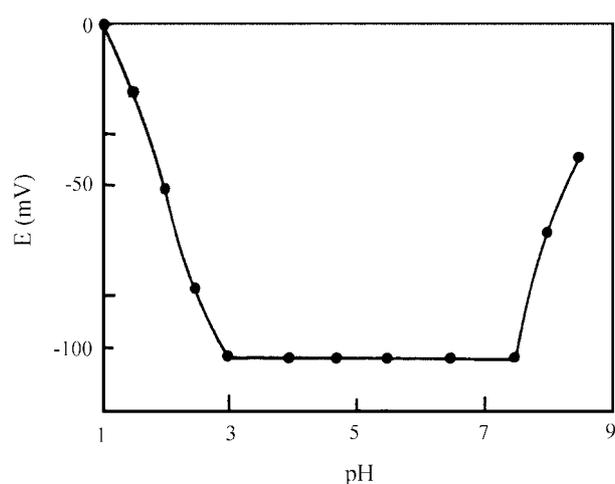


Figure 4. Effect of pH of test solution on the potential response of the Ag^+ ion-selective electrode.

change in response time, slope, or detection limit.

The PVC-membrane electrode prepared and operated under optimal experimental conditions shows a linear response to the activity of Ag^+ ion in the range of 1.7×10^{-6} to 1.0×10^{-1} M (Fig. 3). The slopes of the calibration plots were 60.2 ± 0.7 mV per decade of silver activity change at 25°C . The limit of detection was 7.0×10^{-7} M (0.076 ppm), as determined from the intersection of the two extrapolated segments of the calibration graph. The standard deviation of ten replicate potential measurements was ± 0.5 mV.

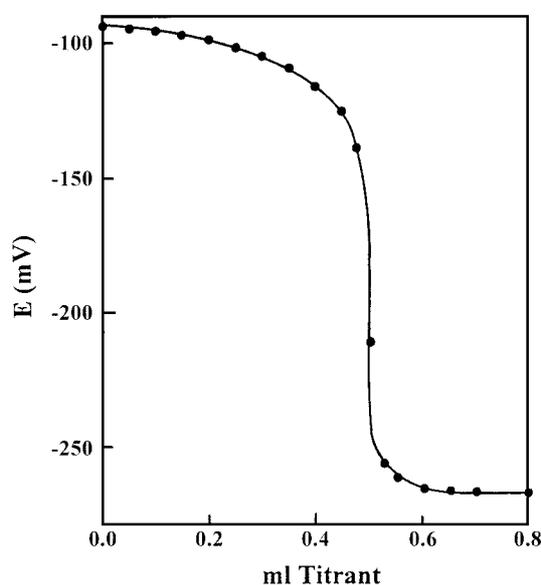
The influence of the pH of the test solution on the potential response of the Ag^+ -selective electrode was tested at a 5.0×10^{-5} M concentration over the pH range 1.0–8.5, (adjusted by either HNO_3 or KOH), and the results are shown in Figure 4. As seen, the potential remained constant from pH 3.0 to 7.5, and the membrane electrode can be suitably used in this range of pH. The observed drift at higher pH values could be due to the interfering effect of the K^+ ion added (as KOH). At low pH, the potentials increased, indicating that the membrane electrode responds to hydrogen ions.

The selectivity behavior is obviously one of the most important characteristics of a membrane electrode, determining whether a reliable measurement in the target sample is possible.^{44,51} To assess the selectivity of the proposed silver ion-selective electrode over other cations, $\text{M}^{\text{n}+}$, the methods of fixed interference (FIM)⁵² and mixed solution (MSM)⁵³ were employed as described in our previous publications.^{12,13,28-31,40} The resulting $K_{\text{Ag},\text{M}}$ values for the proposed Ag^+ ion-selective electrode are summarized in Table 1. As seen, in all cases studied, the selectivity coefficients are in the order of 10^{-3} and smaller, emphasizing the highly selective behavior of the proposed membrane electrode for Ag^+ ion over many other monovalent and divalent cations of vastly different soft-hard character.⁵⁴ Noteworthy is the fact that in most cases indicated in Table 1, the MSM results in more or less lower selectivity coefficient values than the FIM.

The practical utility of the proposed membrane electrode

Table 1. Selectivity coefficients of various interfering ions

M ⁿ⁺	K _{Ag,M} ^{FIM}	K _{Ag,M} ^{MSM}
Co ²⁺	7.9 × 10 ⁻⁵	4.0 × 10 ⁻⁵
Ni ²⁺	1.6 × 10 ⁻⁴	6.3 × 10 ⁻⁵
Cu ²⁺	2.0 × 10 ⁻⁴	6.3 × 10 ⁻⁴
Pb ²⁺	1.6 × 10 ⁻⁴	2.3 × 10 ⁻⁴
Cd ²⁺	1.2 × 10 ⁻⁴	1.0 × 10 ⁻⁴
Hg ²⁺	1.1 × 10 ⁻²	9.0 × 10 ⁻³
Mg ²⁺	1.9 × 10 ⁻⁴	6.3 × 10 ⁻⁵
Ca ²⁺	1.8 × 10 ⁻⁴	7.9 × 10 ⁻⁵
Sr ²⁺	1.1 × 10 ⁻⁴	5.0 × 10 ⁻⁵
Ba ²⁺	3.3 × 10 ⁻⁴	4.0 × 10 ⁻⁵
Na ⁺	7.9 × 10 ⁻³	1.2 × 10 ⁻³
K ⁺	5.0 × 10 ⁻³	7.9 × 10 ⁻⁴
Tl ⁺	5.1 × 10 ⁻³	2.0 × 10 ⁻³

**Figure 5.** Potentiometric titration curve of 50.0 ml of 4.9×10^{-5} M AgNO₃ solution with 5.0×10^{-2} M KI, using the proposed sensor as an indicator electrode.**Table 2.** Silver content of the final solutions of different samples^a

Sample	Proposed ISE	AAS
Silver solder	$(6.3 \pm 0.2) \times 10^{-5}$ M	$(6.2 \pm 0.1) \times 10^{-5}$ M
Radiological film	$(5.1 \pm 0.3) \times 10^{-5}$ M	$(5.0 \pm 0.1) \times 10^{-5}$ M
Photographic developing solution	$(5.3 \pm 0.3) \times 10^{-5}$ M	$(5.5 \pm 0.1) \times 10^{-5}$ M

^aThe results of three replicate measurements.

was tested by its use as an indicator electrode for the titration of 50.0 mL of 4.9×10^{-4} M silver nitrate with a 5.0×10^{-2} M potassium iodide solution, and the resulting titration curve is shown in Figure 5. As seen, the amount of silver ions can be accurately determined with the electrode. The electrode was also successfully applied to the direct determination of silver content of a solder sample, a developed radiological film and a photographic developing solution, and the results, together

with those obtained by AAS, are summarized in Table 2. As observed from Table 2, the results obtained by the proposed Ag⁺-selective electrode are in satisfactory agreement with those obtained by AAS.

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