A novel silver(I)-selective PVC membrane sensor and its potentiometric applications

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Abstract: Silver(I)-selective sensors were prepared from a solid-state contact polyvinyl chloride (PVC) membrane. (Z)-2-(2-((3-(2-hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol was synthesized as an ionophore molecule and embedded in the silver(I)-selective PVC membrane composition. The optimum membrane composition was determined as 2.5% ionophore, 61.7% bis-(2-ethylhexyl)sebacate, 1.0% potassium tetrakis (p-chlorophenyl) borate, and 34.8% PVC. The developed sensor exhibited a linear potential change $E = 67.42$ (–log [Ag$^+$]) + 1152.9 and $R^2 = 0.9960$) in the varying concentration range of 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1} silver ions. This sensor shows a detection limit of 7.3×10^{-7} mol L^{-1}. The proposed sensor showed a good potential change with high sensitivity even in a wide range of pH values (2.0–11.0). The proposed sensor had a quick electrochemical response of less than 3 s with good selectivity and repeatability. The sensor was also successfully applied in the analysis of real water samples. In real water samples prepared by standard addition method, recoveries in the range of 82.30%–95.15% were obtained.

Key words: Potentiometric sensor, PVC membrane, silver(I)-selective, silver determination

1. Introduction

Silver has wide commercial importance in photography, medicine, optics, mirror alloys, electrical and electronic equipment, dental and medical products, and the photographic and imaging industry, as well as in high capacity silver–zinc and silver cadmium batteries.[1−4] Because of the wide use of silver metal, it can become mixed into natural water sources as pollutants. For this reason, determination of silver in environmental, industrial, and wastewater samples is important.[5,6]

Potentiometric determination of silver offers great advantages such as easy preparation and procedures, short response time, high selectivity, wide linear working range, and low cost[7−12] compared to the other methods.

The design and synthesis of an ionophore as an ion selective electrode is the basis for potentiometric ion determination. In recent years, a great deal of effort has been dedicated to the design of new ionophore molecules for trace elements.[13] The selectivity and lifetime of the known ionophore groups may suffer from high price and reproducibility.

Azadipyrromethene compounds were described as blue pigments 70 years ago but are currently emerging as a near-IR emitter. These molecules are also known as subderivatives of dipyrromethene compounds.

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Azadipyrromethene compounds have been extensively used in pH sensors, anticancer agents, and polymers as a repeating unit.[14,15] Although these compounds have been known about for a long time, studies related to metal complexes have entered the literature only within the last 10 years. Several studies showed that azadipyrromethenes might chelate with d-block elements through pyrolic nitrogens.[16] In a study published by the Gray group in 2007, tetraarylazadipyrromethene compounds were shown to form heteroleptic complexes with silver and other d^{10} metals.[17] The ability of azadipyrromethene to bond with metal centers indicates that these compounds have the potential to be used as ionophores in the structure of ion-selective electrodes.

In the present work, an azadipyrromethene derivative compound [(Z)-2-(2-((3-(2-hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol] (Figure 1) was synthesized according to a procedure similar to the literature[18] and this molecule was used as ionophore in the construction of a silver(I)-selective polyvinyl chloride (PVC) membrane sensor. The potentiometric behaviors of this prepared sensor were tested in static conditions.
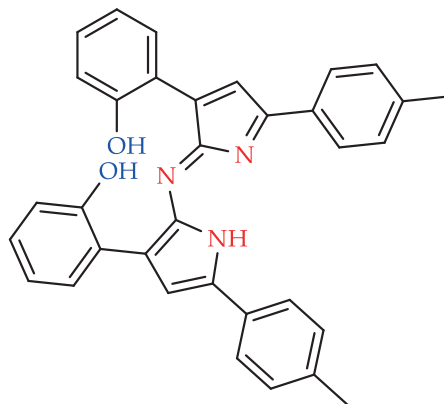

Figure 1. Structure of (Z)-2-(2-((3-(2-hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol.

2. Results and discussion

In the present study, a (Z)-2-(2-((3-(2-hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol molecule was synthesized in 3 steps and this molecule was used as an ionophore in the construction of the all-solid-state contact silver(I)-selective PVC membrane sensor. The potentiometric characteristics of the sensor such as potential operating range, response time, selectivity, reproducibility, and linear work range were investigated under static conditions.

2.1. Potentiometric performance of the silver(I)-selective PVC membrane sensor

The optimum percentage composition was determined by measuring the potentiometric performance of the silver(I)-selective PVC membrane sensor. The calibration curve of the sensor was obtained over the Ag^+ concentration range of 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1}. Figure 2A shows that the silver(I)-selective PVC membrane sensor exhibits a strong potential change. The sensor showed a linear potential change and the linear equation was measured as $E = 67.42$ (–log [Ag^+]) + 1152.9 with a correlation coefficient of $R^2 = 0.9960$ (Figure 2B). The sensor exhibited a potential change of about 65 mV against each ten-fold concentration change in the silver ion.
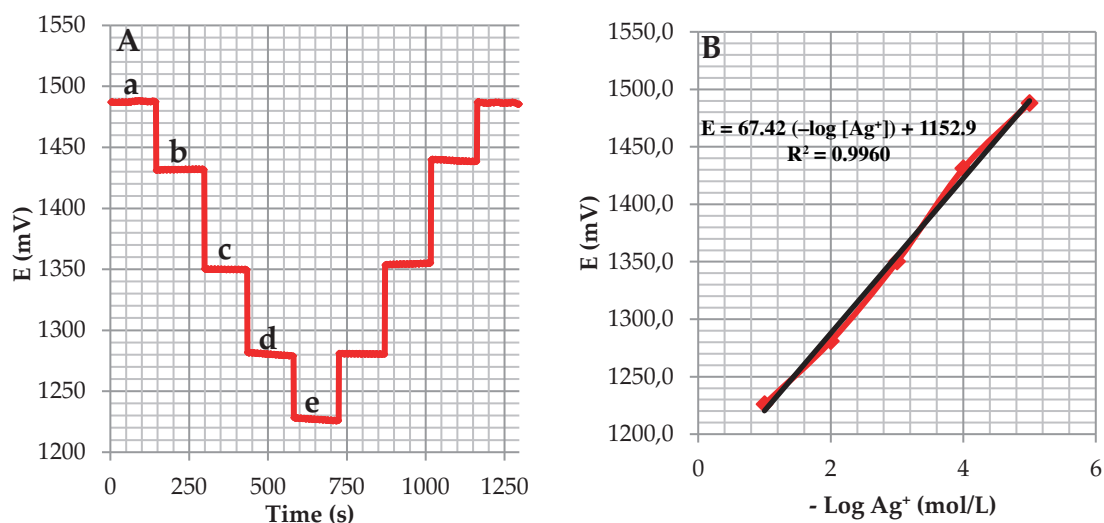
Figure 2. A) The potentiometric response to exhibits of the silver(I)-selective PVC membrane sensor (a: 10^{-1} mol L^{-1}, b: 10^{-2} mol L^{-1}, c: 10^{-3} mol L^{-1}, d: 10^{-4} mol L^{-1}, and e: 10^{-5} mol L^{-1}); B) The variation in average potential values (mV) with $-\log[Ag^+]$ for Ag^+ solutions in the range 1.0×10^{-1}–1.0×10^{-5} mol L^{-1}.

2.2. Selectivity of the silver(I)-selective PVC membrane sensor

One of the most important characteristics of a sensor is that it acts as a selective probe even in the presence of other interfering ions. Potentiometric selectivity coefficients of the silver(I)-selective PVC membrane sensor were calculated according to the IUPAC[19] recommendation by separate solution method. The selectivity of the sensor is summarized in Figure 3 and Table 1. The data show that the sensor is highly selective for Ag^+ ions in the presence of alkali, alkaline earth, and many heavy metal ions.

Table 1. Selectivity coefficients of various interference ions.

| Interfering ions	Selectivity coefficient, $\log k^{pot}_{Ag^+,M^{1+}}$	Interfering ions	Selectivity coefficient, $\log k^{pot}_{Ag^+},M^{1+}$
Fe^{3+}	–2.95	Zn^{2+}	–3.73
Cr^{3+}	–3.36	Ni^{2+}	–3.74
Al^{3+}	–3.53	Sr^{2+}	–3.75
K^+	–3.57	Pb^{2+}	–3.75
Li^+	–3.65	Co^{2+}	–3.77
NH_4^+	–3.65	Bi^{3+}	–3.78
Ca^{2+}	–3.66	Cu^{2+}	–3.78
Na^+	–3.72	Mg^{2+}	–3.80
Cd^{2+}	–3.73		

2.3. Reusability of the silver(I)-selective PVC membrane sensor

The repeatability of the silver(I)-selective PVC membrane sensor was determined by taking repeated measurements at 10^{-2}, 10^{-3}, and 10^{-4} mol L^{-1} Ag^+ concentrations. The potential-time graph was obtained
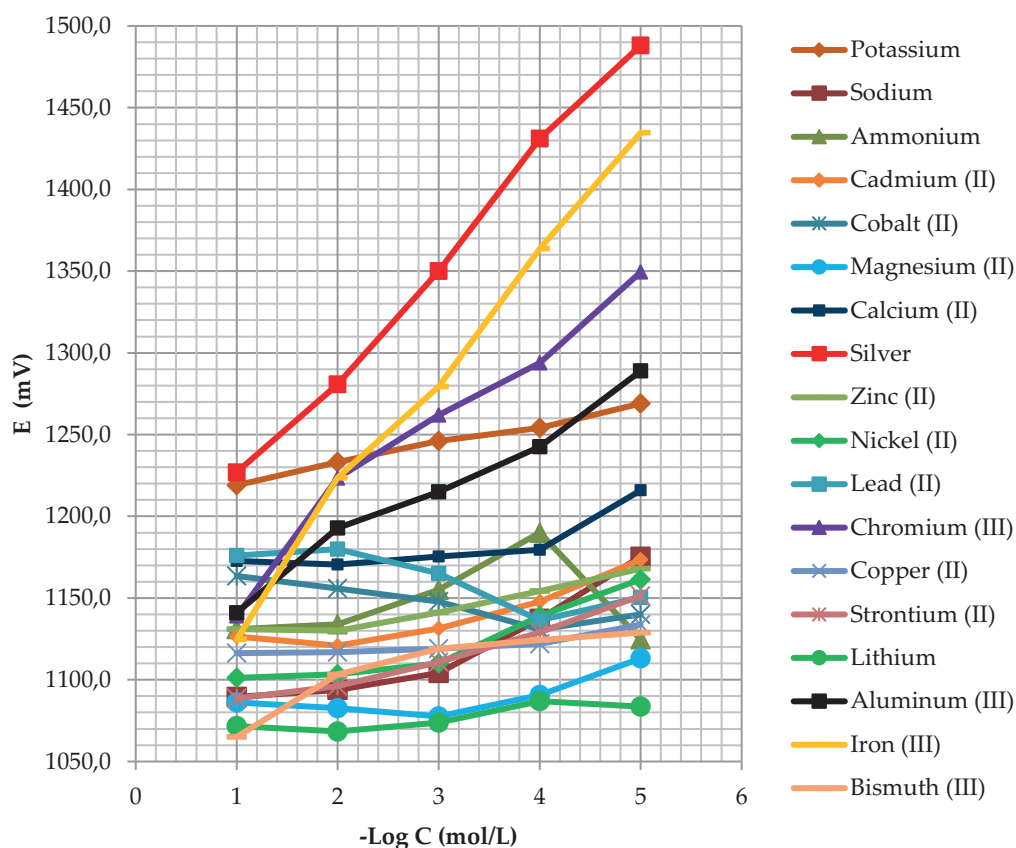
Figure 3. The potentiometric response to exhibits of the silver(I)-selective PVC membrane sensor against interfering ions.

using the measured potential data. Figure 4 shows that the sensor gives reproducible potential values against concentration changes of Ag^+.
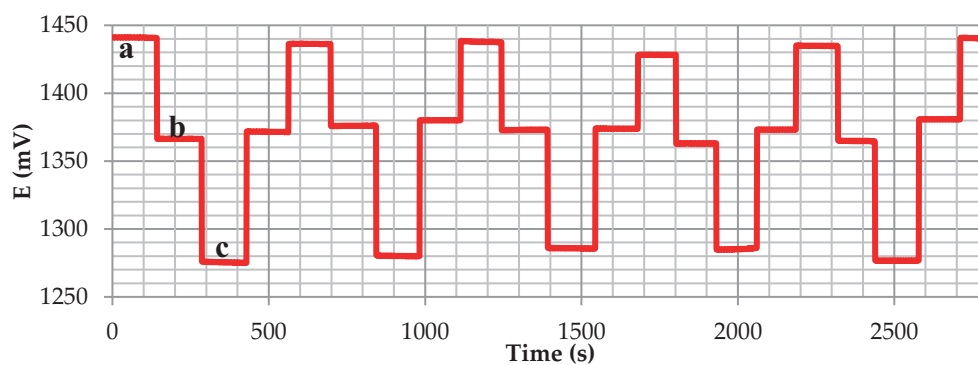
Figure 4. The reusability of the silver(I)-selective membrane sensor (a: 10^{-2} mol L^{-1}, b: 10^{-3} mol L^{-1}, and c: 10^{-4} mol L^{-1}).

2.4. Response time of the silver(I)-selective PVC membrane sensor

The response time at ion-selective electrodes is defined as the elapsed time for 95% of the equilibrium potential with the sensitive part of the membrane when immersed in one solution and then another solution at a ten-fold concentration change.[20,21] In our study, to determine the response time of the silver(I)-selective PVC membrane sensor, the transition times from the 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1} Ag^+ solutions were investigated. The response time of the silver(I)-selective PVC membrane sensor was less than 3 s. This short response time suggests that the sensor membrane can reach a fairly rapid equilibrium.

2.5. pH dependence of the silver(I)-selective PVC membrane sensor

The pH operating range is an important potentiometric performance characteristic that demonstrates the availability of an improved ion-selective electrode in different matrix environments. To determine the pH operating range of the silver(I)-selective PVC membrane sensor, 1.0×10^{-3} mol L^{-1} Ag^+ solutions were prepared with different pH values (pH 2.0–12.0). Measurements were taken for 1.0×10^{-3} mol L^{-1} Ag^+ solutions prepared at different pH values. The pH was adjusted with HCl and NaOH. Measurements were obtained with the silver(I)-selective PVC membrane sensor in pH-adjusted solutions and potential values obtained were recorded. The potential–pH graph displayed by the silver(I)-selective PVC membrane sensor against pH change is shown in Figure 5. According to Figure 5, the change in pH (pH 2.0–11.0) did not affect the potentiometric behavior of the silver(I)-selective PVC membrane sensor. The potential value of the 1.0×10^{-3} mol L^{-1} Ag^+ solutions in the nonacidic medium (approximately 1350 mV) was shown to be unaffected by pH 2.0 to 11.0. The response time of the silver(I)-selective PVC membrane sensor was less than 3 s in the pH range 2.0–11.0.
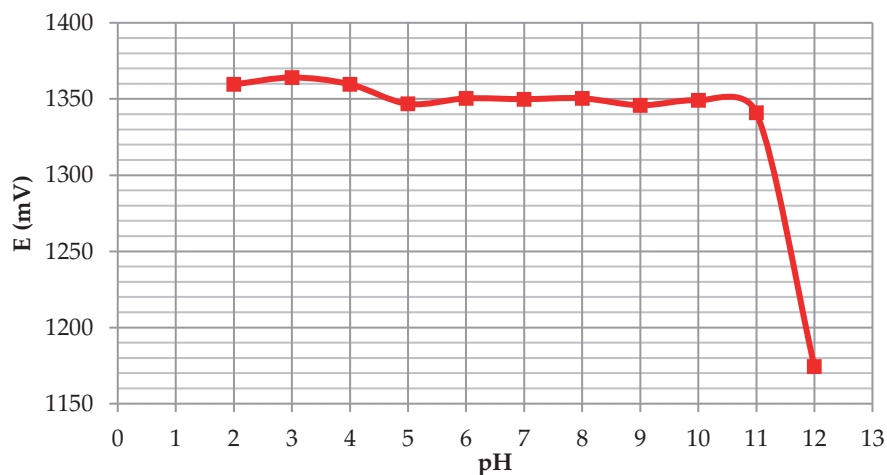

Figure 5. pH dependence of the silver(I)-selective membrane sensor.

2.6. Analytical applications of the silver(I)-selective PVC membrane sensor

Potentiometric titration of NaCl with $AgNO_3$ was investigated to determine the suitability of the silver(I)-selective PVC membrane sensor as an indicator electrode in potentiometric titrations. For this, 50 mL of 1.0×10^{-2} mol L^{-1} $AgNO_3$ solution was taken and 1.0×10^{-2} mol L^{-1} sodium chloride solution was added

continuously. The potential data observed after each silver nitrate addition were recorded. After, the potential-added Ag titration curve was generated using these data (Figure 6). It showed the developed silver(I)-selective PVC membrane sensor was used successfully as an indicator electrode in potentiometric titration of $AgNO_3$ with NaCl. The turning point of the titration was obtained with an error of about 4%.
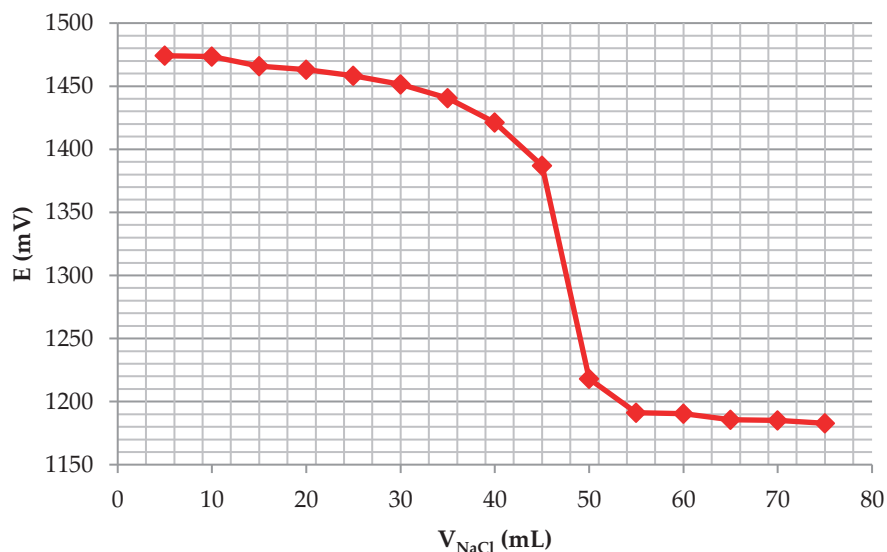
Figure 6. Potentiometric titration of 1.0×10^{-2} mol L^{-1} $AgNO_3$ solution with 1.0×10^{-2} mol L^{-1} NaCl solution.

The actual sample analysis application of the silver(I)-selective PVC membrane sensor was carried out by adding a standard Ag^+ ion to water samples including urban water, river water, spring water, and some commercially available bottled water. For this, a 50-mL portion of the collected water samples was taken and standard Ag^+ ion addition was performed. Before starting the measurement process, calibration was carried out using Ag^+ concentration 1.0×10^{-1}–1.0×10^{-5} mol L^{-1} solutions and the linear equation was obtained. Potential measurements of water samples were carried out, and their potential values were written in their linear equations and the Ag^+ ion concentrations of the samples were calculated. The potential results obtained are shown in Table 2, showing the amount of Ag^+ ions added to each water sample and the Ag^+ amounts obtained from the potentiometric determination of water samples. When the data in Table 2 are examined, it is seen that the potentiometric determination of Ag^+ ions in water samples was successfully performed with the newly developed silver(I)-selective PVC membrane sensor.

Table 2. Real water sample analyses with the silver(I)-selective PVC membrane sensor.

Real sample	Ag^+ quantity, (mol/L)		
	Added Ag^+	Mean ($\pm$SD) found with sensor *	% Regain
River water	1.60×10^{-3}	1.53 ($\pm$0.57) $\times10^{-3}$	95.63
Urban water	1.00×10^{-3}	8.20 ($\pm$0.10) $\times10^{-4}$	82.30
Bottled water 1	1.80×10^{-3}	1.70 ($\pm$0.35) $\times10^{-3}$	94.00
Bottled water 2	1.40×10^{-3}	1.33 ($\pm$0.73) $\times10^{-3}$	95.00
Spring water	1.60×10^{-3}	1.44 ($\pm$0.10) $\times10^{-3}$	90.00

*Mean and standard deviation values are given for three different experimental measurements (n = 3).

2.7. Comparison of the silver(I)-selective electrodes

The developed silver(I)-selective sensor was compared in terms of concentration range, detection limit, pH working range, response time, and real sample applications with other silver(I)-selective sensors previously reported in the literature. According to Table 3, the developed silver(I)-selective sensor is superior to existing sensors in terms of response time, pH working range, and further real sample applications.

Table 3. Comparison of the proposed silver(I)-selective electrode with reported electrodes.

Ionophore	Concentration range (mol L^{-1})	Limit of detection (mol L^{-1})	pH working range	Response time (s)	Real sample applications	Ref.
N,N'-ethylenebis-(3-methoxy salicylaldimine	1.0×10^{-6}–1.0×10^{-1}	8.3×10^{-7}	3.0–8.0	15	Waste water and photographic film	22
5,11,17,23-Tetra-tert-butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4	1.0×10^{-6}–1.0×10^{-2}	8.0×10^{-7}	2.0–6.0	5–10	Not worked	23
1,10-Diaza-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione	1.6×10^{-6}–3.0×10^{-3}	6.3×10^{-7}	4.3–9.4	< 15	Not worked	24
Me$_6$(14)diene.2HClO$_4$	5.0×10^{-6}–1.0×10^{-1}	8.0×10^{-7}	2.5–9.0	< 15	Not worked	25
Schiff base p-tertbutylcalix[4]arene	1.0×10^{-5}–1.0×10^{-1}	6.3×10^{-6}	1.0–6.0	30	Natural water	26
Hexathia-18-crown-6	6.0×10^{-6}–3.2×10^{-3}	4.0×10^{-6}	2.0–7.5	< 10	Not worked	27
Bis-pyridine tetramide macrocycle	4.0×10^{-5}–1.0×10^{-1}	-	-	5	Water samples	28
Isoquinoline-1,3-diones	5.0×10^{-6}–1.0×10^{-1}	5.83×10^{-6}	1.0–5.5	< 12	Tap water samples	29
p-$tert$-Butylthiacalixarene	7.0×10^{-6}–8.0×10^{-3}	3.9×10^{-6}	3.0–5.0	10–20	Pharmaceutical samples	30
Schiff base (N^{2}E,N$^{2'}$E)-N^2,N^2'-bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine	1.0×10^{-7}–1.0×10^{-2}	4.0×10^{-8}	2.0–6.0	9	Not worked	31
(Z)-2-(2-((3-(2-Hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol	1.0×10^{-5}–1.0×10^{-1}	7.3×10^{-7}	2.0–11.0	< 3	Urban water, spring waters, river water, commercially bottled water	This work

2.8. Conclusions

In the present study, an all-solid-state silver(I)-selective potentiometric PVC membrane sensor based on (Z)-2-(2-((3-(2-hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol was developed for fast and simple analysis of silver(I) ions. The developed sensor has potentiometric performance, such as high sensitivity, fast response time <3 s, lower detection limit, good selectivity against silver(I) ion, and a wide pH working range. Moreover, the simple preparation and the low cost of the developed membrane sensor are

significant advantages. It has the potential to be used as a detector in flow injection analysis systems because it can be prepared especially in micro dimensions.

3. Experimental

3.1. Materials

All reagents used in the present study were of analytical purity. At each stage of the study, distilled deionized water was used. High molecular mass polyvinyl chloride (PVC), plasticizer bis-(2-ethylhexyl) sebacate (BEHS), potassium tetrakis (p-chlorophenyl) borate (KTpClPB), tetrahydrofuran (THF), and graphite were obtained from Sigma-Aldrich. Epoxy resins (Macroplast Su 2227) and hardener (Desmodur RFE) was obtained from Henkel and Bayer, respectively. Silver(I)-selective ionophore [(Z)-2-(2-((3-(2-hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol] was synthesized according to a similar procedure published in the literature.[18] Deionized water was obtained by means of a DI 800 Model water deionization system. To perform the selectivity studies, analytical-grade nitrates of Na^+, K^+, NH_4^+, Li^+, Ag^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cr^{3+}, Bi^{3+}, and Al^{3+} nitrate solutions were prepared in deionized water. The stock solutions were diluted gradually from 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1}.

3.2. Apparatus

Potentiometric measurements were performed at room temperature (20 ± 1 °C) using a computer-controlled multichannel potentiometric system. All measurements were performed using the silver(I)-selective PVC membrane electrode and a micro-size silver/silver chloride reference electrode (Thermo-Orion). ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance DPX-400. Melting points were measured on an Electrothermal 9100.

3.3. Method

3.3.1. Synthesis and characterization of (Z)-2-(2-((3-(2-hydroxyphenyl)-5-(p-tolyl)-1H-pyrrol-2-yl)imino)-5-(p-tolyl)-2H-pyrrol-3-yl)phenol

In a 100-mL round-bottom flask 2.38 g (0.01 mol) of 1-(2-hydroxyphenyl)-3-(p-tolyl)prop-2-en-1-one was dissolved in 50 mL of ethanol. To this solution triethylamine (5.05 g, 0.05 mol) and nitromethane (3.05 g, 0.05 mol) were added and the reaction mixture was left to stir at reflux temperature for 48 h. The reaction was monitored by thin layer chromatography. After completion of the reaction, the solvent was removed under vacuum and the brown product was directly used for the next step without further purification. The resulting material was dissolved in 50 mL of ethanol and ammonium acetate (7 g, 0.1 mol) was added to the reaction, and the final mixture was reacted for 48 h at reflux temperature. The solvent was removed under vacuum and the final product was subjected to column chromatography, using neutral aluminum oxide as a stationary phase and a 5:2 hexane–ethyl acetate (v:v) solution as an eluent.

Blue solid, Yield: 50%; mp 187–190 °C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.15 (d, $J = 15.8$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 4H), 7.72 (s, 2H), 7.60 (d, $J = 7.8$ Hz, 4H), 7.31 (d, $J = 8.1$ Hz, 6H) 2.45 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 156.1, 143.5, 140.5, 135.7, 131.6, 129.3, 129.3, 128.7, 122.6, 122.3, 120.5, 116.6, 21.6.

3.3.2. Preparation of PVC membrane electrodes

The preparation of the all-solid-state-contact PVC membrane potentiometric sensor was carried out in two stages. First, solid-state contacts were prepared. For this purpose, the powder graphite, epoxy, and hardener were dissolved in THF in appropriate proportions. After suitable viscosity was obtained, a copper wire (approximately 1 mm thickness and 5–15 cm long) was immersed in this mixture 5–6 times and covered. Then membrane cocktails were prepared in different compositions. The silver(I)-selective sensor was prepared by coating the membrane cocktail on the surface of the solid contacts.

Table 4. Percentage ratios and linear equations of silver(I)-selective membrane compositions.

Membrane no.	Composition (% w/w)				Linear equation	R^2
	Ionophore	PVC	KTpClPB	Plasticizer		
1	2.5	34.8	1.0	61.7	$E= 44.60\ (-\log\ [Ag^+]) + 1152.9$	0.9960
2	3.0	34.5	1.0	61.5	$E= 44.60\ (-\log\ [Ag^+]) + 1318.7$	0.8362
3	3.5	34.6	1.0	60.9	$E= 44.60\ (-\log\ [Ag^+]) + 1491.9$	0.9903

The ionophore, plasticizer, KTpClPB, and PVC mixture were dissolved in THF to determine the most suitable membrane composition (Table 4). The membrane mixture was left to stand until a suitable viscosity was obtained and the membrane cocktail was coated onto the solid-contact surface at a certain thickness. The prepared sensor was allowed to dry for 24 h. Prior to first use, the sensor was conditioned in 1.0×10^{-2} mol L^{-1} silver nitrate solution for 12 h.

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