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Potentiometric sensors for Ag⁺ based on poly(3-octylthiophene) (POT)

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Abstract Potentiometric ion sensors were prepared from the conjugated polymer poly(3-octylthiophene) (POT). The influence of additional membrane components, including silver 7,8,9,10,11,12-hexabromocarborane (AgCB₁₁H₆Br₆) and potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTPFPB) as lipophilic salts, and [2.2.2]p,p,p-cyclophane as silver ionophore, was studied. The membrane components were dissolved in chloroform and membranes were prepared by solution casting on glassy carbon disk electrodes. For comparison, POT-based potentiometric sensors were also prepared by galvanostatic electrosynthesis of POT from the 3-octylthiophene monomer. All the POT-based ion sensors fabricated by solution casting show Nernstian or slightly sub-Nernstian response to Ag⁺, even those based only on POT without any additional membrane components. The potentiometric response of electrochemically polymerized POT depends on the film thickness and the doping anion incorporated in the conducting polymer during polymerization. It is of particular importance that chemically synthesized undoped POT (without any additives) shows a sensitive and selective potentiometric response to Ag⁺ ions although UV-vis results show that POT remains in its undoped form, i.e., POT is not oxidized by Ag⁺. This indicates that undoped POT can exhibit good sensitivity and selectivity to Ag⁺ also in the absence of metallic silver in the polymer film. In this case, the potentiometric response is related to interactions between Ag⁺ and the conjugated polymer backbone.

Keywords Ion-selective electrode · Silver · Poly(3-octylthiophene) · Conducting polymer

Introduction

Typically, commercial silver ion-selective electrodes (Ag⁺-ISEs) have been based on Ag₂S solid-state membranes [1–5]. This type of electrodes show very good selectivity for Ag⁺ against alkali, alkaline earth and most transition metals, except Hg²⁺, which causes significant interference. Thus, an increasing number of publications have focused in the last years on the development of new Ag⁺-ISEs. The synthesis of new silver selective compounds (ionophores) and their inclusion in polymeric membranes (commonly polyvinyl chloride, PVC) has become a promising approach towards the construction of ion-selective electrodes (ISEs) for silver and some other transition metals. Neutral carriers (ionophores) for “soft” metal ions like Ag⁺ usually contain heteroatoms like sulfur, nitrogen or oxygen [6]. Substituted calixarenes [7–15] and other compounds [7, 16–21] including heteroatoms in their chemical structure have been intensively investigated as silver ionophores in conventional (with internal filling solution) [7, 9–15, 17, 18, 21] and solid contact [8, 16, 19, 20] ISEs based on PVC membranes. A lower interference from Hg²⁺ is observed for some of these Ag⁺-ISEs [7, 15, 17, 19] compared to those based on Ag₂S solid-state membranes [1–5]. Recently, cyclophanes have also been used as ionophores in all-solid-state Ag⁺-ISEs based on a conducting polymer as solid contact material [22, 23]. The use of cyclophanes as silver ionophores was based on the π -coordinating properties of these compounds that can bind soft metal ions selectively (cation- π interaction) [23]. The interference from Hg²⁺ in these cyclophane-based Ag⁺-ISEs was related to the π -coordinating phenyl groups of the tetrakis(4-chlorophenyl) borate (TpCIPB⁻) anionic additive acting as a “soft charged carrier” [24]. The substitution of TpCIPB⁻

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by a weakly coordinating carborane anion (7,8,9,10,11,12-hexabromocarborane) ($\text{CB}_{11}\text{H}_6\text{Br}_6^-$) reduced the Hg^{2+} interference by six orders of magnitude resulting in $\log K_{\text{Ag,Hg}} = -3.8 \pm 0.1$ (matched potential method) [24].

Recent studies showed the possibility of using a conducting polymer not only as solid contact but also as an ion-selective membrane for Ag^+ [25]. In those potentiometric sensors, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with *p*-sulfonated calix[4]arene and *p*-methylsulfonated calix[4]resorcarenes was used as the ion-selective membrane [25]. The results obtained revealed that although the doping anion influences the sensitivity and selectivity of the conducting polymer-based potentiometric sensors, the selectivity shown towards Ag^+ is largely a feature of the PEDOT itself. These studies led to the conclusion that the potentiometric response to Ag^+ may partly be due to interactions between Ag^+ and the conjugated polymer backbone, and partly due to the presence of metallic Ag in the polymer film originating from oxidation of the conjugated polymer by Ag^+ (electroless deposition of Ag). A conjugated polymer with a high oxidation potential should suppress the deposition of Ag and help to clarify the role of metallic Ag in the selectivity shown by conjugated polymer-based sensors. The oxidation potential of poly(3-octylthiophene) (POT) [26] is much higher than that of PEDOT [27]. Therefore, POT films should be less susceptible to oxidation by Ag^+ ions than PEDOT films. The undoped (semiconducting) form of POT is very stable in aqueous solutions and shows a cationic potentiometric response [28].

In the present work POT films are used in the construction of potentiometric Ag^+ ion sensors. Films are prepared by solution casting of chemically polymerized POT or by electrochemical polymerization of the 3-octylthiophene monomer in presence of LiBF_4 -propylene carbonate (PC) or $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ -acetonitrile (ACN). The objective is to study the possible effect of silver on the oxidation state of POT films and the potentiometric response of POT films to Ag^+ ions. This paper is an extension of our recent report on Ag^+ -ISEs based on PEDOT doped with *p*-sulfonated calix[4]arene and *p*-methylsulfonated calix[4]resorcarenes [25]. The main goal of the present work is to elucidate the mechanism determining the selectivity shown by conducting polymers towards silver ions.

Experimental

Chemicals

Chemically synthesized poly(3-octylthiophene) (POT) (ACT, Saint-Egrève, France) and 3-octylthiophene (3-OT) (Tokyo Kasei) were used as received. Silver 7,8,9,10,11,12-hexabromocarborane ($\text{AgCB}_{11}\text{H}_6\text{Br}_6$) (Strem Chemicals), [2.2.2]*p,p,p*-cyclophane (Sigma-Aldrich) and potassium tetrakis[3,5-bis(trifluorometh-

yl)phenyl]borate (KTpFPB) (Selectophore reagent, Fluka) were used as received. LiBF_4 (Aldrich, 98%) was dried under vacuum at 80° C for half an hour. Chloroform (99–99.4%) was obtained from BDH. Acetonitrile (ACN) (>99.5%, Riedel-de Haën) was freshly distilled from acetonitrile stored over CaH_2 , and dried over basic alumina (Aldrich). Propylene carbonate (PC) (99%, Aldrich) was dried over basic alumina before use. All other chemicals were analytical-reagent grade. ELGA ultrapure water (resistivity 18.2 M Ω cm) was used to prepare all solutions.

Fabrication of potentiometric sensors by solution casting of soluble POT

Cocktails of different composition were prepared by dissolving POT and other membrane components in chloroform at a total concentration of 6 mg/ml. The electrodes were prepared by applying the membrane solution on top of a glassy carbon disk electrode and then allowing the chloroform to evaporate. The volume of the cocktail was 150 μl per electrode, resulting in a film thickness of ca. 10 μm . The composition of the cocktails studied is shown in Table 1. The chemical structures of the membrane components are shown in Fig. 1.

When preparing cocktails based on POT and $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ in chloroform, partial precipitation of POT was observed, presumably as a result of being oxidized (doped) by silver ions. By using [2.2.2]*p,p,p*-cyclophane as coordinating ligand for Ag^+ [22], oxidation and precipitation of POT may be suppressed [29] as the concentration of free Ag^+ ions in the cocktail solution is reduced. Therefore, stock solutions of $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ and cyclophane at different ratios were prepared in chloroform, and then mixed with different percentages of the stock solution of POT in chloroform. A suspension was then formed. The other cocktails studied were clear solutions.

The resulting electrodes based on chemically polymerized POT (GC/POT) were conditioned in 0.01 M AgNO_3 solution for at least 1 day before further use.

Table 1 Composition of membranes based on chemically synthesized POT in % (w/w)

Electrode	POT	KTpFPB	$\text{AgCB}_{11}\text{H}_6\text{Br}_6$	[2.2.2] <i>p,p,p</i> -cyclophane
1	100	-	-	-
2	90	10	-	-
3	80	20	-	-
4	60	40	-	-
5	90	-	10	-
6	80	-	20	-
7	90	-	3.1 (20) ^a	6.9
8	80	-	10.5 (50) ^a	9.5

^a Values in parenthesis show the mol% of anionic additive versus [2.2.2]*p,p,p*-cyclophane (ionophore)

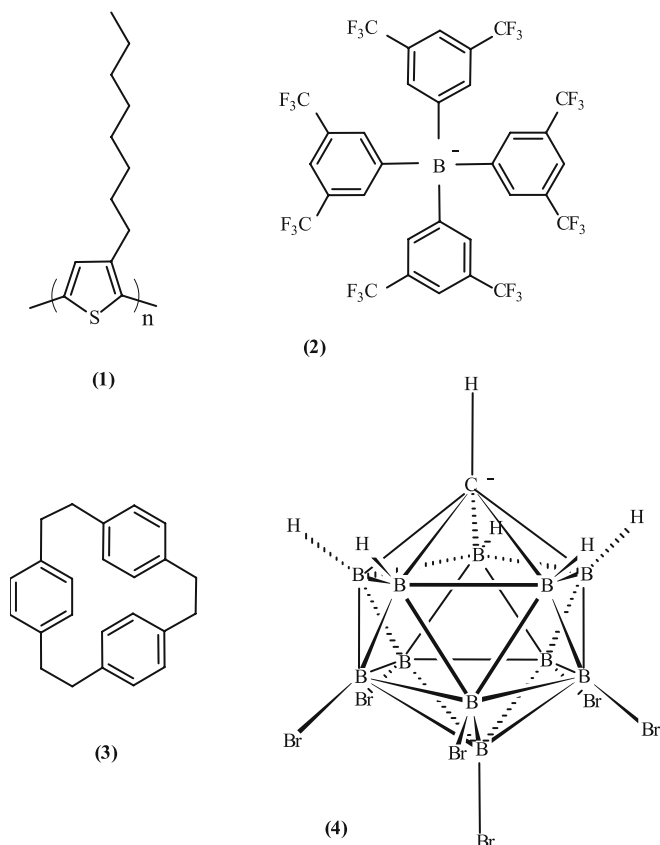


Fig. 1 Chemical structure of POT (1), TpFPB⁻ (2), [2.2.2]p,p,p-cyclophane (3), and CB₁₁H₆Br₆⁻ (4)

These electrodes were kept in 0.01 M AgNO₃ also between measurements.

Fabrication of potentiometric sensors by electrochemical polymerization

Electrochemical synthesis of poly(3-octylthiophene) (POT) was carried out by using an Autolab General Purpose System (AUT20.FRA2-Autolab, Eco Chemie, B.V., Netherlands) connected to a conventional one-compartment three-electrode electrochemical cell. The working electrode was a glassy carbon (GC) disc electrode with an area of 0.07 cm², and a GC rod was used as the auxiliary electrode. An Ag/AgCl wire was used as quasi-reference electrode (calibrated vs the ferrocene/ferrocinium redox couple). Prior to polymerization, the GC working electrode was polished with 0.3 μm alumina, rinsed with water and cleaned ultrasonically for at least 15 min. POT was deposited on the GC electrode surface by galvanostatic electrochemical polymerization from a deaerated solution of the 3-OT monomer (0.1 M) and the supporting electrolyte: 0.1 M LiBF₄-PC or 0.01 M AgCB₁₁H₆Br₆-ACN. A constant current of 0.1 mA (1.43 mA/cm²) was applied in order to produce polymerization charges of 8 mC and 74 mC. These polymerization charges correspond to a film thickness of

approximately 1 μm and 10 μm, respectively, assuming 2.2 electrons/monomer unit and a film density of 1 g·cm⁻³. In order to reproduce electrodes previously used for the construction of potentiometric sensors with a cationic response [28], some of the resulting POT(BF₄) films were electrochemically reduced (undoped) after polymerization by application of a potential of 0 V during 1 min in the polymerization solution. Such cases will be indicated in the text. After polymerization (and undoping), the resulting electrodes were rinsed with the solvents used during polymerization and then with water. Finally, they were conditioned in 0.01 M AgNO₃ solutions for at least 1 day before further use. These electrodes were kept in 0.01 M AgNO₃ also between measurements.

Potentiometric measurements

The potentiometric measurements were performed with a homemade multi-channel mV-meter connected to a PC for data acquisition. The reference electrode was an Ag/AgCl/KCl(3 M). When measuring in nitrate solutions, a salt bridge containing 1 M KNO₃ was used to connect the reference electrode to the test solution.

The potentiometric response of the Ag⁺-sensors was studied in AgNO₃ aqueous solutions with and without background electrolyte (0.1 M KNO₃). Selectivity coefficients were determined by the separate solution method (SSM). SSM was considered to be the fastest method to compare several different types of electrodes in a large number of test solutions. However, considering that in our system ions of different charges are involved this method is not the most appropriate [30]. Nevertheless, the selectivity coefficient values obtained can be used as reference values to compare our POT-based ion sensors with the PEDOT-based sensors studied earlier [25]. The selectivity measurements were done in 0.01 M solutions of the studied ions, except Hg²⁺, Fe²⁺ and Fe³⁺ for which a 10⁻³ M solution at pH 3 was used (pH was fixed by using 10⁻³ M HNO₃ as constant background electrolyte). Contribution of H⁺ to the response in these acidic solutions was canceled by the comparison of the electrode response in acidic solutions of Ag⁺ (10⁻³ M AgNO₃ at pH 3). The rest of the test solutions had pH in the range of 5.1–5.6, and pH = 4.7 in the case of Cu²⁺ and Pb²⁺ cations. Nitrate salts were used for all cations tested.

The activity coefficients were calculated according to the extended Debye-Hückel equation [31]. Correction for the liquid-junction potential was applied (Henderson equation). All the measurements were performed at room temperature (23 ± 2° C).

UV-vis spectroscopy

UV-vis spectra were recorded with a Hitachi U-2001 spectrophotometer at intervals of 1 h during 19 h. The

measurements were done in disposable PS cuvettes (Brand, Germany) with a path length of 10 mm. Films based on chemically polymerized POT, with no additives, were deposited by solution casting (40 μl) on tin oxide (TO) covered quartz glass (thickness: 4 mm), and chloroform was allowed to evaporate. Films based on electrochemically polymerized POT were deposited on the TO layer by galvanostatic polymerization. A Pt wire was used as counter electrode and a Ag/AgCl wire was used as quasi-reference electrode. Prior to polymerization, the TO glass was washed with acetone. The galvanostatic polymerization of POT was done in deaerated solutions of the monomer in presence of the appropriate electrolyte as indicated in **Experimental**. A constant current of 0.46 mA (ca. 1.4 mA/cm²) was applied in order to produce a polymerization charge of 18 mC. Based on the polymerization charge, the resulting film thickness was estimated to be ca. 0.3–0.4 μm .

Results and discussion

Potentiometric response of chemically synthesized POT

The potentiometric response of different GC/POT electrodes in AgNO₃ solutions with 0.1 M KNO₃ as background electrolyte is shown in Fig. 2. The slopes and standard potential values obtained from the calibration curves of the different electrodes shown in Fig. 2 are listed in Table 2.

It can be seen that electrodes 1, 2 and 5 prepared from chemically polymerized POT show good selectivity to Ag⁺, in comparison to K⁺, with slope values ranging from 53 to 57 mV/decade. Examples of calibration plots in AgNO₃ solutions without background electrolyte are shown in the inserted figure in Fig. 2. It can be seen that these electrodes (1, 2, 5) show rather reproducible behavior during calibration from 10⁻¹ M down to 10⁻⁶ M and back to 10⁻¹ M, and no significant hysteresis is observed. Replacing the tetraphenylborate derivative by AgCB₁₁H₆Br₆ was found earlier to dramatically reduce the Hg²⁺ interference of Ag⁺-selective solvent

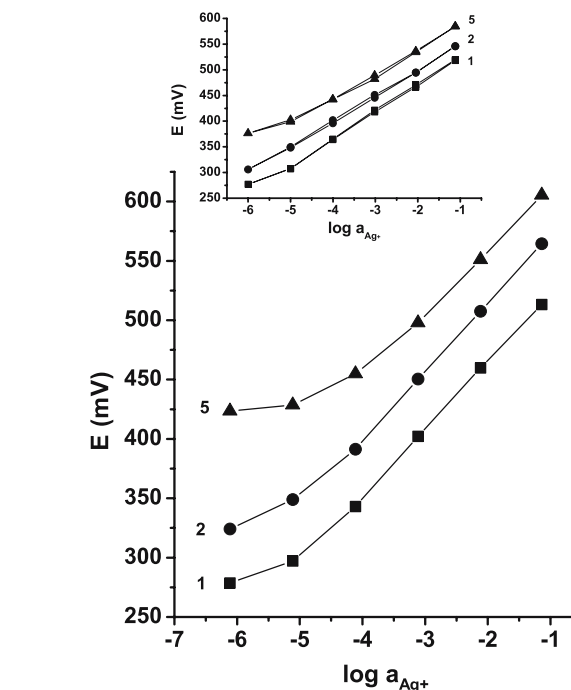


Fig. 2 Calibration plots for electrode 1 (■), electrode 2 (●), and electrode 5 (▲) based on chemically polymerized POT (see Table 1) in AgNO₃ with 0.1 M KNO₃ as background electrolyte, and AgNO₃ without background electrolyte (inserted figure). For clarity the calibration plots in the inserted figure are shifted arbitrarily towards more positive potentials on the y-axis, except that for electrode 1 which has its original values

polymeric membrane electrodes [24]. However, the POT-based electrode 5 containing AgCB₁₁H₆Br₆ as additive deteriorates with time (about 25% loss of slope after 1 month), in contrast to electrodes 1 (no additives) and 2 (containing KTpFPB as additive). The detection limit (D.L.) for electrode 5 is also higher (ca. 10^{-4.5} M) than for electrodes 1 and 2 (ca. 10^{-5.5} M). Response times were measured in AgNO₃ solutions at a constant background (0.1 M KNO₃). The response time is defined as the time required for the electrode potential to become equal to its steady state value within 1 mV after

Table 2 Slope and standard potential (mean values \pm S.D., $n=3$) calculated from the linear range of the calibration plots for GC/POT electrodes prepared by solution casting and conditioned in 0.01 M AgNO₃ solutions. The composition of the different electrodes is shown in Table 1

Electrode	Calibration in AgNO ₃ ^a		Calibration in AgNO ₃ + 0.1 M KNO ₃ ^b	
	Slope (mV per decade)	Standard potential (mV)	Slope (mV per decade)	Standard potential (mV)
1	49 \pm 2	572 \pm 5	53 \pm 4	573 \pm 4
2	49 \pm 3	574 \pm 4	57 \pm 2	580 \pm 5
3	55.1 \pm 0.7	596 \pm 2	57 \pm 2	592 \pm 4
4	56.0 \pm 0.7	589.1 \pm 0.4	56.6 \pm 0.8	585.9 \pm 0.7
5	49.1 \pm 0.5	564.2 \pm 0.8	54.7 \pm 0.3	568 \pm 2
6	49 \pm 2	585 \pm 3	51 \pm 5	581 \pm 9
7	51.2 \pm 0.9	570 \pm 2	55.3 \pm 0.9	567 \pm 1
8	50.0 \pm 0.7	580.5 \pm 0.7	50 \pm 2	578 \pm 4

^a Linear range 10⁻¹–10⁻⁴ M

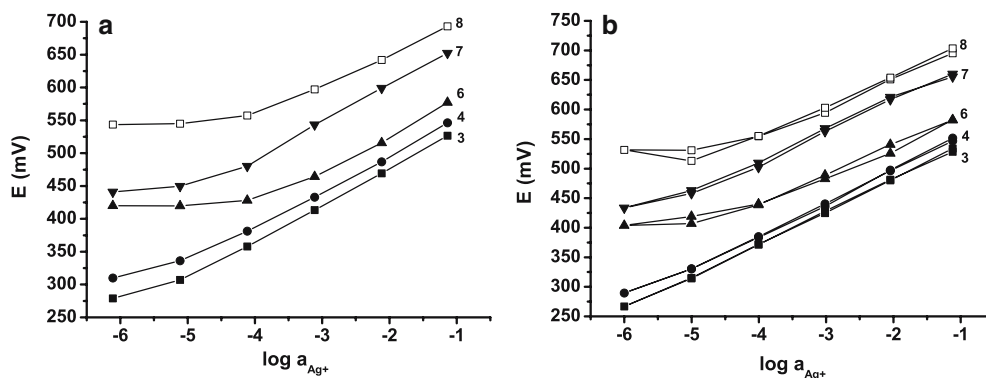
^b Linear range 10⁻¹–10⁻³ M

increasing the concentration of Ag^+ from 10^{-3} to 10^{-2} M. The response times are in the range of 47–57 s for electrodes **1**, **2** and **5** ($n=3$). The short-time potential drift at the two concentrations considered is between -1.2 and 1.0 mV/min for electrode **1**, and between -0.2 and 0.8 mV/min for electrodes **2** and **5**.

By increasing the amount of KTpFPB in the polymer membrane (see Table 1), the electrode performance is slightly improved (Fig. 3), as shown by the slope values obtained in AgNO_3 solutions without background electrolyte for electrodes **3** and **4** (Table 2). Figure 3b shows also that the reproducibility of the electrodes at different concentrations is quite good regardless of the concentration in the lipophilic anion (TpFPB $^-$) present in the polymer matrix. No deterioration in the response was observed for these electrodes with time (electrodes used for ca. 1 month). The D.L. for both electrodes is the same as for electrode **2** (ca. $10^{-5.5}$ M). The response times are ca. 70 s for electrode **3** and 33 s for electrode **4** ($n=3$). The short-time potential drift at the two concentrations considered is between 0.9 mV/min and 1.0 mV/min for electrode **3** and -0.1 mV/min and 2.4 mV/min for electrode **4**.

On the other hand, some deterioration in the electrode performance is observed when the concentration of $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ in the polymer matrix is increased from 10% (electrode **5**) to 20% (w/w) in electrode **6** (Fig. 3). The D.L. is higher for electrode **6** (ca. $10^{-3.8}$ M) than for electrode **5** (ca. $10^{-4.5}$ M) and a slightly lower slope value is obtained for the calibration of electrode **6** in AgNO_3 solutions with background electrolyte (Table 2). A more pronounced hysteresis is also observed for electrode **6** (Fig. 3b). As for electrode **5**, the response of electrode **6** deteriorates with time (about 12% loss of slope in 2 weeks). In addition, the response time is improved for electrode **6** (23 s) ($n=3$) but the short-time potential drift is slightly higher (-1.1 – 0.3 mV/min) than for electrode **5**.

Fig. 3 Calibration plots for electrode **3** (■), electrode **4** (●), electrode **6** (▲), electrode **7** (▼), and electrode **8** (□) based on chemically polymerized POT (see Table 1) in AgNO_3 with 0.1 M KNO_3 as background electrolyte (a), and AgNO_3 without background electrolyte (b). For clarity the calibration plots are shifted arbitrarily towards more positive potentials on the y -axis, except those for electrode **3** that have their original values



In electrodes **7** and **8**, the silver ionophore [2.2.2] p,p,p -cyclophane is also included in the polymer membrane composition together with the $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ additive (see Table 1). As shown by Fig. 3 and Table 2, the behavior of electrode **8** seems to be dominated by the total amount of additives incorporated in the membrane (20% w/w), and it is only slightly influenced by the ratio of $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ /cyclophane present. Electrode **8** shows also some deterioration in the response with time (about 16% loss of slope after 3 weeks). The performance of electrode **7** (10% w/w of additives) (D.L. ca. 10^{-5} M) is improved with respect to electrode **5** due to the presence of cyclophane in the membrane (Fig. 3 and Table 2). No deterioration in the response of electrode **7** is observed during the period of electrode testing (ca. 2 weeks). However, as shown in Fig. 3b, a small deviation from the linearity is observed at the highest concentration (10^{-1} M) for electrode **7**. Furthermore, the response time for electrode **7** is the longest among the electrodes prepared with $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ as additive (87 s) ($n=3$), and the short-time potential drift is the highest (2.3–2.5 mV/min) at the two concentrations considered.

Selectivity coefficients for Ag^+ -ISEs based on chemically synthesized POT

Figure 4 shows the selectivity coefficients calculated by the SSM. It can be seen that the $\log K_{\text{Ag},j}$ values are very similar for electrodes based on chemically polymerized POT with no additives (electrode **1**) and with 10% (w/w) TpFPB $^-$ as anionic additive (electrode **2**) (see Table 1). Usually, lipophilic anions such as TpFPB $^-$ need to be included in the membrane composition of cation-selective electrodes based on neutral ionophores in order to prevent anions from interfering with the cationic response. However, no interference from anions is observed for electrode **1** in the solutions tested. These results show that POT alone works as a Ag^+ -selective electrode (Ag^+ -ISE). In particular, this means that the Ag^+ selectivity is a feature of POT itself, i.e., the selectivity towards Ag^+ is mainly determined by the interactions between silver ions and the conjugated polymer backbone. Based on the $\log K_{\text{Ag},j}$ values, electrodes based on POT are even more selective to Ag^+

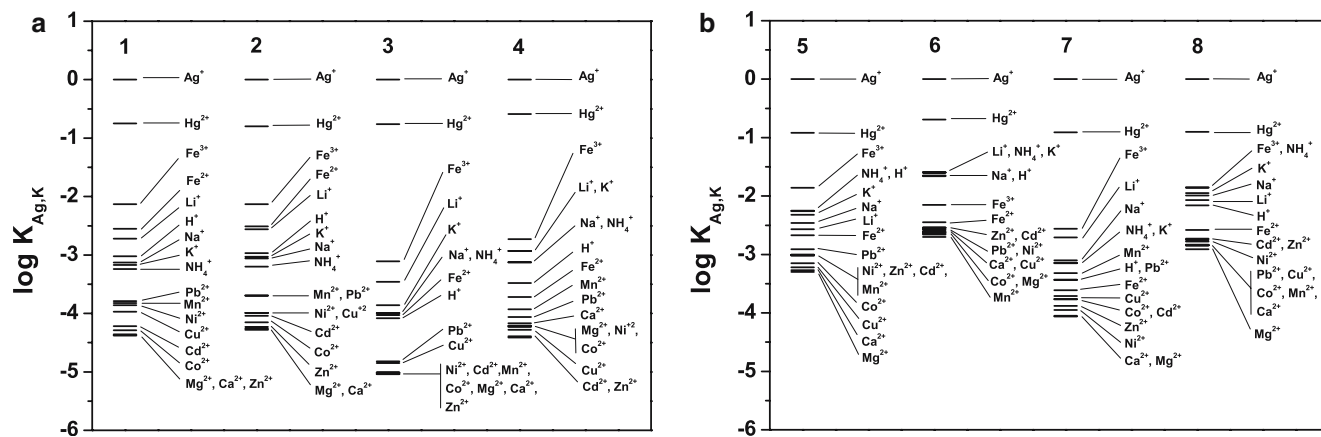


Fig. 4 Selectivity coefficients ($\log K_{Ag,j}$) calculated by the separate solution method (SSM) for electrodes based on chemically polymerized POT. The electrode numbers are indicated in the figure legend (see Table 1)

than those based on PEDOT, where deposition of metallic Ag takes place [25]. Furthermore, the selectivity obtained for electrode 2, based on chemically polymerized POT and 10% (w/w) TpFPB⁻ (Table 1), can be remarkably improved by increasing the amount of the anionic additive present in the polymer membrane to 20% (w/w) (electrode 3). Electrode 3 shows good selectivity towards silver against the alkali, alkaline earth and transition metals tested ($\log K_{Ag,j} < -3$). In general, electrode 3 shows a decrease in the interferences of 1–2 orders of magnitude compared to the electrodes based on PEDOT previously studied [25], except for Hg²⁺ interference that is very similar. Actually, the Hg²⁺ interference ($\log K_{Ag, Hg(II)} = -0.8$) for electrode 3 is close to that observed for some Ag₂S-based Ag⁺-ISEs ($\log K_{Ag, Hg(II)} = -1, \dots, -2$) [1–5]. Tetraphenylborate derivatives may exhibit high affinity towards Hg²⁺ [24], which is a typical interferant for Ag⁺-selective electrodes. However, this effect is less pronounced in the POT-based electrodes, because by increasing the amount of TpFPB⁻ from 10 to 40% (w/w), the $\log K_{Ag, Hg(II)}$ values increase only slightly.

Finally, as shown in Fig. 4, electrode 5 based on chemically polymerized POT with 10% (w/w) CB₁₁H₆Br₆⁻ as anionic additive (Table 1) is less selective to Ag⁺ compared to electrodes based on chemically polymerized POT with no additives (electrode 1) or with TpFPB⁻ as anionic additive (electrodes 2–4), except for the Hg²⁺ ion ($\log K_{Ag, Hg(II)} = -0.9$). This agrees again with the results obtained previously where CB₁₁H₆Br₆⁻ showed less affinity to Hg²⁺ than the tetraphenylborate derivative potassium tetrakis(4-chlorophenylborate) [24]. A higher concentration of AgCB₁₁H₆Br₆ in the membrane (electrode 6) (see Table 1) increases the interferences from all ions, except for Fe³⁺ that is another typical interferant for Ag⁺-selective electrodes. The addition of the silver ionophore [2.2.2]*p,p,p*-cyclophane into the membrane composition (see Table 1) up

to a total content of 10% (w/w) in polymer additives results in a better electrode performance with higher selectivity to Ag⁺ (electrode 7), although the interference from Hg²⁺ is not altered ($\log K_{Ag, Hg(II)} = -0.9$). When the total content of polymer additives is increased to 20% (w/w), a decrease in the selectivity to Ag⁺ is observed for electrode 8 compared to electrodes 5 and 7.

Potentiometric response of electrochemically synthesized POT

Examples of calibration curves for electrodes based on electrochemically polymerized POT are shown in Fig. 5. The slopes and standard potential values obtained from the calibration curves of these electrodes are listed in Table 3.

In contrast to electrodes based on chemically polymerized POT, the electrodes fabricated by electrochemical deposition of thin films of POT doped with CB₁₁H₆Br₆⁻ (9) and BF₄⁻ (11) show poor sensitivity to Ag⁺ (slope values < 40 mV/decade). The performance of electrode 12 is similar to that of electrode 11, indicating that the electrochemical undoping of POT after polymerization plays a minor role. The reason for this is that POT films undergo spontaneous reduction in aqueous solutions [28]. The POT films of electrodes 9, 11 and 12 are considerably thinner (ca. 1 μm) than those prepared by solution casting (ca. 10 μm), which may be one reason for the poor Ag⁺ response of the former. Therefore, electrodes based on electrochemically polymerized POT were prepared with approximately the same thickness as those prepared by solution casting (ca. 10 μm). As shown in Fig. 5, also the electrodes based on thick films of POT doped with BF₄⁻ (electrodes 13 and 14) respond only at the highest concentrations of Ag⁺ (10⁻²–10⁻¹ M). In fact, electrode 13 shows a super-Nernstian behavior in that concentration range and a non-linear behavior in the concentration range 10⁻²–10⁻⁶ M. Moreover, electrodes based on POT doped with BF₄⁻ show rather unstable potential. On the contrary, electrode 10 based on POT doped with CB₁₁H₆Br₆⁻ and a film thickness of ca. 10 μm shows a sub-Nernstian

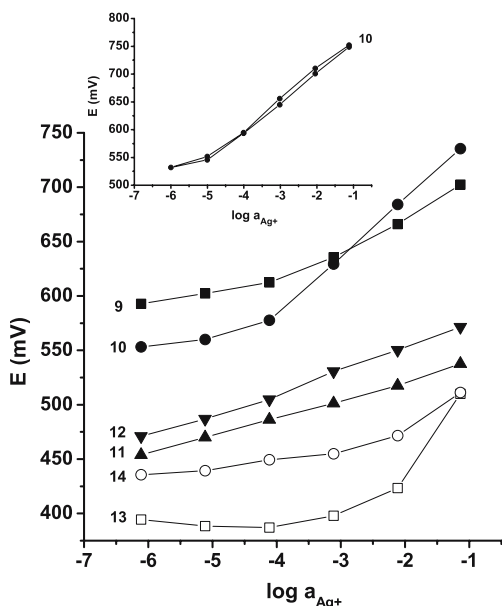


Fig. 5 Calibration plots for electrode **9**(▲), electrode **10**(●), electrode **11**(▲), electrode **12**(▼), electrode **13**(□), and electrode **14**(⊘) based on electrochemically polymerized POT (see Table 3), in AgNO_3 with 0.1 M KNO_3 as background electrolyte, and AgNO_3 without background electrolyte (inserted figure)

response to Ag^+ in a wider concentration range (D.L. ca. $10^{-4.5}$ M) (Table 3). The improved cationic response of electrode **10** compared to **13** and **14** can be related to the immobilization of the large and lipophilic doping anion ($\text{CB}_{11}\text{H}_6\text{Br}_6^-$) in the conducting polymer film. In fact, electrode **10** is the only one from all the POT-based electrodes fabricated by electrochemical polymerization that shows a similar potentiometric behavior as the POT-based electrodes fabricated by solution casting. As shown by the inserted figure in Fig. 5, only a slight hysteresis is present in the calibration of the electrode **10**. The response time is 73 s ($n=3$), and the short-time potential drift at the two concentrations considered is between 1.1 and 2.0 mV/min. Thus, it can be concluded

that the thickness of the film is definitely affecting the potentiometric response of the electrode, as the different potentiometric response for electrode **9** (ca. 1 μm) and **10** (ca. 10 μm) indicates. Furthermore, the doping anion plays a crucial role in the case of electrochemically synthesized POT.

Selectivity coefficients for Ag^+ -ISEs based on electrochemically synthesized POT

In Fig. 6, it can be seen that selectivity coefficients for electrode **10** ($\log K_{\text{Ag},j} \approx -2.5, \dots, -3.5$) are very similar, or slightly more negative, than those shown by electrode **5** (with 10% w/w of $\text{AgCB}_{11}\text{H}_6\text{Br}_6$ as lipophilic additive) (Fig. 4b), except for cases where $j = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Hg}^{2+}$. Actually, the best value obtained for $\log K_{\text{Ag}, \text{Fe(II)}}$ is the one shown by electrode **10** ($\log K_{\text{Ag}, \text{Fe(II)}} = -4.2$). The same is true for Hg^{2+} ion ($\log K_{\text{Ag}, \text{Hg(II)}} = -2.6$). This value represents a reduction in the Hg^{2+} interference of

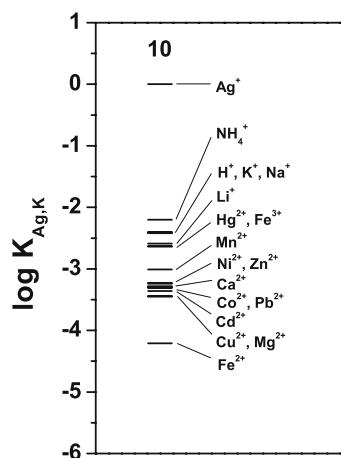


Fig. 6 Selectivity coefficients ($\log K_{\text{Ag},j}$) calculated by the separate solution method (SSM) for electrode **10** based on electrochemically polymerized POT (see Table 3)

Table 3 Slope and standard potential (mean values \pm S.D., $n=3$) calculated from the linear range of the calibration plots for GC/POT electrodes prepared by electrochemical polymerization and conditioned in 0.01 M AgNO_3 solutions

Electrode	Doping anion	Charge (mC)	Calibration in AgNO_3^a		Calibration in $\text{AgNO}_3 + 0.1 \text{ M KNO}_3^b$	
			Slope (mV per decade)	Standard potential (mV)	Slope (mV per decade)	Standard potential (mV)
9	$\text{CB}_{11}\text{H}_6\text{Br}_6$	8	31 ± 3	751 ± 4	38 ± 7	747 ± 6
10	$\text{CB}_{11}\text{H}_6\text{Br}_6$	74	50 ± 3^d	821 ± 14^d	48 ± 8^d	803 ± 8^d
11	BF_4	8 ^c	24 ± 2	569 ± 7	21 ± 3	554 ± 11
12	BF_4	8	35 ± 4^d	665 ± 11^d	24 ± 5^d	603 ± 10^d
13	BF_4	74 ^c	10 ± 4	600 ± 10	55 ± 12^e	561 ± 30
14	BF_4	74	31 ± 2	583 ± 34	33 ± 7	551 ± 10

^a Linear range 10^{-1} – 10^{-4} M

^b Linear range 10^{-1} – 10^{-3} M

^c After polymerization the POT films were electrochemically reduced (undoped) by applying 0 V for 1 min

^d $n=2$

^e Non-linear behavior and super-Nernstian slope (see Fig. 5)

more than one and a half orders of magnitude compared to the rest of electrodes tested. Actually, the Hg^{2+} interference shown by electrode **10** is smaller than that observed for Ag_2S -based [1–5] and PEDOT-based [25] Ag^+ -ISEs, and close to that shown by the best PVC-based Ag^+ -ISEs using neutral carriers as silver ionophores [7, 15, 17, 19, 24].

UV-vis measurements

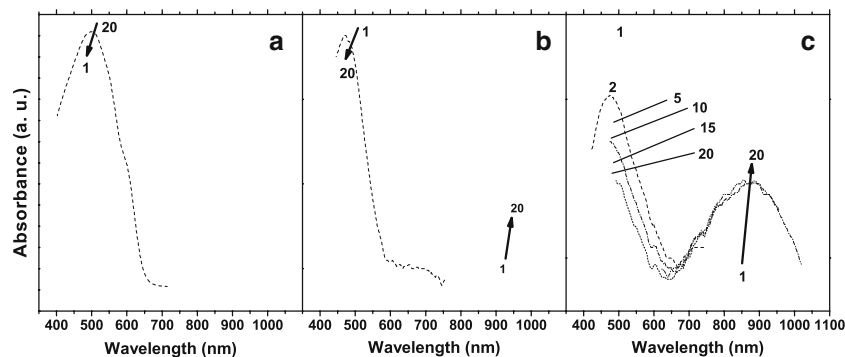
Figure 7 shows the UV-vis spectra of films of chemically polymerized POT (Fig. 7a), and electrochemically polymerized POT with BF_4^- (Fig. 7b) and $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ (Fig. 7c) as doping anions. The spectra are taken during the conditioning step in 0.01 M AgNO_3 solutions, after film deposition. The spectrum recorded for chemically polymerized POT (Fig. 7a) shows the typical features for a conjugated polymer in the neutral (undoped) state [32, 33]: the $\pi\text{-}\pi^*$ absorption band with a maximum at ca. 496 nm. It is also observed that no significant changes take place during the conditioning, and POT remains in the neutral state even after 19 h in 0.01 M AgNO_3 solution. Figures 7b and 7c show the spectra recorded for electrochemically polymerized POT in which the $\pi\text{-}\pi^*$ absorption band (ca. 475 nm) is followed by a second band located at longer wavelengths. These features indicate that electrochemically polymerized POT films are not completely undoped, but exist in a slightly oxidized state [32, 33]. In the case of $\text{POT}(\text{BF}_4)$ only minor changes in the UV-vis spectrum are observed after 19 h (Fig. 7b). On the contrary, the UV-vis spectrum of $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$ changes significantly already after 1 h of conditioning in 0.01 M AgNO_3 solution (curve 2, Fig. 7c). The continuing decrease with time in the $\pi\text{-}\pi^*$ transition peak and the simultaneous increase in the second band indicates that $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$ is gradually oxidized by Ag^+ ions present in the conditioning solution [29]. A typical isosbestic point that indicates the

change from neutral to conducting form is clearly seen for the $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$ film. The reason for the difference in the doping level of $\text{POT}(\text{BF}_4)$ and $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$ films after conditioning in 0.01 M AgNO_3 solutions seems to be the different oxidation potential exhibited by the two polymers. For reasons not yet known, polymerization of 3-octylthiophene in $\text{AgCB}_{11}\text{H}_6\text{Br}_6\text{-ACN}$ solution results in films with lower oxidation potential than POT films polymerized in $\text{LiBF}_4\text{-PC}$ solution. Therefore, $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$ films are more easily oxidized by Ag^+ ($E^0_{\text{Ag}/\text{Ag}^+} = 0.558$ V vs SCE) than $\text{POT}(\text{BF}_4)$ films. This is reflected also in a higher standard potential for electrodes based on $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$ compared to those based on $\text{POT}(\text{BF}_4)$, as shown in Table 3. Upon conditioning in 0.01 M AgNO_3 , the standard potential of the electrodes based on $\text{POT}(\text{BF}_4)$ are drifting from potentials that were initially even higher than those shown by electrodes based on $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$ films, toward potentials very similar to those shown by electrodes based on chemically polymerized POT. In contrast to $\text{POT}(\text{CB}_{11}\text{H}_6\text{Br}_6)$, the $\text{POT}(\text{BF}_4)$ films are gradually reduced by water and develop the red color typical for POT in the neutral form when in contact with aqueous solutions.

Conclusions

Potentiometric sensors based on POT were studied as Ag^+ -selective electrodes. POT films were prepared from chemically polymerized POT (solution casting), and electrochemically polymerized POT. Results reveal that all the ion sensors fabricated by solution casting show Nernstian or slightly sub-Nernstian response to Ag^+ . The selectivity and lifetime of the electrodes are affected by the composition of the POT membranes. Actually, electrodes based on POT and 20% (w/w) TpFPB^- show high selectivity to Ag^+ in comparison to alkali, alkaline earth and transition metals ($\log K_{\text{Ag}, j} = -3, \dots, -5$), except for Hg^{2+} ($\log K_{\text{Ag}, \text{Hg(II)}} = -0.8$). Among the sensors prepared by electrochemical polymerization only those based on thick films of POT doped with the immobile and lipophilic anion $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ show a proper (sub-Nernstian) response to Ag^+ ions. The interference from Hg^{2+} is significantly lower for electrodes based on electrochemically synthesized

Fig. 7 UV-vis spectra recorded during the conditioning of films based on chemically polymerized POT with no additives (a), electrochemically polymerized POT doped with BF_4^- (b) and electrochemically polymerized POT doped with $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ (c) in presence of 0.01 M AgNO_3 . The spectra were recorded at intervals of 1 h during 19 h



POT(CB₁₁H₆Br₆) films compared to electrodes based on chemically synthesized POT films. It is of particular importance that chemically synthesized undoped POT (without any additives) shows a sensitive and selective potentiometric response to Ag⁺ ions although UV-vis results show that POT remains in its undoped form, i.e. POT is not oxidized by Ag⁺. This indicates that undoped POT can exhibit good sensitivity and selectivity to Ag⁺ also in absence of metallic silver in the polymer film. In this case, the potentiometric response is related to interactions between Ag⁺ and the conjugated polymer backbone. This is likely, because Ag⁺ is known to interact with sulfur atoms [6] and double bonds (π -coordination) [10, 23, 34], both of which are present in POT and other polythiophenes. These results show that electroless reduction of Ag⁺ in the conducting polymer film is not a prerequisite for Ag⁺ selectivity of conjugated polymers.

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