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Potentiometric sensors based on poly(3,4-ethylenedioxythiophene) (PEDOT) doped with sulfonated calix[4]arene and calix[4]resorcarenes

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Abstract Potentiometric ion sensors have been prepared by galvanostatic electrosynthesis of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) doped with *p*-sulfonated calix[4]arene (C[4]S) and *p*-methylsulfonated calix[4]resorcarenes (R_n [4]S) with alkyl substituents of different chain length ($R_1 = \text{CH}_3$; $R_2 = \text{C}_2\text{H}_5$; $R_3 = \text{C}_6\text{H}_{13}$). The bowl-shape of these doping ions makes them suitable as ionic recognition sites, and their bulky character is expected to prevent them from leaching out of the conducting polymer membrane. For comparison, sensors based on PEDOT doped with poly(styrene sulfonate) (PSS) and poly(vinyl sulfonate) (PVS) were also constructed. The resulting GC/PEDOT electrodes were conditioned in $0.01 \text{ mol L}^{-1} \text{ AgNO}_3$ and their performance as Ag^+ ion-selective electrodes (ISEs) studied. Results reveal that selectivity and lifetime of the electrodes is affected by the doping anion structure, although all electrodes show selectivity towards Ag^+ ions. Interaction of Ag^+ with sulfur atoms present in the conducting polymer backbone is considered to be the main reason for this behavior. A second set of electrodes was constructed and conditioned in $0.1 \text{ mol L}^{-1} \text{ KCl}$. These electrodes were tested in chloride solutions of quaternary ammonium cations, showing that C[4]S and R_2 [4]S exhibit significant sensitivity towards pyridinium.

Keywords Ion-selective electrode · Silver · Calix[4]arene · Calix[4]resorcarene · Conducting polymer

Introduction

Potentiometric ion sensors based on conducting polymers (CPs) is a field that has grown significantly over the last decade [1]. The unique properties of CPs as ion-to-electron transducers make them very suitable for use as solid contact materials in ion-selective electrodes (ISEs) based on plasticized PVC membranes [2]. In solid contact ISEs (SCISEs) the selectivity is induced by immobilization of ionophores (ion-recognition molecules) in the PVC matrix. However, as a consequence of new market requirements, miniaturization has become one of the main issues in sensor construction for applications in very different fields such as clinical analysis [3] or environmental monitoring [4]. Therefore, new approaches in sensor development are needed in order to simplify the construction procedure and to facilitate miniaturization. Following this premise, elimination of the plasticized PVC membrane from solid contact ISEs by inclusion of ion-recognition molecules in the bulk of the CP enables simplification of the sensor. Thus, electrochemical polymerization of a conducting polymer in presence of a bulky ion with ion-recognition properties is a simple one-step process that results in immobilization of the ion-recognition sites in the CP matrix [5]. In such a design, the resulting CP membrane has both ion-recognition and transduction properties.

In this work, *p*-sulfonated calix[4]arene (C[4]S) and *p*-methylsulfonated calix[4]resorcarenes (R_n [4]S) have been used as doping ions in the galvanostatic electrosynthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) for construction of potentiometric ion sensors. PEDOT is used as the CP on the basis of its suitability as ion-to-electron transducer [6, 7]. Calix[*n*]arenes and

Dedicated to Professor György Horányi on the occasion of his 70th birthday in recognition of his outstanding contributions to electrochemistry

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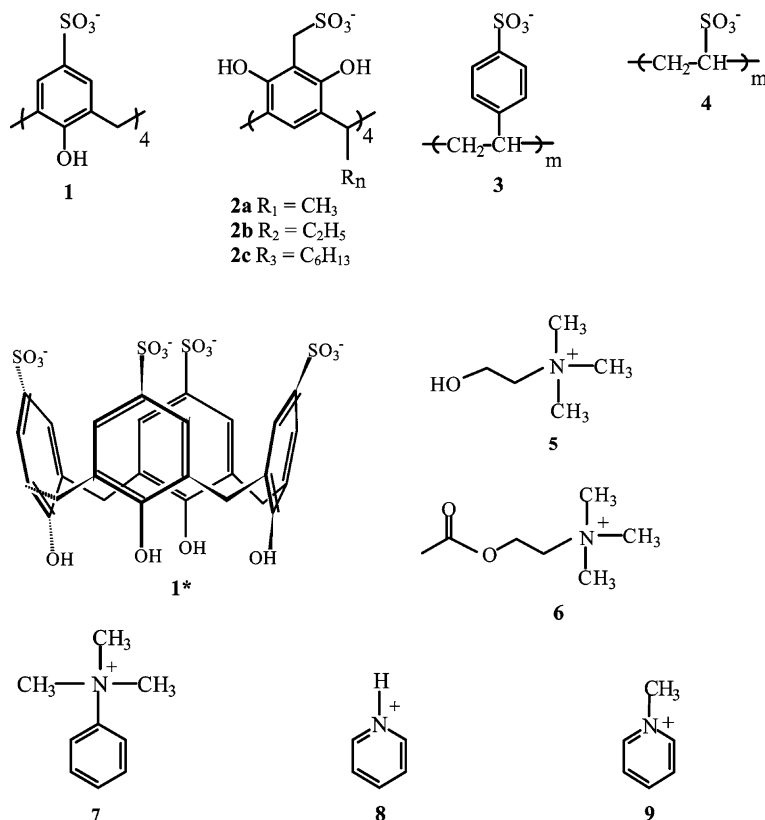
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calix[*n*]resorcarenes form a huge group of bowl-shaped molecules that can easily be functionalized. The size of the cavity and the type of substituent aid molecular recognition, which makes them very attractive in host-guest and supramolecular chemistry [8]. Water-soluble sulfonated calix[*n*]arenes [9] have previously been used as doping ions in the conducting polymers polypyrrole (PPy) [10, 11] and polyaniline (PANI) [12]. The main objective of this work was to study the performance of these types of conducting polymer-based electrode as potentiometric sensors and to determine possible differences between sensor selectivity based on the different structures of the doping anions.

Both C[4]S and R_n [4]S have a bowl-shaped structure, but a different number of -OH groups placed in different positions. The position of the sulfonate group is also different. The acidic character of the molecules is, therefore, not the same. R_n [4]S with different alkyl substituents is used to study the effect of alkyl chain length on the performance of the sensor. PEDOT doped with the bowl-shaped C[4]S and R_n [4]S are compared with PEDOT doped with poly(styrene sulfonate) (PSS). PSS is a linear molecule with sulfonate-substituted aromatic rings as pendant groups. For comparison, poly(vinyl sulfonate) (PVS) is also used as doping anion. PVS is also a linear molecule with sulfonate groups, but without aromatic rings. In this way, the role played by the aromatic ring of the doping anion can be evaluated. The chemical structures of the different dopants studied are shown in Fig. 1.

Fig. 1 Chemical structures of *p*-tetrasulfonated calix[4]arene (1), *p*-tetra(methylsulfonated) calix[4]resorcarene (2), poly(styrene sulfonate) (3), poly(vinyl sulfonate) (4), (semi) 3D representation of *p*-tetrasulfonated calix[4]arene (1*), choline (5), acetylcholine (6), trimethylphenylammonium (7), pyridinium (8), and *N*-methylpyridinium (9)



Experimental

Chemicals

p-Tetrasulfonated calix[4]arene (4-sulfonic calix(4)arene) (C[4]S) in the acid form is commercially available and was obtained from ACROS organics. *p*-Tetra(methylsulfonated) calix[4]resorcarenes (R_n [4]S) ($R_1 = \text{CH}_3$; $R_2 = \text{C}_2\text{H}_5$; $R_3 = \text{C}_6\text{H}_{13}$), as the sodium salts, were synthesized by following Kazakova's procedure [13]. A small change in the procedure was made in the R_3 [4]S synthesis, however—no addition of acetone was necessary to precipitate the end product, because this precipitated during the neutralization step. Poly(sodium 4-styrene sulfonate) (NaPSS, MW~70,000) and poly(sodium vinyl sulfonate) solution (NaPVS) were obtained from Aldrich. The monomer 3,4-ethylenedioxythiophene (EDOT, >97%) was obtained from Bayer. All other chemicals were analytical-reagent grade. ELGA ultrapure water (resistivity 18.2 M Ω cm) was used to prepare all solutions.

Fabrication of the potentiometric sensor by electrochemical polymerization

Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) was carried out by using an Autolab General Purpose Electrochemical System (AUT20).

FRA2-Autolab, Eco Chemie, The Netherlands) connected to a conventional one-compartment electrochemical cell. The working electrode was a glassy carbon (GC) disc electrode with an area of 0.07 cm^2 . A GC rod was used as the auxiliary electrode. No reference electrode was used, in order to prevent any anion other than the desired doping anion from being trapped in the polymer film during the electropolymerization procedure. Prior to polymerization, the GC working electrode was polished with $0.3 \mu\text{m}$ alumina, rinsed with water and cleaned ultrasonically for at least 15 min. PEDOT was deposited on the GC working surface by galvanostatic electrochemical polymerization from a deaerated aqueous solution containing 0.01 mol L^{-1} EDOT and the supporting electrolyte: 1 mmol L^{-1} H(C[4]S), 1 mmol L^{-1} Na(R_{*n*}[4]S), 0.1 mol L^{-1} NaPSS or 0.1 mol L^{-1} NaPVS. The chemical structures of the anions of the supporting electrolytes used are shown in Fig. 1; hereafter they will be denoted by the abbreviations **(1)**=C[4]S, **(2a)**=R₁[4]S, **(2b)**=R₂[4]S, **(2c)**=R₃[4]S, **(3)**=PPS, and **(4)**=PVS. To produce a polymerization charge of 25 mC, a constant current of 0.014 mA (0.2 mA cm^{-2}) was applied for 1785 s in the process of polymerization of PEDOT. The resulting electrodes based on PEDOT (GC/PEDOT) doped with different doping anions were conditioned in 0.1 mol L^{-1} KCl solution for at least 1 day before further use. These electrodes were kept in 0.1 mol L^{-1} KCl between measurements. A second set of all the different GC/PEDOT electrodes was conditioned in 0.01 mol L^{-1} AgNO₃ prior to measurements and from now on they will be called Ag⁺-ISEs when considered as a group. The Ag⁺-ISEs were kept in 0.01 mol L^{-1} AgNO₃ 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 Ag|AgCl|KCl (3 mol L^{-1}). When measuring in nitrate solutions, a salt bridge containing 1 mol L^{-1} KNO₃ was used to connect the reference electrode to the test solution.

The potentiometric response of GC/PEDOT electrodes conditioned in 0.1 mol L^{-1} KCl was studied in KCl aqueous solutions with and without background electrolyte (0.1 mol L^{-1} NaCl). Selectivity coefficients were determined by the separate solution method (SSM). When a large number of cations are tested this method is undoubtedly the fastest compared with any other available method. We therefore decided that SSM was the best method in our work, despite its limitations [14], to compare several different types of electrode in a large number of test solutions. Selectivity measurements were done in 0.01 mol L^{-1} solutions of different alkali, alkaline earth, and organic cations. The pH of the test solutions was usually in

the range 5.3–6.9 except for solutions containing acetylcholine (ACh⁺) and pyridinium (Py⁺), for which the pH was in the range 3.7–4.3, and of course solutions containing H⁺ as the only cation (pH=2). Chloride salts were used for all cations tested except for the *N*-methylpyridinium cation (MPy⁺), for which the iodide salt was used.

The potentiometric response of the Ag⁺-ISEs was studied in AgNO₃ aqueous solutions with and without background electrolyte (0.1 mol L^{-1} KNO₃). Selectivity coefficients were determined by the SSM. Selectivity measurements were done in 0.01 mol L^{-1} solutions of the studied ions, except for Hg²⁺, Fe²⁺ and Fe³⁺ for which a $10^{-3} \text{ mol L}^{-1}$ solution at pH 3 was used (pH was fixed by using $10^{-3} \text{ mol L}^{-1}$ HNO₃ as constant background electrolyte). The contribution of H⁺ to the response in these acidic solutions was cancelled by comparison with the electrode response in acidic solutions of Ag⁺ ($10^{-3} \text{ mol L}^{-1}$ AgNO₃ at pH 3). The other test solutions had pH in the range 5.1–5.6, and pH=4.7 for Cu²⁺ and Pb²⁺ cations. Nitrate salts were used for all cations tested.

The activity coefficients were calculated according to the extended Debye–Hückel equation [15]. Correction for the liquid-junction potential was applied (Henderson equation). All the measurements were performed at room temperature ($23 \pm 2^\circ\text{C}$).

Cyclic voltammetry (CV) measurements

Cyclic voltammetry (CV) measurements were performed by using an Autolab General Purpose Electrochemical System (AUT20.FRA2-AUTOLAB, Eco Chemie, The Netherlands). CV measurements were done in a one-compartment three-electrode electrochemical cell where the GC/PEDOT electrode under study was connected as the working electrode. A GC rod was used as the auxiliary electrode and the reference electrode was an Ag|AgCl|KCl (3 mol L^{-1}) electrode. When measurements were performed in nitrate solutions, the reference electrode was connected to the solution via a salt bridge containing 1 mol L^{-1} KNO₃ solution. For all the measurements temperature was $23 \pm 2^\circ\text{C}$.

Results and discussion

Calix[*n*]arenes are known to be selective for organic cations (quaternary ammonium cations) [8, 16]. This is why electrodes based on PEDOT doped with C[4]S and R_{*n*}[4]S were tested in chloride solutions of organic cations after being conditioned in 0.1 mol L^{-1} KCl solutions. Calix[*n*]arenes are also known to host soft metals [8, 17] such as Ag⁺. Therefore, another set of electrodes based on PEDOT doped with C[4]S and R_{*n*}[4]S were conditioned in 0.01 mol L^{-1} AgNO₃ and are referred to as Ag⁺-ISEs.

Sensitivity and selectivity of GC/PEDOT electrodes conditioned in 0.1 mol L⁻¹ KCl

The potentiometric response of the electrodes based on PEDOT doped with the different anions (1)–(4) in KCl solutions with and without 0.1 mol L⁻¹ NaCl as background electrolyte is shown in Fig. 2. For easier comparison of the different electrodes, the calibration plots in Fig. 2a, are shifted relative to each other on the y-axis, except for curve (1), that has its original potential values. The calibrations in KCl solutions without background electrolyte (Fig. 2a), were done in solutions from 10⁻¹ to 10⁻⁶ mol L⁻¹ and back to 10⁻¹ mol L⁻¹ in order to check the reproducibility of the response.

As can be seen in Fig. 2a, hysteresis is present in all the electrode responses. The slope and standard potential values for the calibration curves in Fig. 2a, are shown in Table 1.

All electrode types show sub-Nernstian cationic responses in the concentration range studied (10⁻¹–

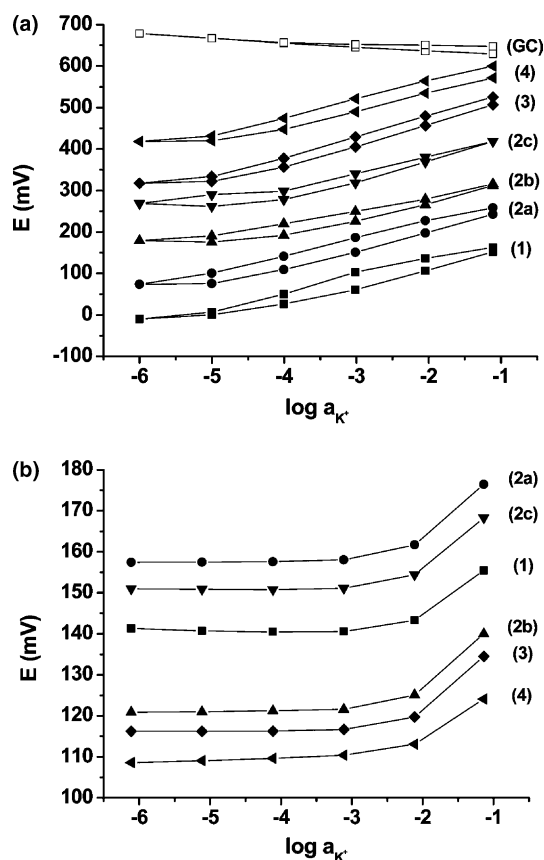


Fig. 2 Calibration plots for electrodes based on PEDOT doped with (filled square) C[4]S (1), (filled circle) R₁[4]S (2a), (filled triangle) R₂[4]S (2b), (inverted filled triangle) R₃[4]S (2c), (filled diamond) PSS (3) and (filled sideways triangle) PVS (4) determined in **a** KCl and **b** KCl+0.1 mol L⁻¹ NaCl. All PEDOT-based electrodes were previously conditioned in 0.1 mol L⁻¹ KCl. The calibration curve for a bare GC electrode is also shown (open squares). For clarity the calibration plots in (a) are shifted arbitrarily toward more positive potentials on the y-axis, except for curve (1) that has its original values

Table 1 Slope and standard potential (mean values \pm SD, $n=3$) calculated from the linear range of the calibration plots (10⁻¹–10⁻⁴ mol L⁻¹) for GC/PEDOT electrodes after conditioning in 0.1 mol L⁻¹ KCl solution

Doping anion	Slope (mV decade ⁻¹)	Standard potential (mV)
C[4]S	42.0 \pm 0.4	204 \pm 1
R ₁ [4]S	43.9 \pm 0.6	223 \pm 2
R ₂ [4]S	39.3 \pm 0.9	206 \pm 4
R ₃ [4]S	46.0 \pm 0.3	214 \pm 3
PSS	52.6 \pm 0.1	197.6 \pm 0.4
PVS	45 \pm 3	162 \pm 7

10⁻⁶ mol L⁻¹) with slopes ranging from 39 to 46 mV decade⁻¹, except for electrodes based on PEDOT doped with PSS (PEDOT/PSS) that have a higher slope (52.6 \pm 0.1 mV decade⁻¹). Considering the large size of the doping anions used they are expected to be immobilized in the conducting polymer film due to steric impediments. Therefore, the electrodes show cationic responses [6]. For comparison, the potentiometric response of bare glassy carbon electrodes in KCl solutions is shown in Fig. 2a. Finally, electrodes based on PEDOT doped with PVS (PEDOT/PVS) showed the lowest reproducibility between samples (SD \pm 3) and the fastest deterioration of the potentiometric response, leading to the conclusion that they are less stable electrodes than the rest. Furthermore, the standard potential shown by PEDOT/PVS electrodes is lower than those shown by the other electrodes.

In Fig. 2b, examples of calibration plots determined in KCl solutions with a constant background (0.1 mol L⁻¹ NaCl) in the concentration range 10⁻¹–10⁻⁶ mol L⁻¹ are shown. It can be seen that electrodes based on PEDOT doped with the anions (1)–(4) are not selective for K⁺ ions, in comparison with Na⁺. Even at high concentrations of K⁺ the slopes of the calibration lines are very low (ca. 15 mV decade⁻¹). Response times were calculated in KCl solutions with a constant background (0.1 mol L⁻¹ NaCl). The response time was defined as the time required for the electrode potential to become equal to its steady state value within 1 mV after increasing the concentration of K⁺ from 10⁻³ to 10⁻² mol L⁻¹ in the same sample solution. The response times were in the range 10–30 s, and the short-term potential drift at the two concentrations considered was between -0.3 and 0.1 mV min⁻¹.

Selectivity coefficients were estimated by using the SSM in solutions of alkali, alkaline earth, and organic cations considering K⁺ as the main ion for the selectivity coefficient calculations (Fig. 3). The selectivity coefficients values obtained cannot be regarded as absolute values, because of the inaccuracy of the SSM method in our system where ions of different charge are involved [14], but they are still useful in order to compare the performance of our different electrodes.

First, electrodes based on PEDOT doped with C[4]S and R_n[4]S are more sensitive to H⁺ than those for which PSS and PVS are used as dopants.

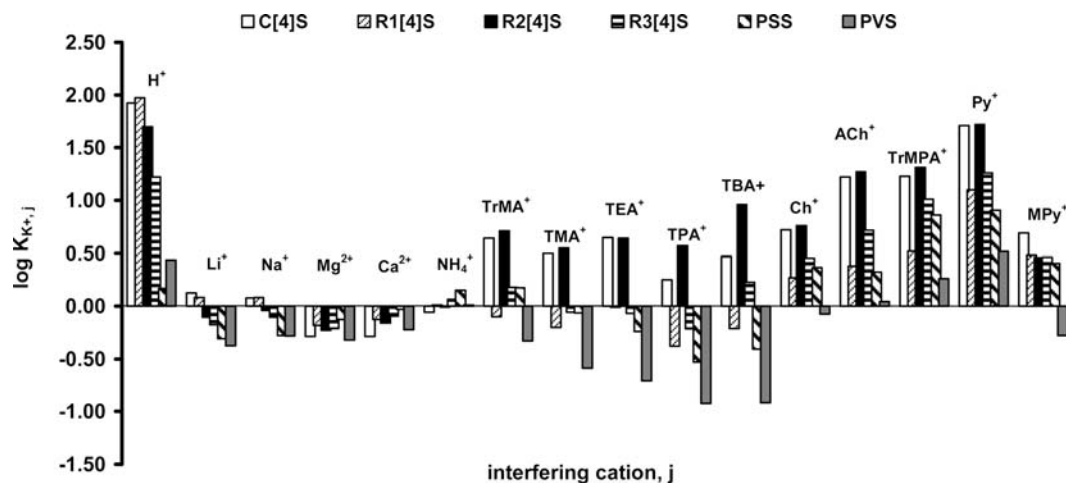


Fig. 3 Selectivity coefficients ($\log K_{K^+, j}$) calculated by the SSM method for electrodes based on PEDOT doped with different doping anions and previously conditioned in 0.1 mol L^{-1} KCl. *TrMA*⁺ trimethylammonium, *TMA*⁺ tetramethylammonium, *TEA*⁺ tetraethylammonium, *TPA*⁺ tetrapropylammonium, *TBA*⁺ tetrabutylammonium, *Ch*⁺ choline, *ACh*⁺ acetylcholine, *TrMPA*⁺ trimethylphenylammonium, *Py*⁺ pyridinium, *MPy*⁺ *N*-methylpyridinium

Furthermore, a decrease in the length of the alkyl chain of the calix[4]resorcarene doping anions increases the pH sensitivity of the sensor. Electrodes based on C[4]S and R₂[4]S as dopants have very similar behavior, exhibiting the highest $\log K_{K^+, j}$ for the organic cations, compared with the other dopants. Special attention should be paid to their affinity towards Py⁺, which might be because of cation- π interaction between the positive charge of the guest cation and the aromatic rings of the host (or doping anion) [8, 18]. Also hydrogen bonding between the N-H groups of Py⁺ and the -OH groups of C[4]S and R_{*n*}[4]S might contribute to the selectivity towards Py⁺. Actually, all the electrodes tested show higher affinity for Py⁺ compared with the other cations tested (with the exception of H⁺ in the cases mentioned previously). However, the affinity of PEDOT/PVS for Py⁺ cannot be attributed to cation- π interactions or hydrogen bonding with the doping anion, because of the lack of aromatic rings in the structure of PVS. This indicates that interactions also occur between the organic cation and the conducting polymer backbone itself. The selectivity of the PEDOT-based electrodes is relatively independent of the lipophilicity of the organic cations (TMA⁺, TEA⁺, TPA⁺, TBA⁺). This is in contrast with the behavior of ion-selective electrodes based on plasticized PVC membranes, for which selectivity toward the tetraalkyl ammonium cations normally increases with the lipophilicity of the cation [18]. In the case of the dopants R₁[4]S, R₃[4]S, PSS, and PVS, the values of $\log K_{K^+, j}$ ($j = \text{TMA}^+, \text{TEA}^+, \text{TPA}^+, \text{TBA}^+$) are rather similar to the values shown for alkali and alkaline earth metal cations, or even more negative, as for PVS.

Sensitivity and selectivity of GC/PEDOT electrodes conditioned in 0.01 mol L^{-1} AgNO₃ (Ag⁺-ISEs)

The potentiometric response of Ag⁺-ISEs in AgNO₃ solutions with and without 0.1 mol L^{-1} KNO₃ as background electrolyte are shown in Fig. 4. For easier comparison of the different electrodes the calibration plots in Fig. 4 are shifted relative to each other on the *y*-axis, except curves (1) and (GC) that have their original potential values.

From the calibrations in AgNO₃ solutions without background electrolyte (Fig. 4a) it can be seen that the electrodes have rather reproducible behavior during calibration from 10^{-1} down to $10^{-6} \text{ mol L}^{-1}$ and back to $10^{-1} \text{ mol L}^{-1}$, at least for electrodes based on PEDOT doped with the C[4]S and R_{*n*}[4]S ($n = 1, 2, 3$) anions. Fig. 4b shows that all the electrodes are selective to Ag⁺, in comparison to K⁺. The slopes and standard potential values for the calibration curves in Fig. 4 are shown in Table 2.

All electrodes show Nernstian (or slightly super-Nernstian) response to silver with rather good reproducibility between samples ($n = 3$), except for the PEDOT/R₁[4]S-based electrodes that exhibit higher standard deviations (SD). The detection limit (DL) for these electrodes is in the range of ca. $10^{-4.5}$ – $10^{-4.8} \text{ mol L}^{-1}$, except for PEDOT/R₃[4]S electrodes (DL ca. $10^{-5.3} \text{ mol L}^{-1}$). Surprisingly, the bare GC electrode is also sensitive to Ag⁺ ($62.0 \pm 0.1 \text{ mV decade}^{-1}$, $n = 2$) as shown in Fig. 4b (DL ca. $10^{-5} \text{ mol L}^{-1}$). This might indicate that metallic Ag is deposited on the GC surface when the GC electrode is in contact with Ag⁺ in solution [19, 20]. The reproducibility of the response for different bare GC electrodes tested in AgNO₃ solutions without constant background (0.1 mol L^{-1} KNO₃) is poor, which is in contrast with the response of the PEDOT-based Ag⁺-ISEs. Deterioration in the response of PEDOT/PSS and PEDOT/PVS is also observed with aging (about 8% loss of slope after 1 month). The response times for Ag⁺-ISEs were calculated in AgNO₃ solutions at a constant background (0.1 mol L^{-1} KNO₃) as indicated in the previous

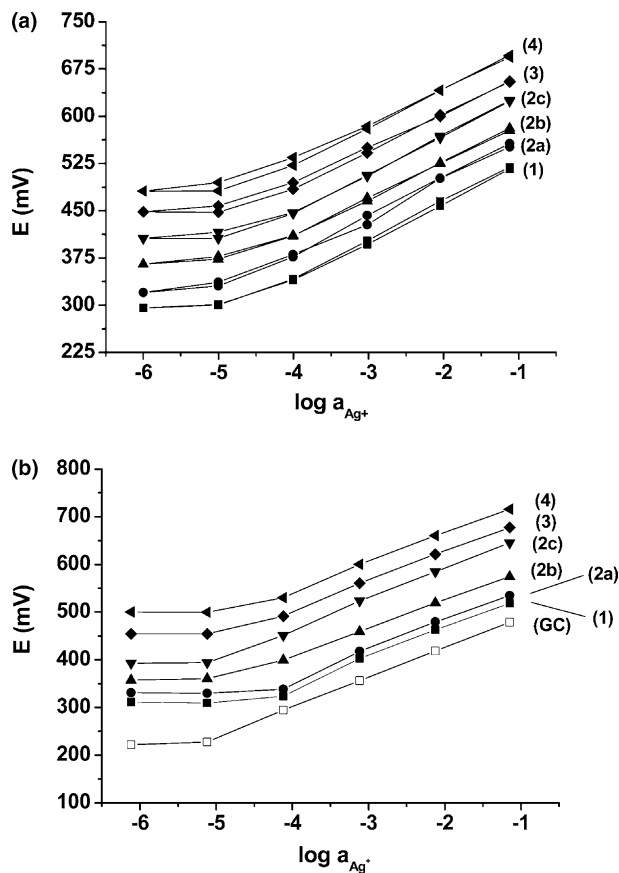


Fig. 4 Calibration plots for electrodes based on PEDOT doped with (filled square) C[4]S (1), (filled circle) R₁[4]S (2a), (filled triangle) R₂[4]S (2b), (inverted filled triangle) R₃[4]S (2c), (filled diamond) PSS (3) and (filled sideways triangle) PVS (4) determined in **a** AgNO₃ and **b** AgNO₃ + 0.1 mol L⁻¹ KNO₃. All PEDOT-based electrodes were previously conditioned in 0.01 mol L⁻¹ AgNO₃. Also shown is the calibration curve for a bare GC electrode (open square). For clarity the calibration plots in (a) and (b) are shifted arbitrarily toward more positive potentials on the y-axis, except curves (1) and (GC) that have their original values

section. The response times were in the range 27–87 s, and the short-time potential drift at the concentrations considered (10⁻³ and 10⁻² mol L⁻¹) was between -1.8 and -0.1 mV min⁻¹.

The influence of the doping anion on the selectivity is shown in Fig. 5. As discussed before, selectivity coeffi-

cient values calculated by SSM for our system cannot be regarded as absolute values, but only as relative values for comparing our different electrodes.

It can be seen that the responses to alkali (log $K_{Ag^+, j} \approx -2, \dots, -2.5$) and alkaline earth (log $K_{Ag^+, j} \approx -3, \dots, -3.5$) metals are very similar for all types of PEDOT-based Ag⁺-ISEs. The electrodes based on PEDOT doped with R₁[4]S (the shortest alkyl-substituted calix[4]resorcarene) show higher log $K_{Ag^+, j}$ values than the other electrodes. The interference from H⁺ (log $K_{Ag^+, H^+} = -0.4$) and Fe³⁺ (log $K_{Ag^+, Fe^{3+}} = -0.8$) is particularly significant for PEDOT doped with R₁[4]S. In general, all Ag⁺-ISE show affinity toward Fe³⁺, typically one of the main interferences for Ag⁺-selective electrodes because of the interaction of Fe³⁺ with sulfur atoms [21]. Actually, all electrodes used in this work have sulfur atoms in the conducting polymer backbone (PEDOT). Another typical interferent in Ag⁺ detection by Ag⁺-ISEs is Hg²⁺ [21, 22]. The Hg²⁺ interference is significant also for the PEDOT-based electrodes (log $K_{Ag^+, Hg^{2+}} \approx -0.5, \dots, -1$).

Finally, as seen in Fig. 5 bare GC electrodes show very low selectivity coefficient values for all the cations tested (log $K_{Ag^+, j} \approx -3, \dots, -4$) except for Hg²⁺ and Fe³⁺. Actually, log $K_{Ag^+, Fe^{3+}} > 0$, which represents the main interference obtained in our measurements. A possible explanation for this interference could be that the silver deposited on the electrode surface during measurements in silver nitrate solutions will be oxidized by Fe³⁺ which is a strong oxidizing agent. Then, the selectivity of bare GC electrodes towards Ag⁺ is lost.

Electroactivity of Ag in the film

The effect of the presence of metallic Ag in the film after conditioning in 0.01 mol L⁻¹ AgNO₃ can be seen in Fig. 6 for the Ag⁺-ISE based on PEDOT doped with R₃[4]S.

The initial cyclic voltammogram shows the beginning of an oxidation peak at ca. 0.4–0.5 V and a clear reduction peak at ca. 0.27 V, which are superimposed on the redox (doping) process of PEDOT (curve 1 in Fig. 6). The oxidation peak at ca. 0.4–0.5 V can be attributed to oxidation of Ag (Ag⁰ → Ag⁺ + e⁻) and the

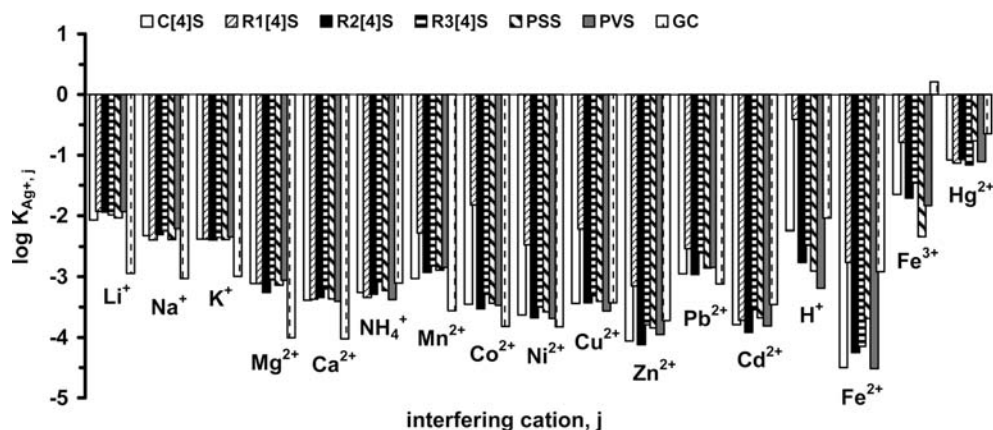
Table 2 Slopes and standard potentials (mean values ± SD, $n = 3$) calculated from the linear range of the calibration plots for GC/PEDOT electrodes after conditioning in 0.01 mol L⁻¹ AgNO₃ solution

Doping anion	Calibration in AgNO ₃ ^a		Calibration in AgNO ₃ + 0.1 mol L ⁻¹ KNO ₃ ^b	
	Slope (mV decade ⁻¹)	Standard potential (mV)	Slope (mV decade ⁻¹)	Standard potential (mV)
C[4]S	60.7 ± 0.3	586.8 ± 0.4	59.1 ± 0.4	588 ± 1
R ₁ [4]S	60 ± 3	600 ± 4	61 ± 5	582 ± 14
R ₂ [4]S	58.8 ± 0.9	573 ± 2	60 ± 1	572 ± 3
R ₃ [4]S	61.1 ± 0.6	569 ± 2	61.5 ± 0.3	566.1 ± 0.8
PSS	56 ± 1	543 ± 4	59.4 ± 0.4	546.1 ± 0.4
PVS	57.8 ± 0.4	536.3 ± 0.9	58.7 ± 0.1	534.2 ± 0.2

^aLinear range 10⁻¹–10⁻⁴ mol L⁻¹

^bLinear range 10⁻¹–10⁻³ mol L⁻¹

Fig. 5 Selectivity coefficients ($\log K_{Ag^+,j}$) calculated by the SSM method for electrodes based on PEDOT doped with different doping anions (figure legend) and previously conditioned in $0.01 \text{ mol L}^{-1} \text{ AgNO}_3$



reduction peak at ca. 0.27 V to the reduction of Ag^+ ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$) in the polymer film. Pretreatment of the electrode by applying a potential of 0.4 V for 3 min has only a minor effect on the cyclic voltammogram (curve 2 in Fig. 6). However, after application of 0.5 and 0.6 V the redox waves at ca. 0.4 – 0.5 and ca. 0.27 V disappear (curves 3 and 4 in Fig. 6). This indicates that oxidation of metallic Ag to Ag^+ causes a loss of silver from the polymer film. However, the cyclic voltammogram still contains some features that indicate the presence of traces of silver in the film. These features are seen most clearly as a step-wise increase in the reduction current at ca. 0.1 – 0.2 V and a step-wise decrease in the oxidation current at ca. 0.4 V . This means there is an

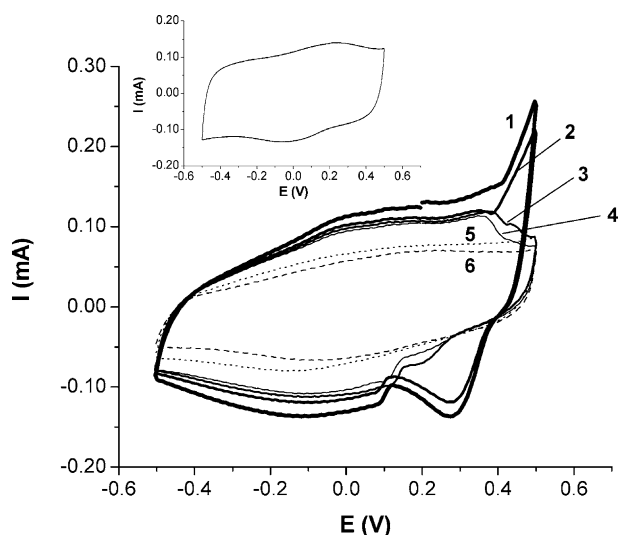


Fig. 6 Cyclic voltammograms for PEDOT($\text{R}_3[4]\text{S}$) electrodes previously conditioned in $0.01 \text{ mol L}^{-1} \text{ AgNO}_3$ (for at least 1 day) after no pretreatment (1) and after applying a potential of 0.4 V (2), 0.5 V (3), 0.6 V (4), 0.7 V (5) and 0.8 V (6) for 3 min in a pretreatment step. Cyclic voltammograms recorded after polymerization of PEDOT($\text{R}_3[4]\text{S}$) before any conditioning are shown in the inserted figure. All voltammograms shown are the tenth scan of a series, except for the voltammogram after no pretreatment (1) and polymerization (inserted figure) that are the third scan of a series. Voltammograms were recorded in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ at 0.1 Vs^{-1} scan rate

additional broad reduction wave from $+0.1$ to -0.5 V and a corresponding oxidation wave up to ca. $+0.4 \text{ V}$. This additional current might arise from Ag^+ complexes (with lower redox potentials than free Ag^+) present in the polymer film. It is known that complexation of Ag^+ by strong coordinating ligands can shift the reduction potential of Ag^+ by 0.5 V in the negative direction, which has been utilized in “solvo-controlled doping” of conducting polymers [23]. After application of even higher positive potentials (0.7 and 0.8 V) the current decreases in the whole potential range studied (curves 5 and 6 in Fig. 6) and the shape of the cyclic voltammogram becomes similar to that of the PEDOT electrode obtained after polymerization before any conditioning in AgNO_3 (Fig. 6, inserted figure). This indicates that Ag^+ ions bound to the polymer can be removed by applying a sufficiently positive potential that creates strong electrostatic repulsion between Ag^+ and the positive charges of oxidized PEDOT. However, some loss in electroactivity of the PEDOT/ $\text{R}_3[4]\text{S}$ film is seen after total stripping of silver. This might be because of irreversible structural changes in the CP film caused by anodic stripping of silver. The same behavior was also observed for electrodes based on PEDOT doped with PVS after conditioning in $0.01 \text{ mol L}^{-1} \text{ AgNO}_3$. In contrast, no loss of electroactivity was seen for PEDOT/ $\text{R}_3[4]\text{S}$ films conditioned in KCl (without silver in the film) under the same experimental conditions. This loss of electroactivity at the positive potentials applied can therefore be related to the stripping of silver from the CP film, and not to overoxidation of the CP film.

Conclusions from these experiments are in good agreement with the observation of metallic deposits in the CP layer after conditioning of the electrodes in $0.01 \text{ mol L}^{-1} \text{ AgNO}_3$. Visual inspection of the electrodes also reveals the presence of a grey layer on top of the CP film. Such features may result from oxidation of the conducting polymer by Ag^+ giving rise to deposits of metallic silver in the polymer film, as previously described for polyaniline [24], poly(1,8-diaminonaphthalene) [25], poly(3-alkylthiophene) [23] and polypyrrole [26]. In addition to complexation of Ag^+ by the polymer, the presence of metallic Ag in the polymer film

might also contribute to the sensitivity and selectivity towards Ag^+ shown by the PEDOT-based electrodes studied.

Conclusions

Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with sulfonated calix[4]arenes and calix[4]resorcarenes were studied as potentiometric sensors for inorganic and organic cations. The results show that the doping anions influence the sensitivity and selectivity of the conducting polymer-based potentiometric sensors. Measurements made in solutions of alkali metals, alkaline earth metals, and organic ammonium cations reveal different selectivity patterns for the PEDOT-based electrodes doped with different anions. Significant sensitivity to pyridinium was observed when C[4]S and R₂[4]S were used as dopants. However, PEDOT doped with sulfonated calix[4]arenes and calix[4]resorcarenes is more sensitive to pH than PEDOT doped with PSS and PVS. All PEDOT-based electrodes studied show high selectivity to Ag^+ ions. The lifetimes of the electrodes were found to depend on the structure of the doping anions. PEDOT doped with PSS and PVS have shorter lifetimes than the other PEDOT-based electrodes studied. The doping ion influences also the selectivity to Ag^+ . However, the results indicate that the Ag^+ selectivity is largely a feature of PEDOT itself. Even PEDOT doped with NO_3^- were found to be selective to Ag^+ (results not shown). The potentiometric response to Ag^+ might be partly because of interactions between Ag^+ and the sulfur atoms present in the backbone of PEDOT and partly because of the presence of metallic Ag in the polymer film.

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