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Modification of Potentiometric Selectivity of Polypyrrole Films Doped with Metal Complexing Ligands (PPy-MCL films)

by Jan Migdalski

Faculty of Material Science and Ceramics, University of Mining and Metallurgy, Al. Mickiewicza 30, PL–30059 Kraków, Poland

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It has been shown that the potentiometric selectivity of PPy–MCL films (MCL — Metal Complexing Ligand) can be adjusted by changing the redox status of the PPy film. Conducting polymer based potentiometric sensors with selectivities similar to those observed for commercial ISE membranes can be obtained by proper oxidation of the PPy–MCL films.

Jak wykazano, selektywność filmów polipirolowych PPy domieszkowanych anionami kompleksonów MCL (MCL — Metal Complexing Ligand) może być modyfikowana przez zmianę stopnia utlenienia tych filmów. Odpowiednie utlenienie filmów PPy–MCL pozwala uzyskać polipirolowe czujniki potencjometryczne o selektywności zbliżonej do tej, obserwowanej w konwencjonalnych elektrodach jonoselektywnych.

Dynamic progress in the field of genetic engineering, clinical chemistry or biotechnology demands increasingly sophisticated chemical sensors with reduced size, improved stability and reliability, *etc.* These demands may be met by applying conducting polymers and many reviews on this can be found [1–6]. Recently they are widely used as mediating layers of the potentiometric sensors without internal solution [7–11]. They were used also as an active part (membrane) of amperometric [12–13] or potentiometric sensors, designed *e.g.* for sulfide determination [14]. A successful use of such conducting polymer based membranes for potentiometric detection of ionic surfactant was also described [15].

One of the first and the most investigated conducting polymers, polypyrrole (PPy) [16–26], can be conveniently prepared by electro-oxidation in aqueous or organic solutions. The polymer is then simultaneously doped by the electrolyte anion.

The size and chemical properties of the doping anion as well as subsequent conditioning of the film determine the ionic sensitivity of the PPy film (which can be anionic, cationic or mixed), its selectivity and the rate of redox response [28–29].

According to the literature data, the anionic or cationic sensitivity of PPy films can be obtained by doping them with: a) small and mobile anions, which can be exchanged with those from solution, and b) big anions (usually organic) immobilized into the PPy film.

In the first case, the anionic sensitivity obtained is a result of the anion exchange between the film and solution phases. Almost all small and mobile anions can be involved in the exchange process and for this reason the observed anionic response is non-selective [30]. Moreover, such anionic sensitivity is dependent on the oxidation status and it disappears during the film reduction. A non-selective anionic response was observed for the PPy films doped with small inorganic anions, such as chloride [16–17], nitrate [18–19], fluoroborate [20] and perchlorate [21]. Such sensors, although non-selective, are used in clinical chemistry for the chloride determination in blood serum [17,27].

In the second case, large, immobilized anions cannot be exchanged with those from the solution, and no anionic sensitivity is observed. These anions are not removed from the film during its reduction and the cation uptake took place to preserve the film neutrality. The cationic sensitivity of the reduced film is a result of the cation-exchange processes. Since the cation bonding by the sulfonate group is not a selective process, almost all the small and mobile cations can be involved in the exchange process and the observed cationic response of the film is not selective. Such non-selective cationic responses have been successfully induced for the PPy films doped with dodecylosulfonate [22], indigo carmine [23,32] and naphtalenosulfonate [24]. The ionic response of this type disappears or becomes mixed during the film re-oxidation. Since both PPy⁰ and PPy⁺ are present in the PPy backbone, the redox response of the film is also observed.

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The mixed, redox and ionic sensitivity of conducting polymers has been described mathematically [31] and confirmed experimentally [26,32–35].

Cationic sensitivity and improved selectivity of the PPy films can be obtained by doping them with large-molecular-weight metal-complexing ligands (MCL) [36–41]. Such ligands contain one or more protonated sulfonate groups $-SO_3H$ used in the doping of PPy and electron-donor sites (Metal Complexing Groups MCG, *i.e.* –OH, –COOH) responsible for complexing cations. It was shown previously that the MCL molecules retain their complexing properties in the film and that they allow the complex formation inside the PPy layer [37–38].

The cationic sensitivity of the PPy–MCL films can be induced by two distinctively different, although in practice concurrent processes, *i.e.* either by the film reduction or by the complex formation inside the film.

In the former process, accidental cations are attracted to the polymer film due to the demand for the charge compensation. It leads to inducing the non-selective cationic sensitivity, which disappears during the film oxidation.

The second process is caused by the complex formation with MCG groups. This leads to inducing the selective cationic sensitivity, which is independent of the polypyrrole film oxidation state. Effective procedures for inducing the desired cationic sensitivity of the PPy–MCL films have been described by Migdalski *et al.* elsewhere [41]. Sensors of this type have been used in the analytical practice [39–40].

In this work, comprehensive studies on the selectivity of the PPy–MCL film's potentiometric response are described. As it will be shown, the selectivity can be adjusted by properly choosing the deposition conditions as well as the oxidation and reduction states of the existing PPy–MCL film.

EXPERIMENTAL

Chemicals

The selected MCL ligands:

- 2-(o-arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic sodium salt, C₁₆H₁₁O₁₁N₂S₂AsNa₂, (Arsenazo I);
- [1-(1-hydroxy-2-naphthylazo)-2-naphtol-4-sulfonic]sodium salt, C₂₀H₁₃N₂NaO₅S, (Calcon);
- 1-hydroxy-4-sulfobenzoic acid p.a., $C_7H_6O_6S \cdot H_2O(SSA)$;
- 1,2-dihydroxybenzene-3,5-disulfonic disodium salt p.a., $C_6H_4O_8S_2Na_2H_2O_3$, (Tiron);
- C₃₀H₁₄O₂₂N₄S₆Na₅,H₂O (calcion or calcichrome), were all obtained from POCh.

All the listed MCL ligands contained one or more $-SO_3^-$ anionic groups and were introduced to the PPy films as immobilized doping anions. All MCLs studied preserved their complexing properties in the PPy films and were able to form complexes with Ca⁺², Mg⁺² and Cu⁺² cations.

Pyrrole (Merck) was purified by double distillation under argon and then was stored under argon at low temperature and was protected from light.

The CaCl₂ p.a. (POCh), MgCl₂ p.a (POCh), MgO p.a. (POCh), CaO p.a. (POCh), KCl p.a. (Sigma Chemicals), NaCl p.a. (Merck), HCl p.a. (POCh), H_2SO_4 p.a. (POCh), CuSO₄ p.a. (Merck), $K_3Fe(CN)_6$ p.a (POCh) and $K_4Fe(CN)_6$ p.a. (POCh) were used as received.

Water, re-distilled from quartz, was used to prepare the solutions. All the solutions with concentrations lower then $0.01 \text{ mol } L^{-1}$ were prepared just before use.

Instrumentation

The electrochemical polymerization of pyrrole was performed using an EA–9C type electrochemical analyser (MTM Poland). The polymerization was performed in a single-compartment, three-electrode electrochemical cell. The working electrode, to be covered with a PPy film, was a platinum (Pt) or glassy carbon (GC) disc electrode of the area of about 0.03 cm² or 0.07 cm². The reference electrode was an Ag/AgCl/sat.KCl electrode, which was connected to the cell *via* a bridge filled with supporting electrolyte solution. A Pt wire (of the area of about 2 cm²) was used as the auxiliary electrode.

Before polymerization of pyrrole, the Pt or GC discs were polished with 0.3 μ m alumina and carefully rinsed with water. Next, the electrode to be covered with PPy was immersed in ethanol and placed in an ultrasonic bath for about 10 min. Just after this, the electrode was rinsed with water and immediately immersed in the solution used for the electropolymerization. Electrodeposition was performed from the solution containing 0.1 mol L⁻¹ pyrrole and selected MCL with the given concentration: 0.025 mol L⁻¹ Arsenazo-I, pH = 1.6; 0.01 mol L⁻¹ Calcon (pH = 1.5); 0.1 mol L⁻¹ Tiron (pH = 0.9); 0.1 mol L⁻¹ SSA (pH = 1); saturated Calcichrome (pH = 1.5).

Prior to use, the sodium cations were removed from sodium salts of MCL with DOWEX 50WX8 50/ 100 ion exchanger. The solutions were saturated with argon for at least 20 min before polymerization, and argon was passed over the solution during electropolymerization.

Polypyrrole was electrochemically deposited on the working electrode by cycling the potential at a scan rate of 20 mV s⁻¹, or potentiostatically, under constant potential.

The maximal ranges of potential cycling were as follows: from -0.5 to +0.65 V for Arsenazo-I; from -0.2 to +0.8 V for SSA; from -0.4 to +0.65 V for Tiron; from -0.3 to +0.65 V for Calcon and from -0.3 to +0.7 V for Calcichrome.

The deposition time was dependent on the selected potential range and was equal to 20-40 subsequent 2-way scans .

Under the potentiostatic conditions, the most positive potential value was chosen and the deposition time was usually equal to 10 min. The PPy films obtained were $10-50 \,\mu$ m thick, smooth and shiny, and they had good mechanical properties. The cationic sensitivity was induced by soaking in alkaline medium containing main ion or under electrochemical condition as described elsewhere [41].

All the potentiometric measurements were performed using a home-made 8-channel set-up. The input impedance was greater than 10¹³ ohms and the input current was lower then 0.1 pA for each 8 inputs as well as for the reference electrode input. The multi-channel potential-meter was coupled with a personal computer equipped with a 16-bit-resolution data-acquisition card CIO–DAS802/16 (ComputerBoards) and the custom-made software.

Ag/AgCl/sat KCl electrodes were used as the reference electrodes.

All experiments were performed at room temperature (about 24°C).

After the oxidation or reduction the PPy–MCL films were soaked in an appropriate solution without redox agent and the potential drift was monitored. When the potential drift was below 0.2 mV min⁻¹ the open cir-cuit values were measured.

RESULTS AND DISCUSSION

The nature of the cationic sensitivity of the PPy-MCL films

As it was shown previously [37–41], the desired cationic sensitivity can be induced in the PPy films doped with the MCL ligands. In contrast to the former observations, the ionic sensitivity of such sensors was independent on the oxidation state of the PPy films, and a dual sensitivity of those films could be exploited in the course of the potentiometric titrations [39].

To explain this unusual behaviour, the titration of selected MCL's with concentrated NaOH was performed. Figure 1 shows the titration curves obtained for Arsenazo-I alone and for a mixture of Arsenazo-I with Cu^{+2} ions. Prior to the titration the sodium cations were removed from the sodium salt of Arsenazo-I with the DOWEX 50WX8 50/100 ion exchanger and substituted with protons. A single and high potential jump (as expected for the strong acid titration), and a small titrant consumption was observed during the titration of a 0.1 mmol Arsenazo-I sample. It looks that only protonated sulfonate groups were neutralised during this stage of titration. If the titration of Arsenazo-I was stopped at pH = 10 and $CuSO_4$ was added, the solution rapidly re-acidified and pH dropped to 1.3. This proves that a copper complex was formed with the MCG groups (-OH and $-AsO_3H_2$) and the MCG protons were substituted with the copper cations. Continuation of the titration brings a titration curve similar to that observed for the sample containing a mixture of 0.1 mmol Arsenazo-I and 0.1 mmol Cu^{+2} .



Figure 1. Titration curve of the selected MCL ligand, Arsenazo-I, with 2 mol L⁻¹ NaOH solution; (A) 0.1 mmol Arsenazo-I, (B) a mixture of 0.1 mmol Arsenazo-I and 0.1 mmol Cu⁺²

Without addition of Cu⁺², or, in general, other complexing cations, the MCG protons do not become neutralised, even in a strong alkaline environment. The protons of weak acidic groups of MCG can be removed in the course of complexation with metal ions. The same behaviour was observed for other MCL ligands such as SSA, Tiron and Calcon. Two important points follow from the above:

- 1) MCGs do not belong to an anionic group and cannot act as doping anions during the film oxidation or reduction;
- 2) the complex formation is a selective process (the presence of Cu⁺², not Na⁺, was needed for the complex formation) and may contribute to the final selectivity of the cationic-sensitive conducting polymer films.

This means that the complexed cations could not be removed from the film during its oxidation, in contrast to those bounded by the sulfonate groups. Moreover, only a limited group of cations can be exchanged with the complexed ones, and a more or less selective cationic response should be induced in this way. A cationic sensitivity of such a kind should be independent of the PPy film oxidation status. Additionally, an improvement in potentiometric selectivity can be expected after the film oxidation, because only accidental cations M_i (which neutralised the negative charge of the sulfonate groups), not the complexed Me cations, will be removed. The ion-exchange processes determined initially by both Me and M_i cations will be determined by the complexed Me cation, only after the film oxidation, see Figure 2. Consequently, the film selectivity should become better and better during its oxidation.

In particular, Me and Mi can be the same cations bounded in the form of a complex with the MCG groups and in the form of a salt with the sulfonate groups.



Figure 2. Cation-exchange processes for reduced and oxidized PPy–MCL film. The R-(MCG)-SO₃H composition of MCL was assumed for simplicity

The cationic response of the oxidized PPy-MCL films

As it was assumed, the complexed cation should not be removed from the film during its oxidation and the cationic response should be independent of the oxidation status of the PPy–MCL film. As an example, two ionic calibration curves of the calcium-sensitive PPy–Calcichrome film divided by its redox calibration are shown in Fig. 3.



Figure 3. Ionic calibration curves with CaCl₂ before (a) and after (c) redox calibration (b) for calciumsensitive PPy–Calcichrome film; redox calibration was performed with K₃Fe(CN)₆/ K₄Fe(CN)₆ solution, 0.001 mol L⁻¹ total concentration and indicated molar ratio

The PPy–Calcichrome films were obtained dynamically and the potential range of cycling was $-0.3\div0.7V$. Each film was conditioned at 0.5 V for 5 min after the deposition. The calcium sensitivity was induced by soaking the film in saturated calcium hydroxide, pH = 12.5, for two weeks. It can be seen that the initially observed calcium response (Fig. 3a) remains unchanged after the film oxidation (Fig. 3c) during its redox calibration (Fig. 3b). As a result of the film oxidation, the calibration curve 3c shifts towards more positive potentials, but its slope is unchanged, which indicates that the calcium ions cannot be removed from the film. The presence of the main ion (Ca⁺², Mg⁺² or Cu⁺²) prior to and after the film oxidation was additionally confirmed by the EDAX experiments. As an example, the EDAX spectra for magnesium sensitive PPy–Tiron film before (a) and after oxidation (b) with hexacyanoferrate are shown in Figure 4.



Figure 4. EDAX spectra for magnesium sensitive PPy–Tiron film before (A) and after its oxidation (B) with K₃Fe(CN)₆/K₄Fe(CN)₆ solution, 1:1 molar ratio, 0.0001 mol L⁻¹ total concentration

Influence of the electropolymerization conditions on PPy–MCL film cationic sensitivity and selectivity.

It is well known that the existing PPy film is oxidized and doped during the electrodeposition which is because the PPy film oxidation potential is lower than that needed for the monomer oxidation. After the deposition from MCL solution, the R-(MCG)-SO₃⁻ anions are immobilized as the [R-(MCG)-SO₃⁻(PPy⁺)] groups, which cannot be removed from the film during its reduction. Moreover, only the hydrogen and R-(MCG)-SO₃⁻ ions are present in the solution of the acidic form of MCL, *i.e.* an uptake of the big R-(MCG)-SO₃⁻ anions should be prohibited during the film oxidation. Consequently, only the hydrogen cation uptake or removal can be expected during the film reduction or oxidation.

With this assumption, and also assuming the most oxidized initial state of PPy and an insignificant anion uptake, *i.e.* that σ and δ are equal to 0, one can write:

 $\alpha[(PPy^{0})] \beta[R-(MCG)-SO_{3}(PPy^{+})]^{+} \gamma[e^{-}] + \gamma[H^{+}] \Leftrightarrow (\alpha + \gamma)[(PPy^{0})] \gamma[R-(MCG)-SO_{3}H] (\beta - \gamma)[R-(MCG)-SO_{3}(PPy^{+})]$

Coefficients α and β indicate the reduced and oxidized and doped with R-(MCG)-SO₃⁻ fragments of the PPy backbone. The greek symbols used are the same as those proposed earlier by Lewenstam *et al.* [31].

Depending on the redox status of the PPy film, one or two parallel processes of cation uptake are possible during the chemical conditioning of such films (which leads to inducing its cationic sensitivity):

— complex formation with the MCG group only, if $\gamma = 0$

— complex and salt formation with the MCG and sulfonate groups if $\gamma > 0$

As it was assumed, the salt cations can be exchanged with any other (in contrast to those bounded as a complex with the MCG groups). Therefore, the PPy–MCL film se-lectivity should be a function of its oxidation state. To verify this assumption, two groups of film were electropolymerized under different conditions:

- for the first group the reduction of the growing PPy film was avoided such films were electrodeposited under both, potentiostatic or dynamics conditions;
- the films of the second group were deposited dynamically and were periodically oxidized and reduced. An additional electrochemical reduction was performed after the deposition process was completed.

As an example, the results for the Ca-sensitive PPy–Arsenazo films are shown below. Both groups of films were obtained dynamically and the potential range of cycling was $0.3\div0.65$ V for the first group, and $-0.15\div0.65$ V for the second. Each film from the second group was conditioned at -0.15V for 5 min after the deposition. The calcium sensitivity was induced under the same conditions for both groups of the

films, *i.e.* by soaking in saturated calcium hydroxide of pH = 12.5 for two weeks. After the conditioning, a similar calcium response was observed for the films in both groups and the slope values were equal to 30.6, 28.5, 29,8 and 30.5 mV/pCa, respectively, as it can be seen in Figure 5A. On the other hand, the response in the presence of sodium cations was diametrically different in both groups. Figure 5B shows the potential changes caused by an increase of sodium ion concentration (under constant calcium ion concentration). The films in the first group were practically insensitive towards the sodium ion. In the second group, a potential increase of 50–60 mV was observed. As expected, the E⁰ values were also different and equalled 158.9 and 185.8 mV for the films in first group and 107.6 and 112.9 mV for the second group.



Figure 5. Calibration curves (A) and selectivity test with sodium ion (B) for calcium-selective PPy–Arsenazo films; the films were electrodeposited without reduction (solid line, triangle) or periodically reduced and oxidized during deposition (dotted line, circle)

To explain the differences in the selectivity described above, it must be noticed that for both groups of the films the total polymerization charge, as well as the doping level were similar. This follows from the identical oxidation potential of +0.65 V and the identical number of scans. A similar doping level (*i.e.* $\beta_1 \approx \beta_2$) means that, after sufficiently long chemical conditioning, the total amount of the complexed cations is similar in both groups of the films and proportional to β . The salt content proportional

to γ should be different and much higher for the second group of films, *i.e.* $\gamma_2 \gg \gamma_1 \ge 0$ (films of the first group can be accidentally reduced after the electrodeposition and for them it is assumed that γ_1 can be also greater than 0). As a result, the final $\beta/(\beta + \gamma)$ ratios for both groups of films and their selectivities should be different as well.

After the conditioning in calcium hydroxide, the same Me and M_i cation, *i.e.* Ca⁺², determines the ion-exchange processes (see Fig. 2), and the calcium sensitivity for both groups of films should be independent of the $\beta / (\beta + \gamma)$ factor and similar, see Fig. 5A.

In contrast, the potentiometric selectivity should be dependent on the complex-tosalt ratio, described operationally by the $\beta / (\beta + \gamma)$ factor, and becomes better when the γ value is closer to 0. In fact, much better selectivity was observed for the first group of films (Fig. 5B).

Influence of redox status of the PPy-MCL films on their selectivity

The apparent value of the $\beta / (\beta + \gamma)$ factor can be modified to be higher or lower by doing the oxidation or reduction, and adequate changes in the PPy–MCL film selectivity should be observed. Consequently, the selectivity of the second group of films (with lower PPy oxidation state) may be improved by doing the re-oxidation.

As previously, two groups of PPy-MCL films were always investigated. The films of the first group were deposited without their reduction, whereas the films of the second group were periodically oxidized and reduced during the electrodeposition. As an example, the results obtained for the PPy-Tiron films are presented. The films in both groups were obtained dynamically and the potential range of cycling was $0\div0.65$ V for the first group, and $-0.4\div0.65$ V for the second. Each film from the second group was conditioned at -0.4 V for 5 min after the deposition. The chemical conditioning with saturated magnesium hydroxide induced the magnesium sensitivity. After 4 weeks of conditioning, the same slope, equal to 26.6 mV/pMg was observed for each film tested, however, the E^0 values were different and higher for the first group of films. As previously, a different response to sodium ion addition was observed and the selectivity of the first group of PPy-Tiron films was much better, see Figure 6A. After the oxidation with a mixture of $K_4Fe(CN)_6/K_4Fe(CN)_6$, 1:1 molar ratio and the total concentration of 0.0001 mol L⁻¹, the selectivity of the second group of films significantly improved, see Figure 6B (the size of the hexacyanoferrate anions prevents its uptake during the film oxidation [25,26]). A positive shift of E⁰ values (by about 100 mV) was observed during the film oxidation, but the magnesium sensitivity remained unchanged after that. It should be emphasised that the good selectivity of the oxidized films was unchanged during 6 months of soaking in saturated magnesium hydroxide.



Figure 6. Selectivity test with sodium ions for magnesium-sensitive PPy–Tiron films before (A) and after their oxidation (B) with $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution, 1:1 molar ratio, 0.0001 mol L⁻¹ total concentration; the films were electrodeposited without reduction (solid line, triangle) or periodically reduced and oxidized during deposition (dotted line, circle)

A convincing proof for the relation between the film selectivity and the oxidation state was obtained from a potentiometric titration using the PPy–MCL films as the indicator electrode. For example, Figure 7 shows the titration curves of the calcium ions with sodium oxalate, which were obtained with the calcium-sensitive PPy–Arsenazo films as well as with a commercial Ca–ISE. Two groups of PPy–Arsenazo films were used: deposited and sensitised towards calcium as described earlier (Fig. 5). The film deposited without reduction (s = 29.3 mV/pCa, $E^0 = 113.1 \text{ mV}$) was insensitive towards sodium ions and its potential changes were similar to that for the commercial Ca–ISE. In contrast, the second film (periodically reduced and oxidized during the deposition, s = 28.2 mV/pCa, $E^0 = 99.1 \text{ mV}$) was sensitive to the sodium ions also. As a result, a much smaller potential jump and the characteristic potential change were observed (Fig. 7A).

After the oxidation with a mixture of $K_3Fe(CN)_6/K_4Fe(CN)_6$, 1:1 molar ratio and the total concentration of 0.0001 mol L⁻¹, the titration curves of both the PPy–Arsenazo films as well as commercial Ca–ISE films was similar — *i.e.* the selectivity of the second film was improved after its oxidation, (Fig. 7B).



Figure 7. Titration curves of calcium ion with sodium oxalate for: calcium-sensitive PPy–Arsenazo film deposited without reduction (thin, solid line), calcium-sensitive PPy–Arsenazo film periodically reduced and oxidized during deposition (thick, solid line), and Ca–ISE (dotted line). The titrations were performed before (A) and after (B) oxidation of the PPy–Arsenazo films with $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution, 1 : 1 molar ratio, 0.0001 mol L⁻¹ total concentration



Figure 8. Titration curves of calcium ion with sodium oxalate. The same calcium-sensitive PPy–Arsenazo film was used before (solid, thin line) and after its reduction with 0.0002 mol L⁻¹ sodium ascorbate, 0.004 mol L⁻¹ CaCl₂, pH = 7 solution (solid, thick line); the curve with Ca–ISE (dotted line) is shown for comparison

According to my assumption, a lower value of the $\beta / (\beta + \gamma)$ factor and a worse selectivity may be attributed to the reduction of the PPy–MCL film. As example, in Figure 8, two subsequent titration curves obtained with the same calcium-sensitive PPy–Arsenazo film before and after its reduction with 0.0002 mol L⁻¹ sodium ascorbate, 0.004 mol L⁻¹ CaCl₂ of pH = 7, are presented. The E⁰ value of the PPy–Arsenazo film was decreased by 63 mV and equal to 117 mV after the reduction, but the initial slope value (29.8 mV/pCa) remained unaffected. As it can be seen, the initially good selectivity towards sodium ion (thin solid line) deteriorated after the film reduction (thick solid line). The titration curve with the commercial Ca–ISE is shown for comparison (dotted line).

The improved selectivity due to the oxidation was also observed for the coppersensitive PPy–SSA, PPy–Arsenazo and PPy–Calcon films. As it was shown earlier, those films were electrochemically oxidized during the preparation [41]. In spite of the low pH of copper salt solution, the PPy–MCL film deprotonation was difficult to perform and the chemical conditioning was an ineffective method for inducing copper sensitivity. In fact, after 3 weeks of conditioning, the PPy-Arsenazo film had no copper sensitivity, but it was sensitive to the hydrogen and sodium ions. After electrochemically inducing copper sensitivity, the film was oxidized and the salt cations (hydrogen ions here) were removed. As a result, the response towards copper (23.6 mV/ pCu), depressed the response towards hydrogen and no response towards the sodium ions was obtained, see Figure 9.



Figure 9. The copper (A), sodium (B) and pH sensitivity (C) of the PPy–Arsenazo film before (solid, thick line, empty circle) and after (solid thin line, filled circle) electrochemical inducing its cooper sensitivity; the results for Cu–ISE are shown for comparison (dotted line)

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An evidence for the influence of complex formation process on potentiometric selectivity of the PPy–MCL films was also obtained. As it was shown earlier, the noncomplexed cations can be removed from the oxidized PPy–MCL films, and a good selectivity towards them is established. However, a poor selectivity can be expected if the complexed cation may be exchanged, *i.e.* when an interfering cation can also form the complex with the MCL ligands. Such behaviour should be observed for the magnesium- and calcium-sensitive PPy–MCL films when the calcium or magnesium ions are used as the interferent; both cations can form complexes with the Calcon, Arsenazo and Tiron ligands and the stability constant of the complexes is similar. As an example, Figure 10 shows the response of the magnesium-sensitive films: PPy–Calcon (29.1 mV/pMg), PPy-Arsenazo (28.5 mV/pMg) and PPy–Tiron (27.9 mV/pMg), on the interfering cation concentration increase. The selected interfering ions were Na⁺, K⁺ and Ca⁺². These films were sodium- and potassium-insensitive, but the response towards calcium was evident. Interestingly, a similar calcium response was observed for the commercial Mg–ISE.



Figure 10. Selectivity test towards sodium, potassium and calcium ions of the magnesium-sensitive PPy films doped with Calcon, Arsenazo-I and Tiron ligand

CONCLUSION

The oxidation and reduction can modify the potentiometric selectivity of the PPy– MCL films, with the strongly oxidized films being the most selective. Such films, enriched with the complexed main cation only, can be used as a solid contact to co-operate with a selected PVC ion-selective membrane. The cation activity in such solid contact (which acts as a solid internal solution) is buffered, and the potential drop at the PPy–MCL/PVC membrane interface is determined and constant. The main ion activity is dependent on the stability constant of the MCL–Me complex and may be set to be very low. According to the results described by Sokalski *et al.* [42] it can be important for the design of robust, maintenance-free potentiometric sensors with a low detection limit.

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