

# A New Method Based on the Butler–Volmer Formalism to Evaluate Voltammetric Cation and Anion Sensors

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Received: June 13, 2008; Revised Manuscript Received: September 9, 2008

A new method based on the Butler–Volmer formalism is applied to assess the capability of two voltammetric ion sensors based on polypyrrole films: PPy/DBS and PPy/CIO<sub>4</sub> modified electrodes were studied as voltammetric cation and anion sensors, respectively. The reversible potential versus electrolyte concentrations semilogarithm plots provided positive calibration slopes for PPy/DBS and negative ones for PPy/CIO<sub>4</sub>, as was expected from the proposed method and that based on the Nernst equation. The slope expressions deduced from Butler–Volmer include the electron-transfer coefficient, which allows slope values different from the ideal Nernstian value to be explained. Both polymeric films exhibited a degree of ion-selectivity when they were immersed in mixed-analyte solutions. Selectivity coefficients for the two proposed voltammetric cation and anion sensors were obtained by several experimental methods, including the separated solution method (SSM) and matched potential method (MPM). The *K* values acquired by the different methods were very close for both polymeric sensors.

## 1. Introduction

In order to characterize ion-selective electrodes the expressions used until present have been based on the Nernst relationship.<sup>1</sup> Bond et al.<sup>2,3</sup> adapted the potentiometric equation to voltammetric ion sensors, changing the electromotive force (EMF) for  $E_R$  and considering an activity coefficient close to unity. These authors successfully applied eqs 1 and 2 to tetracyanoquinodimethano (TCNQ) and tetrathiofulvaleno (TTF) immobilized on electrode surfaces, respectively

$$E_R = E^{\circ'} + S \log[M_A^+] \quad (1)$$

$$E_R = E^{\circ'} - S \log[X^-] \quad (2)$$

where  $[M_A^+]$  and  $[X^-]$  are the cation and anion concentrations, respectively, and  $E_R$  is the reversible potential, defined by

$$E_R = \frac{E_p^{\text{red}} + E_p^{\text{ox}}}{2} \quad (3)$$

$E_p^{\text{red}}$  is the reduction peak potential and  $E_p^{\text{ox}}$  is the oxidation peak potential. These equations were also applied recently to check a TTF-TCNQ/poly(vinyl chloride) (PVC) composite for use as ion selective electrode.

Equations 1 and 2 demonstrate a direct relation between  $E_R$  and the logarithm of the electrolyte concentration, where *S* is the slope derived from the plot, which has positive or negative

values for cationic or anionic movement, respectively. Ideally, *S* will be equal to  $2.303RT/nF$ .

A similar linear dependence of the potential versus the logarithm of ion activity has frequently been reported for electrochemical ion sensors based on polymeric materials. In this case, a negative slope is recorded for anion exchanging polymer and a positive slope is obtained for cationic exchanger polymeric materials. Although this linear relationship is mainly based on the Nernst equation,<sup>5–9</sup> recently a treatment based on the Butler–Volmer expression has been reported to explain the direct relationship between the potential and the logarithm of the electrolyte concentration.<sup>10</sup>

Polymers, such as polypyrrole (PPy), polyaniline (PANI) or polythiophene (PTH), offer great possibilities for improving selectivity, by partly changing the chemical structure of the polymer backbone and partly due to the many possible counterions or neutral molecules that can be trapped inside the polymer.<sup>10–13</sup> Hence, the use of anions of different size means that polypyrrole films can be used as cationic and anionic potentiometric ion sensors.<sup>6,10–16</sup>

In PPy polymers doped with small-anions, it is considered that the anions are expelled during the reduction process, while they are included again inside the polymer during oxidation. However, it is normally accepted that PPy films doped with large anions, such as DBS<sup>−</sup>, the anions are fixed inside the polymer matrix, providing cationic transport when the polymer is subjected to a redox process.<sup>15,17–19</sup>

Recently, in a short communication, we introduced a new method based on the Butler–Volmer equation to assess the capability of voltammetric ion sensors.<sup>20</sup> In the present work, this method is revised and it is used to evaluate both PPy/DBS and PPy/CIO<sub>4</sub> films as voltammetric cation and anion sensors, respectively. We then examine whether both of these PPy modified electrodes retain their ion selectivity in mixed-ion solutions. Also, selectivity coefficients of these voltammetric sensors are calculated by different methods. In this sense, the

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increase in the midpoint reversible potential ( $\Delta E_R$ ) will be used for the first time to apply the matched potential method (MPM) to voltammetric ion sensors.

## 2. Experimental Section

Pyrrole monomer (Fluka, >97%) was distilled under vacuum before use. Sodium dodecylbenzene sulfonate (Aldrich),  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ ,  $\text{NaF}$ ,  $\text{NaNO}_3$ , and  $\text{NaCl}$  (Merck) were used as received. Millipore water with resistivity of  $>18 \text{ M}\Omega \text{ cm}$  was used.

PPy/DBS and PPy/ $\text{ClO}_4$  films were generated by electrochemical oxidation on Pt foil electrodes, applying a constant potential of +0.8 V versus Ag/AgCl for 60 s. A 0.1 M pyrrole and 0.1 M DBS aqueous solution was used to generate the PPy/DBS polymers and a 0.1 M pyrrole and 0.1 M  $\text{LiClO}_4$  solution was used to synthesize the PPy/ $\text{ClO}_4$  films. Once the polymer film was deposited on the Pt foil, the modified electrode was taken out of the solution, washed with water, dried, and stored at 4 °C.

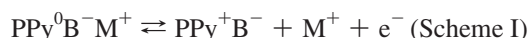
The electrochemical polymerization and the voltammetric measurements were performed with a PAR 273A potentiostat/galvanostat. A three electrodes cell composed of Pt foil working electrode (area  $1 \text{ cm}^2$ ), an Ag/AgCl reference electrode, and a Pt wire as the auxiliary electrode was used. All the solutions were purged with  $\text{N}_2$  gas for 15 min.

With the aim of preventing an ohmic distortion, a voltammetric  $iR_u$  compensation of  $50 \Omega$ , which was calculated as the mean for the different solutions used, was applied to the voltammetric measurements.

Each experimental potential ( $E_R$ ) was determined from at least three measurements. The results were virtually identical, which testifies to the high reproducibility of the polymer modified electrodes.

## 3. Results and Discussion

**3.1. Butler–Volmer Treatment.** Anions of different sizes can be used to dope PPy during the polymerization process, providing polymeric systems with different electrochemical properties.<sup>14–16</sup> Hence, a PPy film can be used as cationic or anionic ion sensor, depending on the anion type used during polymeric synthesis. For the theoretical treatment based on the Butler–Volmer equation, we will consider the oxidation/reduction process of two polymeric systems: one cationic exchanger polymer, such as PPy/DBS, and another anionic exchanger, such as PPy/ $\text{ClO}_4$ . Thus, the basic redox reactions for the prevailing interchange of cations or anions, respectively, could be proposed as



where  $\text{B}^-$  is a large anion, such as  $\text{DBS}^-$ , used to dope the



polymeric material during the synthesis, and  $\text{M}^+$  and  $\text{A}^-$  represent the small cations and anions present in the test solutions when the polymeric material is used as voltammetric sensor.

Therefore, during the reduction of a polymer as PPy/DBS,  $\text{DBS}^-$  anions will remain fixed inside the polymer, making it necessary for the electrolyte cations to enter. These cations will be expelled to the solution during the subsequent oxidation

[Scheme I]. However, when a polymer such as PPy/ $\text{ClO}_4$  is reduced,  $\text{ClO}_4^-$  anions are expelled from the film, and during the subsequent oxidation small anions will again enter the polymer from the solution.

In the simplest approximation and considering an equilibrium condition, the electrochemical potential for these reactions could be described by the Nernst equation as, respectively

$$\begin{aligned} E &= E^{0'} + \frac{RT}{nF} \ln \frac{|\text{PPy}^+\text{B}^-||\text{M}^+|}{|\text{PPy}^0\text{B}^-\cdot\text{M}^+|} \\ &= E^{0'} + \frac{RT}{nF} \ln \frac{|\text{PPy}^+\text{B}^-|}{|\text{PPy}^0\text{B}^-\cdot\text{M}^+|} + \frac{RT}{nF} \ln |\text{M}^+| \quad (4) \end{aligned}$$

$$\begin{aligned} E &= E^{0'} + \frac{RT}{nF} \ln \frac{|\text{PPy}^+\text{A}^-|}{|\text{PPy}^0||\text{A}^-|} \\ &= E^{0'} + \frac{RT}{nF} \ln \frac{|\text{PPy}^+\text{A}^-|}{|\text{PPy}^0|} - \frac{RT}{nF} \ln |\text{A}^-| \quad (5) \end{aligned}$$

These equations describe the evolution of the redox potential as a function of the electrolyte concentrations, in accordance with eqs 1 and 2. If cationic exchange prevails, the redox potential versus electrolyte concentration plots will show a semilogarithmic increase in the potential with electrolyte concentration (eq 4). On the contrary, a negative slope is predicted (eq 5) when the interchange of small anions prevails.<sup>5–7,10,19–22</sup>

Previously, different research groups have used the Butler–Volmer treatment to study the kinetic of the charge transport of diverse polymeric films.<sup>10,20,23–27</sup> We consider that the Butler–Volmer formalism is more appropriate for describing kinetic processes such as those described by Scheme I and Scheme II.<sup>10,20</sup> In regard to the anodic part of the general process,  $\text{R} \rightleftharpoons \text{O} + n\text{e}^-$  and, considering that only oxidation occurs in this branch of the voltammogram, the Butler–Volmer equation for Scheme I can be expressed by<sup>10,20,28,29</sup>

$$E_a = E^{0'} + \frac{1}{\alpha_a n f} \ln \frac{i_a}{nFAk^0} - \frac{1}{\alpha_a n f} \ln |\text{PPy}^0\text{B}^-\cdot\text{M}^+| \quad (6)$$

where  $i_a$ ,  $E_a$ ,  $E^{0'}$ ,  $\alpha_a$ ,  $k^0$  and  $n_s$  are the anodic current, the anodic potential, the standard potential, the anodic transfer coefficient, the standard rate constant and the  $n$  value of the rate-determining step, respectively. Also,  $|\text{PPy}^0\text{B}^-\cdot\text{M}^+|$  is the reactive compound concentration,  $C_R$ .

Moreover, considering that in the cathodic part of Scheme I, only reduction is presented, the cathodic potential,  $E_c$ , can be expressed by

$$\begin{aligned} E_c &= E^{0'} - \frac{1}{\alpha_c n f} \ln \frac{i_c}{nFAk^0} + \frac{1}{\alpha_c n f} \ln |\text{PPy}^+\text{B}^-| + \\ &\quad \frac{1}{\alpha_c n f} \ln |\text{M}^+| \quad (7) \end{aligned}$$

where,  $i_c$  is the cathodic current,  $\alpha_c$  the cathodic transfer coefficient, while  $|\text{PPy}^+\text{B}^-|$  and  $|\text{M}^+|$  are the concentrations of the product compounds,  $C_O$ .

In this case, considering that solid-state phases confined on the electrode surface, such as  $\text{PPy}^+\text{B}^-$  and  $\text{PPy}^0\text{B}^-\text{M}^+$ , have

activity values equal to unity, eqs 6 and 7 can be transformed into

$$E_a = E^{0'} + \frac{1}{\alpha_a n_s f} \ln \frac{i_a}{nFAk^0} \quad (8)$$

$$E_c = E^{0'} - \frac{1}{\alpha_c n_s f} \ln \frac{i_c}{nFAk^0} + \frac{1}{\alpha_c n_s f} \ln |M^+| \quad (9)$$

At this point, based on the definition of  $E_R$ , eq 3, and substituting  $E_p^{\text{red}}$  and  $E_p^{\text{ox}}$  by  $E_c$  and  $E_a$  from eq 8 and 9, respectively, we can express  $E_R$  for Scheme I as

$$E_R = E^{0'} + \frac{1}{2} \left( \frac{1}{\alpha_a n_s f} \ln \frac{i_a}{nFAk^0} - \frac{1}{\alpha_c n_s f} \ln \frac{i_c}{nFAk^0} \right) + \frac{1}{2\alpha_c n_s f} \ln |M^+| \quad (10)$$

For clarity, the second term can be designated  $Z$ , and thus this equation would be transformed into

$$E_R = E^{0'} + Z + \frac{1}{2\alpha_c n_s f} \ln |M^+| \quad (11)$$

Comparing this expression with eq 1, it should be noted that they are very similar. Moreover, a direct relationship between  $E_R$  and the cation concentration is obtained experimentally, as will be presented below. Hence,  $Z$  has to be a constant term, and thus this equation can be transformed into

$$E_R = H + \frac{1}{2\alpha_c n_s f} \ln |M^+| \quad (12)$$

where  $H$  is the origin coordinate constant.

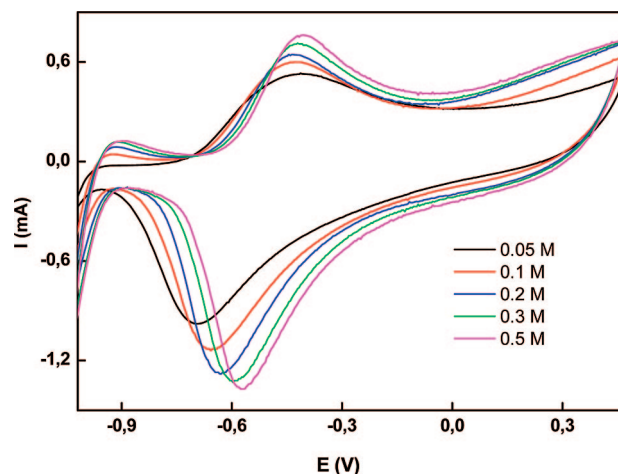
With respect to Scheme II, where anion exchange prevails, eqs 6 and 7 can be expressed by

$$E_c = E^{0'} - \frac{1}{\alpha_c n_s f} \ln \frac{i_c}{nFAk^0} + \frac{1}{\alpha_c n_s f} \ln |PPy^+ \cdot A^-| \quad (13)$$

$$E_a = E^{0'} + \frac{1}{\alpha_a n_s f} \ln \frac{i_a}{nFAk^0} - \frac{1}{\alpha_a n_s f} \ln |PPy^0| - \frac{1}{\alpha_a n_s f} \ln |A^-| \quad (14)$$

Once again, considering that solid-state phases confined on the electrode surface, such as  $PPy^+A^-$  and  $PPy^0$ , have activity values equal to unity, eqs 13 and 14 can be transformed into the form

$$E_c = E^{0'} - \frac{1}{\alpha_c n_s f} \ln \frac{i_c}{nFAk^0} \quad (15)$$



**Figure 1.** Voltammograms of a PPy/DBS modified electrode in diverse concentrations of  $\text{LiClO}_4$  aqueous solutions. Figure indicates the  $\text{LiClO}_4$  concentrations.

$$E_a = E^{0'} + \frac{1}{\alpha_a n_s f} \ln \frac{i_a}{nFAk^0} - \frac{1}{\alpha_a n_s f} \ln |A^-| \quad (16)$$

Proceeding in a similar manner to the way in which eq 10 was deduced, we can obtain  $E_R$  for Scheme II by using eqs 15 and 16

$$E_R = E^{0'} + \frac{1}{2} \left( \frac{1}{\alpha_a n_s f} \ln \frac{i_a}{nFAk^0} - \frac{1}{\alpha_c n_s f} \ln \frac{i_c}{nFAk^0} \right) - \frac{1}{2\alpha_a n_s f} \ln |A^-| \quad (17)$$

Note that in this equation the second term is identical to that obtained for Scheme I in eq 10. Hence, this term will again be designated  $Z$ , and in the same way to the previous case it could be considered as a constant, giving

$$E_R = E^{0'} + Z - \frac{1}{2\alpha_a n_s f} \ln |A^-| \rightarrow E_R = H - \frac{1}{2\alpha_a n_s f} \ln |A^-| \quad (18)$$

In Figure 4, the cathodic and anodic peak currents maintain similar values with the electrolyte concentration. This fact is in accordance with a constant value of  $Z$ . However, it is possible that  $i_c$  and  $i_a$  have different values for each electrolyte concentration (see Figure 1). In this case,  $|i_c|$  and  $|i_a|$  increase uniform and continuously with the concentration. Thus, a relationship between  $i_c$  and  $i_a$  has to exist to make the  $Z$  term constant with the electrolyte concentration.

Furthermore, by substituting  $f$  by its value and using decimal logarithm, eqs 12 and 18 for Scheme I and Scheme II, respectively, could be expressed by

$$E_R = H + 2.303 \frac{RT}{2\alpha_c n_s F} \log |M^+| \quad (19)$$

$$E_R = H - 2.303 \frac{RT}{2\alpha_a n_s F} \log [A^-] \quad (20)$$

Comparing these equations with eqs 1 and 2 reported by Bond et al.,<sup>2,3</sup> the only changes are the slope and the origin ordinate constant. Thus, for cationic exchange, the slope is equal to  $S/2\alpha_c$ , and for anionic movement the slope is equal to  $-S/2\alpha_a$ , while the origin ordinate is  $H$  (equal to  $E^{0'} + Z$ ). Note that for systems where  $\alpha_c = 0.5$  or  $\alpha_a = 0.5$ , the resulting slopes are in accordance with those of Bond equations. Moreover, in systems where  $i_c$  is equal in absolute value to  $i_a$  the origin ordinate constant in eqs 19 and 20 will be equal to  $E^{0'}$ . Hence, in systems where  $\alpha_c = 0.5$  or  $\alpha_a = 0.5$  and  $|i_c| = |i_a|$  the equations obtained using the Butler–Volmer formalism will be similar to those proposed by Bond. Thus, for systems with behaviours close to Nernst, the method proposed by us is still valid.<sup>20</sup>

**3.2. Assessment of the Capability of Polymer Films As Voltammetric Ion Sensors.** As mentioned above, the basis of calibration of the proposed voltammetric cation sensor is a plot of the reversible potential ( $E_R$ ) versus electrolyte concentrations. Equations derived from Nernst or Butler–Volmer provide a linear relationship between  $E_R$  and the logarithm of the ion concentration. Thus, eqs 1 and 19 predict a positive slope and eqs 2 and 20 propose a negative slope for cationic and anionic sensors, respectively.

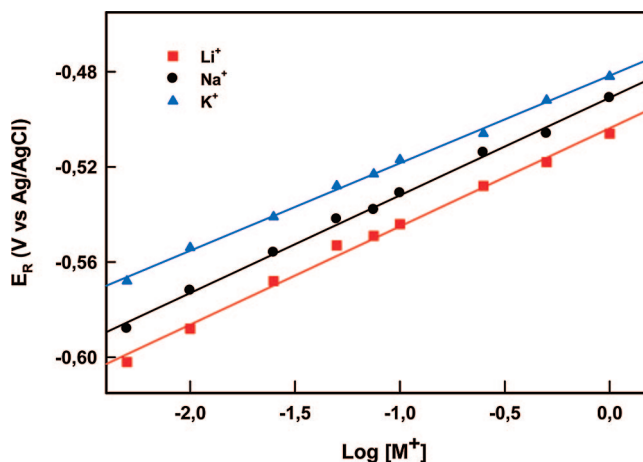
In this section, we will use the Butler–Volmer treatment to assess the capability of a PPY/DBS film as a voltammetric cation sensor and a PPY/ClO<sub>4</sub> polymer as a voltammetric anion sensor.

**3.2.1. Polypyrrole Film Working As a Voltammetric Cation Sensor.** First, we assess the capability of a PPY/DBS modified electrode as a voltammetric cation sensor using the Butler–Volmer based method. Cyclic voltammograms of PPY/DBS films deposited on Pt electrode were obtained at several concentrations of sodium, potassium, and lithium perchlorate aqueous solutions. The potential was cycled between  $-1.0$  and  $0.5$  V at a moderate scan rate ( $\leq 30$  mV·s<sup>-1</sup>), which allowed us the modified electrode to be kept operational for a long period of time. Figure 1 shows the voltammograms registered at 20 mV·s<sup>-1</sup> for a PPY/DBS film immersed in different concentrations of LiClO<sub>4</sub>. As can be seen, the cathodic and the anodic peaks changed with increases in the electrolyte concentration.

By using the corresponding cathodic and anodic peak potentials obtained in eq 3, the  $E_R$  values could be calculated for each electrolyte concentration, and hence the  $E_R$  versus log [LiClO<sub>4</sub>] plot was generated (Figure 2). This plot shows a positive slope for the PPY/DBS polymeric film cycled in different concentrations of LiClO<sub>4</sub> solutions, in accordance with eqs 1 and 19 derived from Nernst and Butler–Volmer, respectively, for cation exchanger systems.

Thus, a positive slope confirms that the redox reaction of this system is described by Scheme I. In this case, the DBS<sup>-</sup> anions are fixed inside the polymer matrix and are not exchanged during the redox process. This behavior means that the cations must penetrate the polymer from the solution during the cathodic branch, and they will be expelled to the solution during the subsequent anodic semicycle, as has been reported previously.<sup>17–19</sup>

In the same way, we also registered the voltammograms for PPY/DBS films in different concentration solutions of KClO<sub>4</sub> and NaClO<sub>4</sub>. A similar shift of the peak potentials with the electrolyte concentration resulted, again providing positive slopes in  $E_R$  versus log [M<sup>+</sup>] plots for these electrolytes (Figure 2). Although these slopes have very similar values for different electrolytes, all of them clearly differ from the ideal Nernstian value:  $2.303RT/nF$  (58.1 mV·dec<sup>-1</sup> for  $T = 25$  °C).



**Figure 2.** Calibration plots of reversible potential,  $E_R$ , versus log [M<sup>+</sup>] for a PPY/DBS modified electrode in aqueous solutions of M<sup>+</sup>ClO<sub>4</sub><sup>-</sup>.  $E_R$  values were obtained including the peak potentials obtained from the voltammograms in eq 3.

**TABLE 1: Voltammetric Parameters for the PPY<sup>+0</sup> Process Obtained by Immersing a PPY/DBS Modified Electrode in 0.1 M M<sup>+</sup>ClO<sub>4</sub><sup>-</sup> Aqueous Solutions<sup>a</sup>**

	potassium	sodium	lithium
$E_p^{ox}$ (mV)	-442	-437	-451
$E_p^{red}$ (mV)	-592	-625	-637
$E_R$ (mV)	$-512 \pm 8$	$-531 \pm 7$	$-542 \pm 6$
$S$ (mV·dec <sup>-1</sup> )	36	39	41

<sup>a</sup> Scan rate: 10 mV·s<sup>-1</sup>.  $S$  values were obtained from Figure 2.

The Bond method based on the Nernst equation cannot explain the values of these slopes values, which differ from the ideal one. Hence, we consider it is more appropriate to apply eq 19, deduced from the Butler–Volmer equation. This equation defines the slope value as

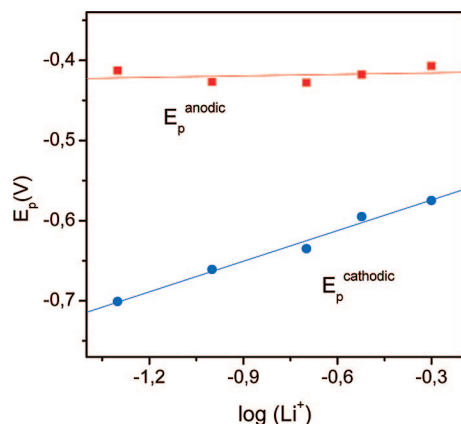
$$S' = 2.303 \frac{RT}{2\alpha_c n_s F} \quad (21)$$

By including the slope values obtained from Figure 2 in this expression, we can estimate the values of the factor  $\alpha_c \cdot n_s$  for the PPY<sup>+0</sup> couple for different cations: 0.82 for K<sup>+</sup>, 0.76 for Na<sup>+</sup>, and 0.72 for Li<sup>+</sup>. Note that the presence of the electron-transfer coefficient in the slope equation allows slope values different from the ideal Nernst value to be explained.<sup>20</sup> Note also that when  $\alpha_c = 0.5$ , eq 21 coincides exactly with the ideal Nernst slope.

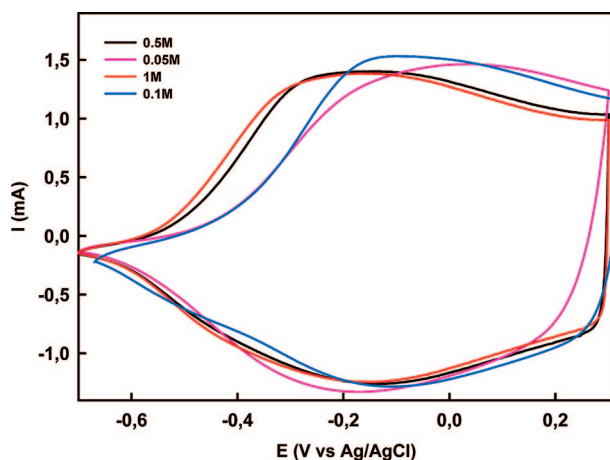
On the other hand, although the slopes values are very similar for all cations, a vertical shift was observed, indicating that the origin constant is different for each cation. Bond et al.<sup>2</sup> explained a similar shift as being due to a change of the formal potential value, although if we use eq 19 derived from Butler–Volmer this explanation is not clear; the standard potential could be similar for the three electrolytes used but only if change the  $Z$  constant value.

With regard to cation identity, from Figure 2 and Table 1, it can be demonstrated that for identical cation concentrations in electrolyte solutions, each cation led to a different voltammetric peak pattern and hence different reversible potential values for the PPY<sup>+0</sup> couple. Thus, the PPY/DBS system can be deemed as a voltammetric sensor analogous to a cation-selective electrode.





**Figure 3.** Variation of the cathodic and anodic peak potentials with the log  $[Li^+]$  for a PPy/DBS modified electrode cycled in  $LiClO_4$  aqueous solutions.



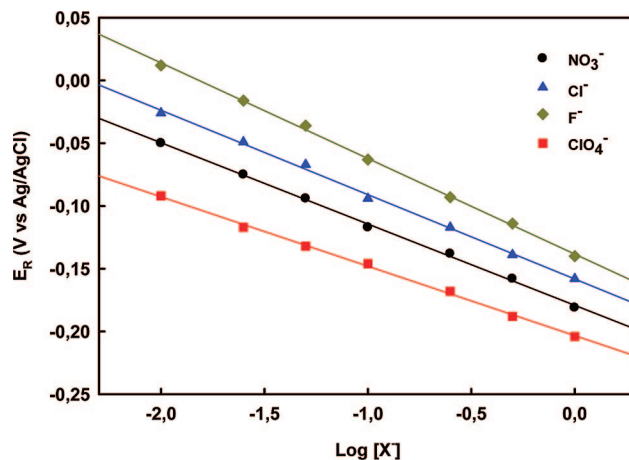
**Figure 4.** Voltammograms of a PPy/ $ClO_4$  modified electrode in diverse concentrations of NaCl aqueous solutions. Figure indicates the NaCl concentrations.

Finally, with the aim of corroborating that the Butler–Volmer formalism could be applied to these polymeric systems, an additional figure has been included. Figure 3 shows the cathodic and anodic peak potentials derived from Figure 1 versus log  $[Li^+]$ . As can be seen, the variation of the cathodic peak potential increases linearly with the logarithm of the electrolyte concentration. However, the anodic peak potential maintains a quasi constant value with the log  $[Li^+]$ . These results are in agreement with eqs 9 and 8, respectively, confirming that the Butler–Volmer-based method is truly applicable to these polymeric systems.

### 3.2.2. Polypyrrole Film As a Voltammetric Anion Sensor.

In the same way as we have used a PPy/DBS modified electrode as a cation sensor, another polypyrrole film will be evaluated in this section as an anion sensor. In this case, we synthesized a PPy film doped with a small anion:  $ClO_4^-$ . The redox reaction of this system is described by Scheme II, which postulates anion interchange during the reduction/oxidation process.

To evaluate this polymeric material as voltammetric anion sensor, we have cycled a PPy/ $ClO_4$  film in four sodium salts of different anions: fluoride, chloride, nitrate, and perchlorate. Cyclic voltammograms of the polymeric modified electrode were obtained in different concentrations of the electrolyte solutions. As for application to cations sensor, a moderate scan rate ( $\leq 30$  mV  $s^{-1}$ ) allowed the polymeric modified electrodes to be kept operational for a long period of time and also permitted one polymeric film to be immersed in different electrolyte solutions.



**Figure 5.** Calibration plots of reversible potential,  $E_R$ , versus log  $[X^-]$  for a PPy/ $ClO_4$  modified electrode in aqueous solutions of  $Na^+X^-$ .  $E_R$  calculated using eq 3.

**TABLE 2: Voltammetric Parameters for the  $PPy^{+/0}$  Redox Process Obtained for PPy/ $ClO_4$  Films Immersing in 0.1 M  $Na^+X^-$  Aqueous Solutions. Scan rate: 30 mV  $\cdot$  s $^{-1}$**

	perchlorate	nitrate	chloride	fluoride
$E_p^{ox}$ (mV)	−113	−32	−92	−16
$E_p^{red}$ (mV)	−179	−202	−96	−110
$E_R$ (mV)	$−146 \pm 4$	$−119 \pm 5$	$−94 \pm 4$	$−62 \pm 2$
$S$ (mV $\cdot$ dec $^{-1}$ )	−56	−64	−67	−76

<sup>a</sup>  $S$  values were obtained from Figure 5.

Figure 4 displays the cyclic voltammograms of a PPy/ $ClO_4$  film registered in different concentrations of NaCl. As before, the use of the peaks potentials values from these voltammograms, allows us to obtain the  $E_R$  values for each NaCl concentration. Hence, the  $E_R$  versus log  $[Cl^-]$  plot is generated and a linear relationship with negative slope resulted (Figure 5).

Proceeding in the same way as with the other electrolyte salts, we observed negative slopes for all of them (Figure 5), in accordance with eq 2, derived from Nernst and eq 20 obtained from Butler–Volmer.

The slopes obtained from Figure 5 have values ranging between  $−56$  mV  $\cdot$  dec $^{-1}$  for  $NaClO_4$  and  $−76$  mV  $\cdot$  dec $^{-1}$  for NaF (Table 2). Although the slope obtained for  $NaClO_4$  is close to the ideal Nernstian value, the other three slope values differ notably from this ideal value. Hence, we again consider that it is more appropriate to use the Butler–Volmer based treatment, eq 20, which can explain these values. From this equation, the value of the slope for an anion sensor is defined by

$$S'' = 2.303 \frac{RT}{2\alpha_a n_s F} \quad (22)$$

Note that where  $\alpha_a$  is equal to 0.5, the slope value obtained from the Butler–Volmer treatment coincides with the slope obtained from Nernst. Accordingly, the Butler–Volmer treatment can be used for a Nernstian system and for a system out of equilibrium.

Through the use of the slope values obtained from Figure 5, eq 22 allows us estimate the values of factor  $\alpha_a \cdot n_s$  for the  $PPy^{+/0}$  couple when different anions are used: 0.39 for  $F^-$ , 0.44 for  $Cl^-$ , 0.46 for  $NO_3^-$ , and 0.53 for  $ClO_4^-$ . It should be noted that when a lower peak potential increment ( $\Delta E_p$ ) is obtained

in the voltammograms a higher error will be involved in the calculus of the  $\alpha_a \cdot n_s$ .

With respect to anion identity, it is demonstrated that for identical anion concentrations in electrolyte solutions, each anion leads to a different voltammetric peak pattern and hence different reversible potential values for the  $\text{PPy}^{+/0}$  couple (Figure 5). Thus, the PPy system can be deemed as a voltammetric sensor analogous to an anion-selective electrode.

The applicability of the Butler–Volmer formalism to these  $\text{PPy}/\text{ClO}_4$  polymeric systems can be demonstrated in a similar way as it was carried out previously in Figure 3 for a  $\text{PPy}/\text{DBS}$  system. Equations 15 and 16 predict, respectively, that the cathodic peak maintains a constant value and the anodic peak decreases linearly with the  $\log [X^-]$ . These predictions are in accordance with the shift of the peak potentials observed in Figure 4.

At this point, we would like to outline the different behavior observed for  $\text{PPy}/\text{DBS}$  and  $\text{PPy}/\text{ClO}_4$  in Figures 1 and 4, respectively. For  $\text{PPy}/\text{ClO}_4$ , the anodic peak is shifted to a more negative potential as the electrolyte concentration increases, while the cathodic peak remains approximately at the same potential for different  $\text{NaCl}$  concentrations. However, in Figure 1 where a  $\text{PPy}/\text{DBS}$  film was cycled, the cathodic peak shifted to more positive values, while the anodic peak maintained a quasi-constant value for the different electrolyte concentrations (Figure 3). This behavior could be explained by eqs 8 and 9 for the  $\text{PPy}/\text{DBS}$  system and eqs 15 and 16 for a  $\text{PPy}/\text{ClO}_4$  of the method presented in this paper. However, an alternative explanation was used previously in the literature to interpret a similar shift of the peak potentials.<sup>6,10</sup>

Thus, it has been reported that the voltammetric peaks corresponding to the insertion of mobile ions are more sensitive to the scan rate, leading to a shift of the peak potential.<sup>6,10</sup> Thus, Ren et al.<sup>6</sup> affirmed that insertion of the mobile ionic species from the solution into the polymer is associated with a larger ohmic potential drop than its expulsion. These authors considered that at the beginning of the part of the potential cycle involving insertion, the ionic resistance of the film is at its maximum value.

Hence, the shift of the cathodic peak for  $\text{PPy}/\text{DBS}$  and the anodic peak in the case of  $\text{PPy}/\text{ClO}_4$  with the electrolyte concentration may be explained by the above evidence.  $\text{PPy}/\text{DBS}$  is a cationic exchanger system and so the cations take up the polymer during the reduction and they are expelled to the solution during the oxidation. Thus, inclusion of the cations occurs during the reduction process and a shift of the cathodic peak potential is observed with the electrolyte concentration. Contrarily, during oxidation, the cations are expelled from the polymer and so the peak potential presents a similar value for all electrolyte concentrations studied.

In the same way,  $\text{PPy}/\text{ClO}_4$  is an anionic exchanger system, and in this case the anions enter the polymer during the anodic branch and they are expelled during the cathodic one. Once again, in Figure 4 the anodic peak, where anion inclusion occurs, shifts with the electrolyte concentration and the cathodic peak, where the anion is expelled, maintains its potential value invariable with the electrolyte concentration.

Furthermore, note that in refs 6 and 10 the peak shifted due to ion inclusion inside the polymer when the scan rate was varied. However, we observed a similar shift related with ion inclusion when the electrolyte concentration was changed. Hence, it can be established that the electrolyte concentration will affect the ionic resistance of the film in similar terms as the scan rate. Thus, for a  $\text{PPy}/\text{DBS}$  system an increasing

electrolyte concentration produces a shift of the cathodic peak to a more positive potential, indicating that a lower overpotential is necessary to reduce the polymer. This behavior can be explained as a diminution of the ionic resistance of the polymer with the electrolyte concentration, facilitating inclusion of the cation in the polymeric matrix.

In the same way, the shift of the anodic peak to a more negative potential for  $\text{PPy}/\text{ClO}_4$  film when the electrolyte concentration increased indicates that a lower overpotential has to be applied to oxidize the polymeric material, facilitating anionic inclusion from the solution. Once again, this behavior is explained by a decrease in the ionic resistance of the film as the electrolyte concentration increases.

**3.3. Detector Responses to Multianalyte Solutions.** The aim of this section is to check whether the PPy films used in the previous sections would retain their cation or anion selectivity in mixed-cation or mixed-anion solutions, respectively.

First, we exam the  $\text{PPy}/\text{DBS}$ -modified electrode in solutions where two different cations have been mixed. Bond et al.<sup>2,3</sup> used an adaptation of the Nicolsky–Eisenman (N-E) type equation for voltammetric sensors

$$E_R = x + S \log([A] + K_{A,B}[B]) \quad (23)$$

where  $E_R$  is the midpoint reversible potential,  $x$  and  $S$  are the origin ordinate and the slope of the calibration plot for the main ion (A), B denotes the “competing” or interfering cation, and  $K$  is the ion selectivity coefficient, which represents the preference of the sensor for the main ion or the interfering one.

In the literature, it has been established that the N-E equation assumes a Nernstian response for the main and the interfering ions.<sup>30,31</sup> However, based on the Butler–Volmer treatment proposed in this work, an equation similar to N-E equations can be deduced, but in this case the  $S$  value is defined by eq 21. Hence, this  $S$  value may coincide or not with the ideal Nernstian slope, as was commented in previous sections, and this fact makes it possible to use the N-E equation for non Nernstian systems, which follows a Butler–Volmer behavior.

With respect to the estimation of the ion selectivity coefficients of a voltammetric sensor, the empirical separate solution method (SSM), based on the following equation, can be used

$$-\log K_{A,B} = \frac{E_{RA} - E_{RB}}{S} \quad (24)$$

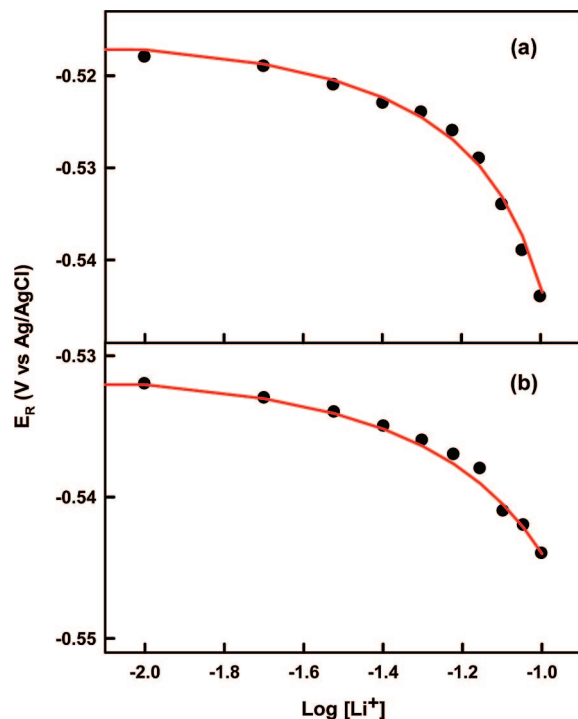
where  $S$  is the average slope for the two competing ions. As mentioned above, the  $S$  values can be deduced for each ion by our method based on the Butler–Volmer treatment. Thus, we can assume the use of  $S$  values differing from ideal Nernstian value.

Using the data included in Table 1 we obtain the following sequence of  $K$  values:

$$K_{\text{Li},K} = 4.73 > K_{\text{Na},K} = 2.24 > K_{\text{Li},Na} = 2.11$$

This result leads to the following cation selectivity sequence:  $K^+ > Na^+ > Li^+$ , which is in accordance with the shift of the calibration lines to more negative values (Table 1 and Figure 2).

Furthermore, in order to confirm that the using of the N-E equation is appropriate to our system, the experimental values of the  $E_R$  obtained by using mixed-cation solutions in variable



**Figure 6.** Reversible potential for the PPY<sup>+/0</sup> couple as obtained by immersing a PPY/DBS electrode in mixed-cation solutions containing variable Li<sup>+</sup>/K<sup>+</sup> ratios (a) and containing variable Li<sup>+</sup>/Na<sup>+</sup> ratios (b) and a constant total cation concentration of 0.1 M. Symbols correspond to experimental data and the solid line to data obtained from eq 23 (see text for further details).

cation ratios were compared with those predicted by the N-E expression. Ten mixed-ion ratios, ranging from 0.1 M of A and 0 M of B to 0 M of A and 0.1 M of B, maintaining a constant ionic strength, were used. Figure 6a shows the results for Li<sup>+</sup>/K<sup>+</sup> mixtures. Circles correspond to experimental data and the solid line to the best fit obtained with equation 23. Consistency between the experimental and predicted data was especially good at  $x = -503$  mV,  $S = 41$  mV·dec<sup>-1</sup>, and  $K_{Li,K} = 4.80$ .

In the same way, Figure 6b depicts the results for selected Li<sup>+</sup>/Na<sup>+</sup> mixtures. Again, the experimental data and the best fit were highly consistent at  $x = -505$  mV,  $S = 40$  mV·dec<sup>-1</sup>, and  $K_{Li,Na} = 2.20$ .

Although the  $K_{Li,K}$  and  $K_{Li,Na}$  values obtained suggest perturbations (competitive selectivity) from the interfering ion in the determination of the main ion, the proposed electrode provides an acceptable response to these types of mixtures. Also, the  $K$  values obtained for the cation-mixture measurements are similar to those provided by eq 24, which confirms the accuracy of the separate solution method approximation.

In 1995 the matched potential method (MPM) was recommended by IUPAC<sup>30,32</sup> as the most appropriate for determining  $K$  values because it is totally independent of the N-E equation or any of its modifications. This recommendation was based on the affirmation that the N-E equation assumes a Nernstian response for the primary and the interfering ions. However, based on the method proposed by us, in our opinion this affirmation is not totally correct, because we have demonstrated that the N-E equation is also valid for systems obeying the Butler–Volmer theory.

Furthermore, Umezawa et al.<sup>30,31</sup> affirmed that the  $K$  values obtained by MPM for cases in which both primary and interfering ions have the same charge and respond in a Nernstian manner should agree well with those obtained by methods based

on the N-E equation. In this sense, we considered that two systems obeying the Butler–Volmer equation should produce similar values of  $K$  as those obtained by SSM and MPM. Therefore, we have obtained the  $K$  values using the MPM to compare them with those resulting from the N-E based method.

The MPM, proposed by Gadzepko and Chirstian<sup>33</sup> in 1984, defines  $K$  as an activity ratio of primary and interfering ions giving the same potential changes under identical conditions. At first, a known activity ( $a_A'$ ) of the primary ion solution is added to a reference solution that contains a fixed activity ( $a_A$ ) of primary ions, and the corresponding reversible potential change ( $\Delta E_R$ ) is recorded. Next, a solution of an interfering ion, whose activity is  $a_B$ , is added to the reference solution until the same reversible potential change ( $\Delta E_R$ ) is reached:

$$K_{A,B} = \frac{a_{A'} - a_A}{a_B} \quad (25)$$

It should be noted that this equation is here adapted for the first time to be applied in voltammetric ion sensors. With this aim, we use the activity values where the same reversible potential change ( $\Delta E_R$ ) is observed, instead of the potential increment ( $\Delta E$ ) used in potentiometric sensors.

We obtained  $K_{Li,K} = 5.18$  and  $K_{Li,Na} = 2.38$  (each value was the average from 9  $K$  values obtained from 9 different  $\Delta E_R$ ), values that are very close to those obtained by the N-E based methods. Hence, we can confirm that for cases in which both primary and interfering ions have the same charge and respond in a Nernstian or Butler–Volmer manner, both of methods provide similar results.

In the same way, we examined the selectivity of a PPY/ClO<sub>4</sub> film in solutions where two different anions have been mixed. Once again, the ion selectivity coefficients,  $K$ , for this voltammetric anion sensor were calculated using the empirical SSM, based on eq 24. The experimental data included in Table 2 were taken to obtain the following sequence of  $K$  values:

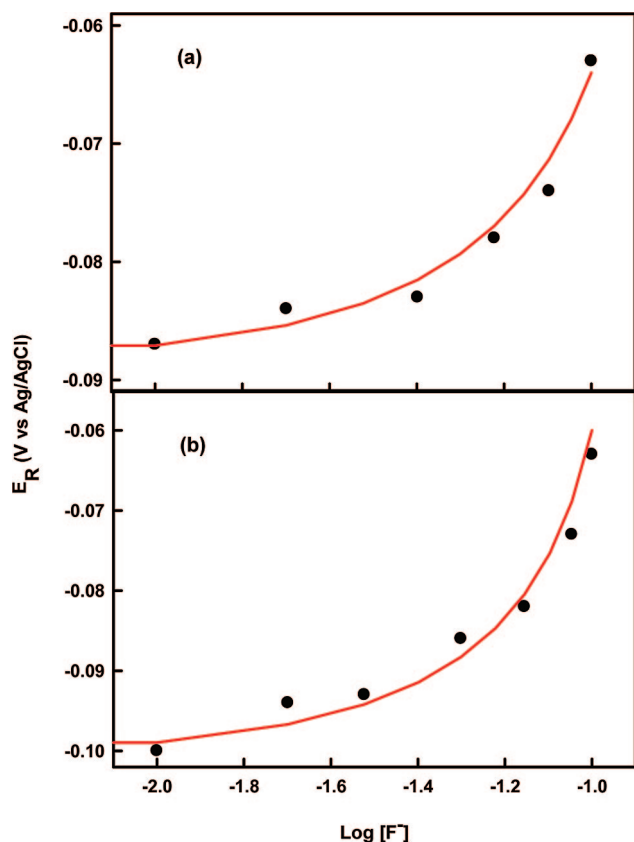
$$K_{F,ClO_4} = 15.3 > K_{F,NO_3} = 5.9 > K_{F,Cl} = 2.76 > K_{Cl,NO_3} = 2.13$$

These  $K$  values lead to the following selectivity sequence: ClO<sub>4</sub><sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > F<sup>-</sup>, which is in accordance with the positive shift of the PPY reversible potential obtained changing the anion included in the electrolyte solution (see Table 2 and Figure 5).

Furthermore, in order to confirm that the using the N-E is appropriate to our system, the experimental values of the  $E_R$  obtained by using mixed-cation solutions in variable cation ratios were compared with those predicted by N-E expression. Several mixed-ion ratios, ranging from 0.1 M of A and 0 M of B to 0 M of A and 0.1 M of B, maintaining a constant ionic strength, were used. Figure 7 shows the results for selected F<sup>-</sup>/Cl<sup>-</sup> (a) and F<sup>-</sup>/NO<sub>3</sub><sup>-</sup> (b) mixtures. Circles correspond to experimental data and the solid lines are the best fits of eq 23. The two were highly consistent at  $x = -120$  mV,  $S = -56$  mV·dec<sup>-1</sup>, and  $K_{F,Cl} = 2.76$  for F<sup>-</sup>/Cl<sup>-</sup> mixtures and at  $x = -116$  mV,  $S = -56$  mV·dec<sup>-1</sup>, and  $K_{F,NO_3} = 5.4$  for F<sup>-</sup>/NO<sub>3</sub><sup>-</sup> mixtures.

Also, the matched potential method (MPM) was used to obtain the anion selectivities coefficients, resulting  $K_{F,Cl} = 2.52$  and  $K_{F,NO_3} = 3.54$ . Although the  $K_{F,NO_3}$  value is lower, the  $K_{F,Cl}$  value is close to that obtained by N-E methods.





**Figure 7.** Reversible potential for the  $\text{PPy}^{+/0}$  couple as obtained by immersing a  $\text{PPy}/\text{ClO}_4$  electrode in mixed-anion solutions containing variable  $\text{F}^-/\text{Cl}^-$  ratios (a) and containing variable  $\text{F}^-/\text{NO}_3^-$  ratios (b) and a constant total anion concentration of 0.1 M. Symbols correspond to experimental data and the solid line to data obtained from eq 23 (see text for further details).

Again, although the  $K_{\text{F,Cl}}$  and  $K_{\text{F,NO}_3}$  values obtained suggest competitive selectivity from the interfering ion in the determination of the main ion, the proposed electrode provides an acceptable response to these types of mixtures.

#### 4. Conclusions

In this work we have demonstrated that the new method proposed based on Butler–Volmer formalism can be successfully applied to assess the capability of the voltammetric ion sensors. Two polypyrrole films,  $\text{PPy}/\text{DBS}$  and  $\text{PPy}/\text{ClO}_4$ , modified electrodes were tested as voltammetric cation and anion sensors, respectively. Both polymeric films produced slope values in the semilogarithm plots that differed from ideal Nernstian values, which could be explained by the inclusion of the electron-transfer coefficient in the equations deduced from Butler–Volmer. Tentative values of electron-transfer coefficients for the different polymeric materials and electrolytes are presented.

Moreover, this new theoretical treatment allows us to include the slope values deduced by the new method in the Nicolsky–Eisenman equation for the determination of the selectivity coefficients ( $K$ ) for systems which respond with a Butler–Volmer, and those obeying the Nernstian equation.

The results show that  $\text{PPy}/\text{DBS}$  and  $\text{PPy}/\text{ClO}_4$  systems can be deemed as voltammetric ion sensors analogous to cation and anion-selective electrodes, respectively, and that they exhibit a degree of ion-selectivity when immersed in mixed-analyte solutions. Selectivity coefficients for the two proposed sensors were obtained by

several experimental methods, including SSM and MPM. The latter is applied for the first time to the voltammetric ion sensors, changing the  $\Delta E$  by  $\Delta E_R$ . The  $K$  values acquired by the different methods were very close.

The acceptable degree of selectivity obtained suggests that these electrodes may be useful for applying in real systems, although a previous preconcentration step may sometimes be necessary. Therefore, to our minds the proposed sensors represent a step forward in the development of new voltammetric lithium (or others cations) or fluoride (or other anions) detectors, providing an acceptable compromise between reliability and ease of preparation and use.

**Acknowledgment.** M.C. and R.R.-A. wish to acknowledge funding by the Spanish Ministerio de Educación y Ciencia within the framework CTQ2004-01677, CTQ2007-60387 and cofunding by FEDER. A.J.F.R. would like to thank the financial support from the Spanish government and from the Seneca Foundation.

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