Ac-Electrogravimetry Study of Electroactive Thin Films. II. Application to Polypyrrole

Claude Gabrielli,*,† Jose J. Garcia-Jareño,†,‡ Michel Keddam,† Hubert Perrot,† and Francisco Vicente‡

UPR 15 du CNRS, Physique des Liquides et Electrochimie, Université Pierre et Marie Curie,
4 place Jussieu, 75252 Paris, France, and Department Química-Física, Universidad de Valencia,
Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

Received: October 23, 2001

Polypyrrole films were investigated by using ac-electrogravimetry, that is, simultaneous impedance and electrogravimetry spectroscopies at various potentials between the reduced and oxidized forms in NaCl solutions. Information about the movement of anions, cations, and solvent during the switching of polypyrrole between oxidation states was obtained. Anions were inserted in the film, whereas cations and solvent were expelled during oxidation. Sodium ions were solvated, but the hydration number was lower at anodic potentials. The insertion/expulsion isotherms and the transfer time constants were obtained for the three species.

Introduction

It is now commonly admitted that anions, cations, and solvent are all involved during the switching between oxidation states of electroactive polymers. The kinetics of the exchange of these species depends on the nature of these ions and the method of fabrication of the polymer.[1,2] Some anions (e.g., ClO_4^-) promote the formation of compact films, while others (SO_4^{2-}, Cl^-) promote more porous films.[3−7] Despite the numerous past studies, there are still many remaining questions regarding their electrochemical growth mechanism, their structure, and even their electrical properties[8] and, in particular, the transfer kinetics of the species, ions and solvent, occurring during a redox reaction.[9,10] In fact, in practical applications, electrode performance is governed by the rate-determining step at which the charges are exchanged. In many cases, ion and solvent transfer at the polymer/solution interface has been found to be slower than electron motion, which balances them to reach electroneutrality.[11,12]

Contrary to electroactive films where only one species is involved in the charge compensation process, for example, Prussian Blue, for which results have been reported in a companion paper, called paper I[13] in the following, three species are often involved in electroactive polymers in the same conditions. Therefore, the understanding of the compensation mechanism is much more difficult. Indeed, the solution of the problem necessitates the analysis of three unknown processes, namely, anion, cation, and solvent transfers, with only two known quantities because the usual quantities measured are current and mass by means of a potentiostatic arrangement coupled with a quartz crystal microbalance (QCM).[14−16] The first investigations have analyzed the current and mass responses to a potential scan. However, these quasi steady state techniques have not been able to separate anion and cation transfers and especially solvent interference. So, only qualitative results were gained by means of these techniques. Two ways have been explored to properly analyze the three species transfers. On one hand, a third measured quantity has been added to separate the processes: the probe beam deflection technique (or mirage effect)[17−25] allows the three unknown transfers (cation, anion,

and solvent) to fit three data sets (charge, mass, and beam deflection). On the other hand, another approach was tested. It was based on time scale variations, which allow the various time constants of the processes to be explored. This can be carried out by resolving the processes in time or in frequency. Changing the sweep rate of the potential scan results in current and mass responses, which can be interpreted in terms of ingress or exit of the species.[26,27] However, the frequency analysis of both current and mass allows a real dissection of the whole process and the separation of the movements of each species. In a first attempt, the impedance alone has been measured,[28−30] but the interpretation of the diagrams is difficult, especially when solvent is involved in the species exchange.[31−36] Then, ac-electrogravimetry, where the usual electrochemical impedance has been simultaneously measured with the mass/potential transfer function, has been proposed.[37−44] Time and frequency resolution, that is, various sweep rates of the potential or perturbation of the potential by a sine wave signal, give, in principle, the same type of information. However, the first technique is a nonlinear technique because large amplitude signals are used, whereas the second one is a small amplitude technique. Then, for the latter, all of the kinetic parameters can be obtained at each potential, whereas these quantities are averaged over the potential for the former. In addition, generally speaking, frequency analysis allows the elementary processes to be easily separated, whereas it is much more difficult for time resolution. This is the same discussion as for the comparison between impedance technique and cyclic voltammetry in classical electrochemistry.

Polypyrrole films were chosen in this work as an illustration of the benefits of ac-electrogravimetry to gain thorough information on the kinetics of the redox processes of electroactive polymers because it is already well-documented in the literature.[45−48]

In this paper, to simplify the problem, we have chosen to study very thin films where charge transport (migration or diffusion) in the polymer is not limiting. The rate-limiting step is now the ionic and solvent transfers at the polymer/electrolyte interface.

Theory

Theoretical Transfer Functions with Two Ions and One Free Solvent. Like in paper I, to illustrate the model behavior,

---

* To whom correspondence should be addressed. cg@ccr.jussieu.fr.
† Université Pierre et Marie Curie.
‡ Universidad de Valencia.

Electroactive Thin Films: Polypyrrole

J. Phys. Chem. B, Vol. 106, No. 12, 2002 **3193**

TABLE 1: Schematic Representation of the Four Transfer Functions, $(\Delta E/\Delta I)(\omega)$, $(\Delta q/\Delta E)(\omega)$, $(\Delta m/\Delta E)(\omega)$, and $(\Delta m/\Delta q)(\omega)F$

i) Cation and solvent expelled; anion inserted	$\frac{\Delta E}{\Delta I}$, Ω cm^2(a)	$\frac{\Delta q}{\Delta E}$, C cm^{-2} V^{-1}(b)
Increasing frequencies : → Values of the parameters : $d_{film} = 0.1\ \mu m$ $K_c = 10^{-3}$ cm s^{-1} $m_c = 39$ g mol^{-1} $G_c = 2\ 10^{-5}$ mol cm^{-2} s^{-1} V^{-1}	[schematic]	[schematic] cation anion
	$\frac{\Delta m}{\Delta E}$, g cm^{-2} V^{-1}(c)	$\frac{\Delta m}{\Delta q}$.F, g mol^{-1}(d)
$K_a = 5\ 10^{-7}$ cm s^{-1} $m_a = 35$ g mol^{-1} $G_a = -1\ 10^{-8}$ mol cm^{-2} s^{-1} V^{-1} $K_s = 5\ 10^{-5}$ cm s^{-1} $m_s = 18$ g mol^{-1} $G_s = 2\ 10^{-6}$ mol cm^{-2} s^{-1} V^{-1} $C_{interface} = 1\ 10^{-5}$ F cm^{-2}	[schematic] anion / solvent cation	[schematic] anion / cation
ii) Cation expelled; anion and solvent inserted	$\frac{\Delta E}{\Delta I}$, Ω cm^2(e)	$\frac{\Delta q}{\Delta E}$, C cm^{-2} V^{-1}(f)
Values of the parameters : same except for : $G_s = -2\ 10^{-6}$ mol cm^{-2} s^{-1} V^{-1}	[schematic]	[schematic] cation anion
	$\frac{\Delta m}{\Delta E}$, g cm^{-2} V^{-1}(g)	$\frac{\Delta m}{\Delta q}$.F, g mol^{-1}(h)
	[schematic] solvent anion / cation	[schematic] cation anion

TABLE 2: Schematic Representation of the Four Partial Transfer Functions, $(\Delta m_{cs}/\Delta E)(\omega)$ and $(\Delta m_{as}/\Delta E)(\omega)$

i) Cation and solvent expelled; anion inserted	$\frac{\Delta m_{cs}}{\Delta E}$, g cm^{-2} V^{-1}(a)	$\frac{\Delta m_{as}}{\Delta E}$, g cm^{-2} V^{-1}(b)
Increasing frequencies : → (same values as in table I)	[schematic] solvent cation	[schematic] anion / solvent
ii) Cation expelled; anion and solvent inserted	$\frac{\Delta m_{cs}}{\Delta E}$, g cm^{-2} V^{-1}(c)	$\frac{\Delta m_{as}}{\Delta E}$, g cm^{-2} V^{-1}(d)
Increasing frequencies : → (same values as in table I)	[schematic] solvent / cation	[schematic] anion / solvent

the main transfer functions, $(\Delta E/\Delta I)(\omega)$, $(\Delta q/\Delta I)(\omega)$, $(\Delta m/\Delta E)(\omega)$, and $(\Delta m/\Delta q)(\omega)$, were calculated from eqs 12, 15, 13, and 17 (paper I[13]), respectively, for three interfering species, anion, cation and solvent, inserted or expelled from the film. In addition, the partial electrogravimetric transfer functions, $(\Delta m_{as}/\Delta E)(\omega)$ and $(\Delta m_{cs}/\Delta E)(\omega)$, were calculated because more than one species is involved in the redox reaction according to eqs 19 and 21 of paper I. Table 1 shows the results for two typical situations: (i) cation and solvent expelled and anion inserted and (ii) cation expelled and anion and solvent inserted. The values of the parameters used to calculate the various transfer functions are given in Table 1. The arrows indicate the direction of increasing frequency.

To counter balance the positive charges created by a potential increase across the electroactive film, that is, for an oxidation step, cations may be expelled and anions inserted. In the first example considered in Table 1, the solvent is expelled. For the electrochemical impedance, $(\Delta E/\Delta I)(\omega)$ (Table 1a and e), the high frequency loop corresponds to charge transfer in parallel to double-layer charging and the straight vertical line, in the lower-frequency range, corresponds to ionic transfer. For $(\Delta q/\Delta E)(\omega)$ (Table 1b and f), two loops corresponding to the anion and the cation are observed. This quantity allows the number of charged species involved in the charge compensation process to be determined. The electrogravimetric transfer function, $(\Delta m/\Delta E)(\omega)$ (Table 1c and g), takes into account all of the species involved in the redox reaction, here, three species: cations for the highest frequencies and anions for the lowest frequencies. Contrary to the case where only one species is involved in the charge compensation process, the low-frequency limit of the transfer function, $(\Delta m/\Delta E)(\omega \rightarrow 0)$, depends on all of the species

that take part in the redox reaction. This is the slope of $m(E)$, which can be measured by using a classical QCM. Contrary to the case where only one species is involved in the charge compensation process, the last transfer function, $(\Delta m/\Delta q)(\omega)$-$F$, is frequency dependent (Table 1d and h).

Theoretical Partial Transfer Functions. By eliminating either the anion or the cation contribution, the partial electrogravimetric transfer functions, $(\Delta m_{cs}/\Delta E)(\omega)$ and $(\Delta m_{as}/\Delta E)$-(ω), respectively, make it possible to determine which loop is related to anion, cation, and solvent (Table 2). If cations and solvent are expelled and anions are inserted in the film (Table 2i), the comparison of the two partial electrogravimetric transfer functions, $(\Delta m_{cs}/\Delta E)(\omega)$ and $(\Delta m_{as}/\Delta E)(\omega)$, allows the attribution of each of the loops: the loop in common between the two partial transfer functions corresponds to the solvent and the additional loop in the two cases, Table 2a and b, to the cation and the anion, respectively. It should be noted that the cation loop (a) and the anion loop (b) are magnified as was demonstrated by examining eqs 19 and 21 from paper I. When the solvent is inserted as shown Table 2ii, the conclusions are identical as previously except for the location of the solvent in the third quadrant.

Experimental Section

Film Preparation. Polypyrrole films can be prepared by using different methods described in the literature.[49] The mechanism of polymerization was already described earlier.[50] The polypyrrole films were prepared from 0.1 M pyrrole + 0.05 M NaDS. This low sodium dodecyl sulfate (NaDS) concentration was chosen to avoid surfactant aggregates and to obtain films of good quality in term of mechanical properties.[51]

From these solutions, a cyclic potential sweep between 0 and 0.675 V vs SCE at a 10 mV s^{-1} rate was applied twice. These films were sufficiently thin to allow the Sauerbrey equation[52] to be used without limitation coming from viscoelastic properties of the polymer film.[27,53] Electrochemical studies were carried out in 0.25 M NaCl to study the influence of the ions present in the bathing solution.

Experimental Setup. The experimental setup is the same as the one used in paper I.[13]

Results and Discussion

First, current and mass responses to a potential scan were simultaneously measured in 0.25 M NaCl solutions. Then, measurements of the electrochemical impedance and the electrogravimetric transfer function were simultaneously carried out.
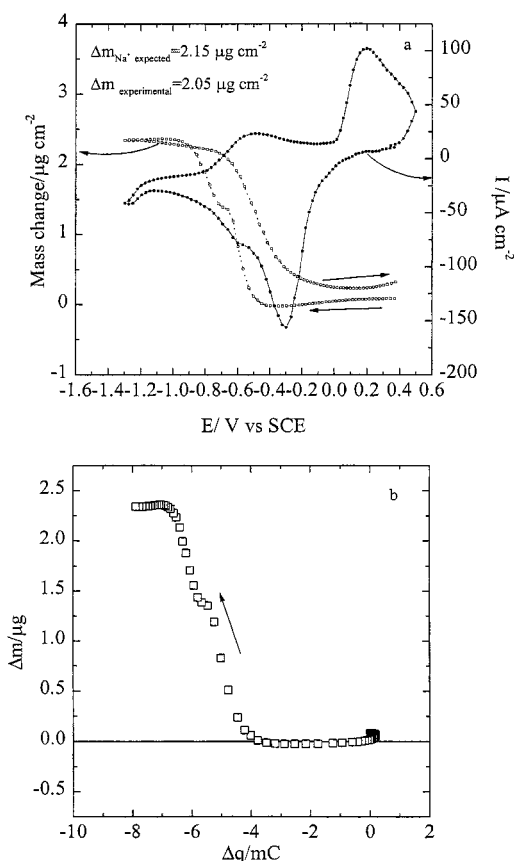
Figure 1. Current and mass responses (a) to forward and backward potential scans for a polypyrrole film in 0.25 M NaCl and (b) curve of mass vs charge for a cathodic sweep, same conditions as in panel a.

Voltammetry and Mass/Potential Curves. The polypyrrole (PPy) films were first studied by cyclic voltammetry, and the mass response to a potential scan was recorded by means of the quartz crystal microbalance. Figure 1a shows the current and mass responses to a potential scan of a PPy film in a 0.25 M NaCl solution. The mass decrease, determined through microbalance measurements, between the reduced and oxidized forms was about 2.05 μg cm^{-2}. Meanwhile, the expected mass change evaluated from the electric charge enclosed within the voltamogram was about 2.15 μg cm^{-2} if only Na$^+$ was supposed to be involved in the charge compensation. However, the reduction process of the film between -0.2 and -0.6 V seemed to demonstrate cation ingress as the film gained mass, and the oxidation process seemed to demonstrate cation expulsion as the film lost mass. However, when oxidation went beyond $+0.3$ V, the film gained mass again showing anion insertion. Therefore, the QCM in quasi steady state led to ambiguous results, as the charge compensation seems to occur not only by cation ingress but also by anion expulsion. Even when the curve $\Delta m - \Delta q$ is plotted (Figure 1b), the conclusions remain ambiguous: by considering the global mass and charge change during the process, the equivalent molar mass obtained is -28 g mol^{-1}, and by taking into account the slope in the linear range, a -90 g mol^{-1} value is delivered.

These results clearly show that charge compensation process during oxidation or reduction of the polypyrrole film occurred by insertion and expulsion of cations and anions. However, it is difficult to separate the various processes.[54] The information obtained from the coupling of the measurement of the electrochemical impedance and the electrogravimetric transfer function will enlighten these points.

Electrochemical Impedance and Electrogravimetric Transfer Function. Polypyrrole films were studied by simultaneous measurements of the electrochemical impedance and electrogravimetric transfer function in 0.25 M NaCl at various potentials after that the steady state was reached. Figures 2 and 3 show the various transfer functions, measured and calculated, for PPy films immersed in a 0.25 M NaCl solution at potentials of -0.55 and $+0.3$ V vs SCE. The electrochemical impedance (Figures 2a and 3a) has the usual shape, when dealing with this kind of ion-blocking electrodes, from which it is difficult to extract information. It should be noted that there is no part with a slope equal to 45° in the electrochemical impedance response (Figures 2a and 3a); therefore, the rate-limiting step is not mass transport in the film but rather ionic transfer between the solution and the film. The electrogravimetric transfer function, $(\Delta m/\Delta E)(\omega)$, shows (Figure 2c), at least, two loops at -0.55 V similar to the theoretical plot given in Table 1c. The high-frequency loop seems to be related to cation expulsion from the film, whereas the low-frequency loop seems to be related to anion ingress in the film. The low-frequency limit of this loop gives a negative value for $(\Delta m/\Delta E)(\omega \rightarrow 0)$; this is in agreement with the slope of the $m(E)$ plot of the mass response to a potential scan given in Figure 1 in this potential range.

Data analysis was conducted in the same way as that for the Prussian Blue films in paper I.[13] The model was tested by taking into account that the possible species involved in the compensation process could be H_2O for the solvent, Cl$^-$ for the anions, and H$^+$ or Na$^+$, hydrated or not, for the cations. Below, examples are detailed for 0.25 M NaCl at $E = -0.55$ and $+0.3$ V vs SCE.

For the two potentials, the plot of the $(\Delta q/\Delta E)(\omega)$ (Figures 2b and 3b) in the complex plane shows two loops. This demonstrates that two charged species are involved in the charge compensation process. For $E = -0.55$ V vs SCE, the plot of $(\Delta m/\Delta q)(\omega)$ shows also two loops such as in Table 1d. This demonstrates that the solvent is involved in the redox reaction in addition to anions and cations. Now, the plots of the partial electrogravimetric transfer function help to identify the loop related to each species.

Figure 2e shows $(\Delta m_{cs}/\Delta E)(\omega)$, obtained by eliminating the anion contribution, that is the electrogravimetric transfer function only related to the contribution of the cation and solvent. By taking $m_a = 35.5$ g mol^{-1}, that is, the molar mass of Cl$^-$ ions, in eq 18 of paper I,[13] the low-frequency loop disappears. This demonstrates that Cl$^-$ is the anion involved in the charge compensation and that it has the lowest time constant.

At last, the plot of the partial electrogravimetric transfer function, $(\Delta m_{as}/\Delta E)(\omega)$, obtained by eliminating the cation contribution, is related to the anion and solvent alone (eq 26 in paper I[13]). By taking m_c as the atomic mass of Na$^+$ + nH$_2$O, where n is the number of solvent molecules, the high-frequency loop disappears for $n = 2$. This demonstrates that the involved cation in the charge compensation process is Na$^+$ hydrated with two molecules of water and that it has the greatest time constant. When the sodium ions were taken without the solvatation shell, the calculations in the cathodic range show a bad agreement between the experimental data and the theoretical simulation.

Therefore, the solvent was related to the intermediate frequency loop and was expelled when polypyrrole was oxidized. This result seems a little bit surprising if compared with results given by Otero et al.[55,56] In fact, the way of polymer electrogeneration (in organic medium) and the condition of the test (low cathodic potential, organic medium) can explain these differences. To fit the $(\Delta m/\Delta E)(\omega)$ data, the solvent molar mass
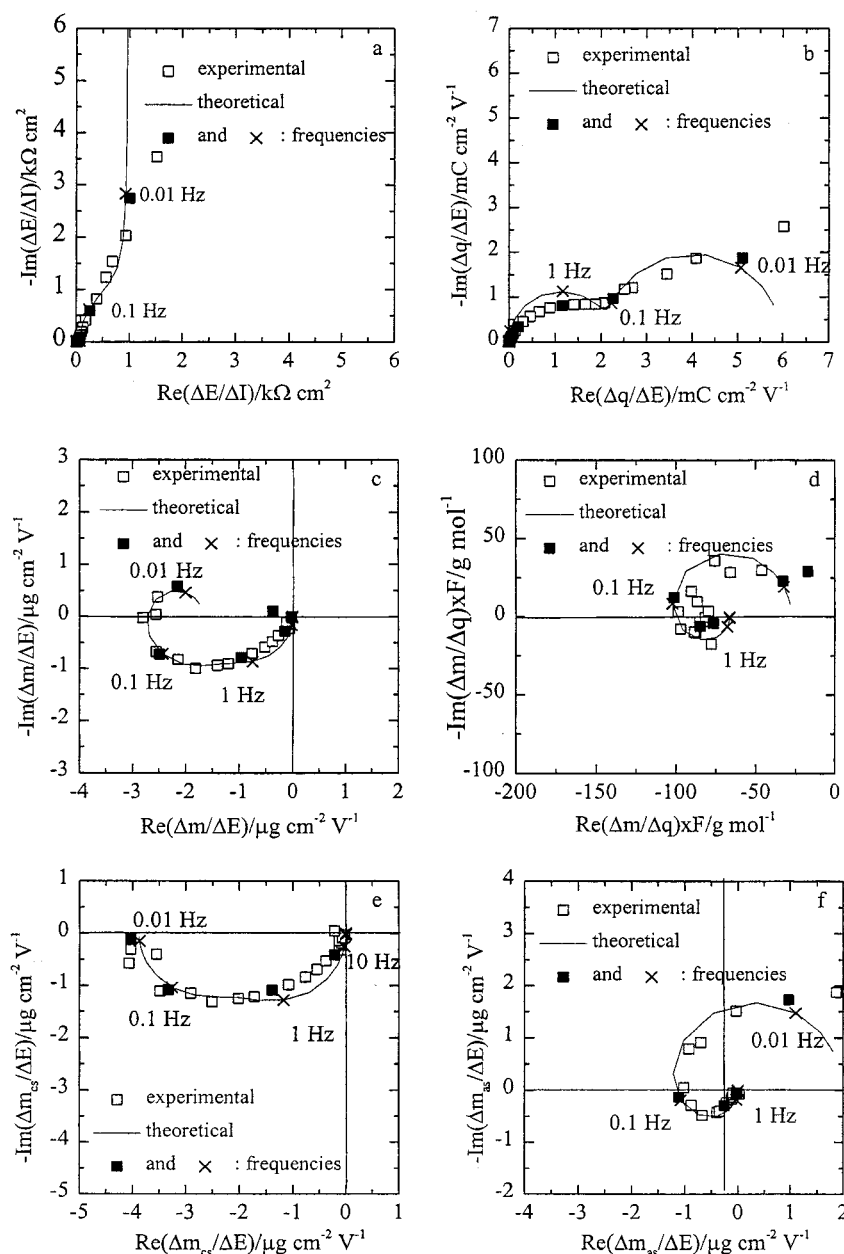
Figure 2. Measured and calculated transfer function quantities for a polypyrrole film in a 0.25 M NaCl solution at -0.55 V vs SCE: (a) $(\Delta E/\Delta I)(\omega)$; (b) $(\Delta q/\Delta E)(\omega)$; (c) $(\Delta m/\Delta E)(\omega)$; (d) $(\Delta m_{as}/\Delta E)(\omega)$; (e) $(\Delta m_{cs}/\Delta E)(\omega)$; (f) $(\Delta m/\Delta q)(\omega)F$. Parameters used for the calculation were as follows: $d_{film} = 0.1\ \mu m$; $C_{interface} = 6.99\ \mu F\ cm^{-2}$; $K_c = 6.9 \times 10^{-5}\ cm\ s^{-1}$; $K_a = 1.13 \times 10^{-6}\ cm\ s^{-1}$; $K_s = 8.8 \times 10^{-6}\ cm\ s^{-1}$; $G_c = 1.5 \times 10^{-7}$ mol $s^{-1}\ cm^{-2}\ V^{-1}$; $G_a = -4.5 \times 10^{-9}\ mol\ s^{-1}\ cm^{-2}\ V^{-1}$; $G_s = 8.8 \times 10^{-9}\ mol\ s^{-1}\ cm^{-2}\ V^{-1}$; $m_a = 35.5\ g\ mol^{-1}$, $m_s = 18\ g\ mol^{-1}$, $m_c = (23 + 36)\ g\ mol^{-1}$.

has to be taken as $m_s = 18\ g\ mol^{-1}$ showing that free water was transferred during the redox process.

For $E = +0.3$ V vs SCE, Figure 3e shows that $(\Delta m_{cs}/\Delta E)(\omega)$, obtained by eliminating the anion contribution, is related to the contribution of the cation and solvent alone. By taking $m_a = 35.5\ g\ mol^{-1}$, that is, the molar mass of Cl$^-$ ions, in eq 18 in paper I,[13] practically all of the diagram disappears demonstrating that at this potential, the redox reaction involves only anions and, in addition, that Cl$^-$ is the anion involved in the charge compensation.

At last, the plot of the partial electrogravimetric transfer function, $(\Delta m_{as}/\Delta E)(\omega)$, obtained by eliminating the cation contribution, is related to the anion and solvent alone. By taking m_c as the atomic mass of Na$^+$ + nH$_2$O like above, the high-frequency loop disappears for $n = 0$ or 1, which is difficult to determine given the weak contribution of the cation at this

potential. This demonstrates that the involved cation in the charge compensation process is Na$^+$ hydrated with one molecule of water or dehydrated.

At $E = +0.3$ V vs SCE, the $(\Delta m/\Delta q)(\omega)$ transfer function is practically reduced to one point at about 35 g mol^{-1} on the real axis in the complex plane, similar to in Table 1b of paper I.[13] This confirms that Cl$^-$ is the predominant species involved in the charge compensation process at $+0.3$ V vs SCE. The motions of both anions and cations have been proposed in other works, realized in the same conditions, with less sophisticated methods and also with less information concerning the subleties of the species transfer between the polymer and the film.[57]

Kinetic Approach. Bruckenstein et al. have already noticed that sodium transfer required water transfer in the same direction.[27] It was shown here that during the charge compensation process occurring when PPY is oxidized solvent leaves the
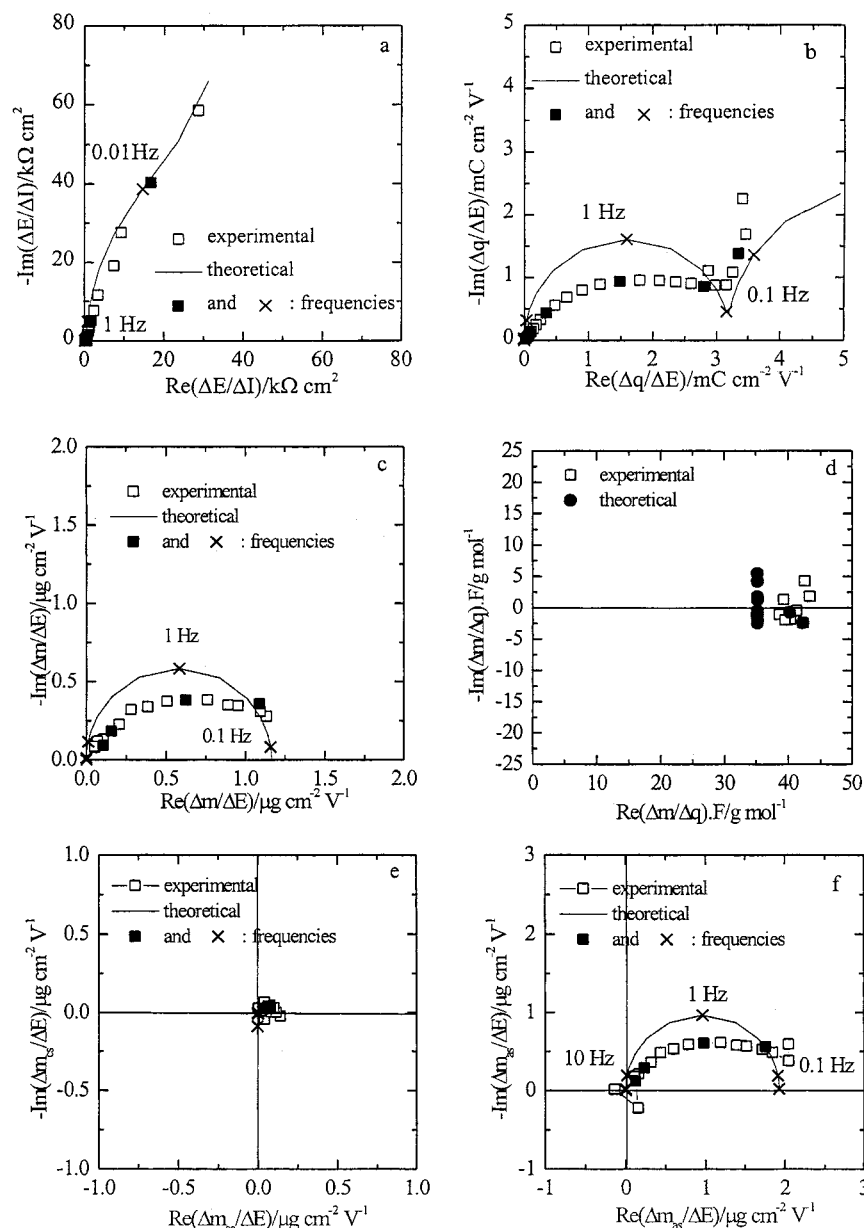
Figure 3. Measured and calculated transfer function quantities for a polypyrrole film in a 0.25 M NaCl solution at +0.3 V vs SCE: (a) $(\Delta E/\Delta I)(\omega)$; (b) $(\Delta q/\Delta E)(\omega)$; (c) $(\Delta m/\Delta E)(\omega)$; (d) $(\Delta m_{as}/\Delta E)(\omega)$; (e) $(\Delta m_{cs}/\Delta E)(\omega)$; (f) $(\Delta m/\Delta q)(\omega)F$. Parameters used for the calculation were as follows: $d_{film} = 0.1~\mu m$; $C_{interface} = 24.7~\mu F~cm^{-2}$; $K_c = 1.8 \times 10^{-7}~cm~s^{-1}$; $K_a = 6.2 \times 10^{-5}~cm~s^{-1}$; $G_c = 9.4 \times 10^{-10}~mol~s^{-1}~cm^{-2}~V^{-1}$; $G_a = -2.0 \times 10^{-7}~mol~s^{-1}~cm^{-2}~V^{-1}$; $m_a = 35.5~g~mol^{-1}$, $m_c = 23~g~mol^{-1}$.

conducting polymer under two forms: free, on one hand, but also bonded to the cation, on the other hand, in a solvation shell. In addition, the hydration coefficient is potential dependent. Na^+ cations are more hydrated in the reduced state, where $n = 3$ at $E = -0.7$ V vs SCE, than in the oxidized state where Na^+ is less or not hydrated. At cathodic potentials, the polymer swells (insertion of solvent) because more free solvent is inserted. Therefore, the ingress of bigger ions such as hydrated cations may be favored by the resultant higher porosity. This phenomenon is due to the release of the polymeric chains resulting from the solvent insertion.

From the experimental curves obtained and the fitting with the theoretical model, some kinetic parameters are determined, in addition to molar masses of species i. First, the parameters K_i, which give the time constant of the relaxation of the movement of species i (Figure 4), are determined. These quantities are decreasing with the potential, especially the time
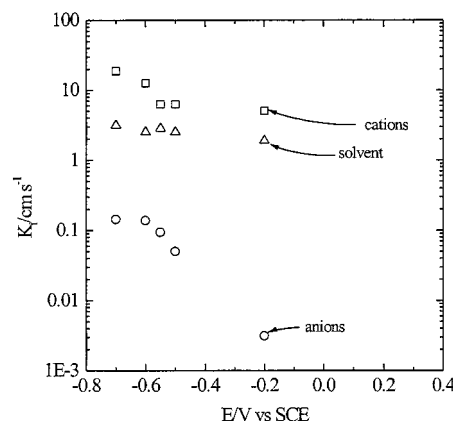

Figure 4. Relaxation time constant, K_i, for cations, anions, and solvent for a polypyrrole film immersed in 0.25 M NaCl.

constant of anions, which are the slowest to transfer. Then, the ratio G_i/K_i gives the derivative of the insertion isotherm of

Electroactive Thin Films: Polypyrrole

J. Phys. Chem. B, Vol. 106, No. 12, 2002 **3197**
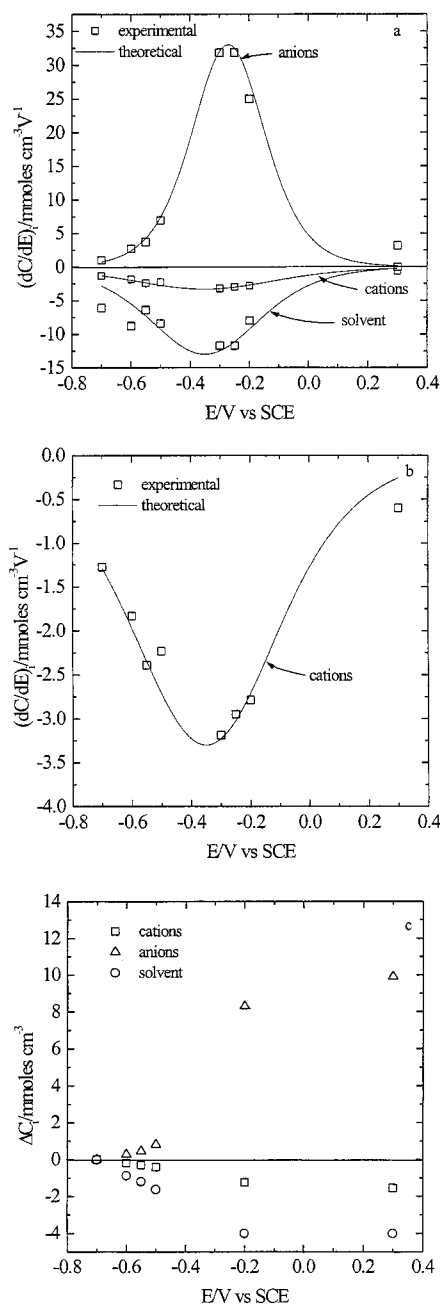
Figure 5. Variation of the derivative of the insertion law for cations, anions and solvent with the potential (a) in polypyrrole immersed in 0.25 M NaCl. Theoretical values were taken in cgs units, and to simplify the calculation, β, γ, and η are defined as follows: $\beta = ((b_i - b_i')/4)(C_{i_{max}} - C_{i_{min}})$, $\gamma = (b_i' - b_i)/2$ and $\eta = -((b_i' - b_i)/2)(E_i^0 - E_i)$; for cation, $\beta = -0.0033$, $\gamma = 3$, and $\eta = 1.05$; for anion, $\beta = 0.033$, $\gamma = -6$, and $\eta = -1.6$; for solvent, $\beta = -0.013$, $\gamma = 4$, and $\eta = 1.4$. Panel b shows the magnification of the derivative of the insertion law for cation under the same experimental conditions and theoretical values as for panel a. Panel c shows the variation of the insertion law, ΔC_i, for cations, anions, and solvent with the potential.

species i, as $G_i/K_i = (dC_i/dE)(\omega \rightarrow 0)$ (Figure 5a,b). Figure 5a,b shows also the plot of the theoretical value of the corresponding quantity (eq 5 of paper I[13]). Integration of the latter against potential gives the insertion isotherm (Figure 5c). From the insertion isotherm of species i, the quantity $C_{i_{max}} - C_{i_{min}}$ can be estimated. At last, the number, n, of water molecules that solvated Na$^+$ ions is plotted in Figure 6 with respect to the potential. It shows that n is potential-dependent: polypyrrole is more hydrated in the reduced state than in the oxidized state.
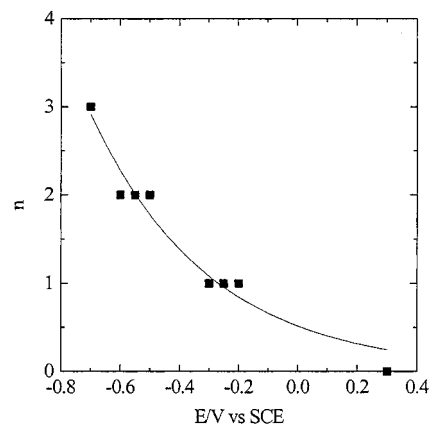
Figure 6. Number of water molecules attached to the Na$^+$ cations during their insertion into or expulsion from polypyrrole immersed in 0.25 M NaCl.

Thermodynamic Approach. Although anion insertion or cation expulsion could be sufficient alone to compensate for the positive charges created when the polymer is oxidized, the results reported here show that both simultaneously occur. As already noticed by Bruckenstein and Hillman,[58,59] thermodynamic restraints may help to describe ions and solvent populations within a polymer immersed in an aqueous solutions. This could be explained by considering the partition coefficients of ions in addition to electroneutrality.

If intermediate concentrations are considered ($C_{i_{min}} \ll C_i \ll C_{i_{max}}$), eq 4 of paper I[13] can be written under the simplified form

$$J_i(d_{film}) = k_i C_i - k_i' C_{i_{sol}} \tag{1}$$

where $k_i'' = k_i' C_{i_{max}}$, $k_i = k_{i_0} \exp b_i E$, and $k_i'' = k_{i_0}'' \exp b_i' E$.

At steady-state, $I = 0$, and $J_i(d_{film}) = 0$ because of boundary conditions at the electrode/film interface where ions cannot cross.

Therefore, if $K_i = C_i/C_{i_{sol}}$ is a generalized partition coefficient at steady-state, as $J_i(d_{film}) = 0$, eq 1 leads to $k_i'/k_i = C_i/C_{i_{sol}}$. Therefore, K_i is potential dependent such as

$$K_i = K_{i_0} \exp\left[+\frac{F}{RT}E\right] \tag{2}$$

if $b_i = -\alpha_{t_i}F/(RT)$, $b_i' = (1 - \alpha_{t_i})F/(RT)$, $K_{i_0} = k_{i_0}'/k_{i_0}$, and only monocharged ions are considered in this part.

Conditions of electroneutrality in the solution and in the polymer give

$$C_{c_{sol}} - C_{a_{sol}} = 0$$

$$C_c + C_\Phi - C_a = 0 \tag{3}$$

where C_Φ is the concentration of some cationic sites in the polymer (e.g., polarons, positive fixed sites).

By eliminating the concentrations of the species in the solution,

$$C_c = -K_c \frac{C_\Phi}{K_c - K_a} \quad \text{and} \quad C_a = -K_a \frac{C_\Phi}{K_c - K_a} \tag{4}$$

Now, if a potential scan is imposed,

$$\frac{\Delta C_c}{\Delta E} = -\frac{\Delta C_\Phi}{\Delta E}\frac{1}{1-\dfrac{K_a}{K_c}} - \frac{\Delta\left(\dfrac{K_a}{K_c}\right)}{\Delta E}\frac{C_\Phi}{\left(1-\dfrac{K_a}{K_c}\right)^2} \tag{5}$$

$$\frac{\Delta C_a}{\Delta E} = -\frac{\Delta C_\Phi}{\Delta E}\frac{1}{\dfrac{K_c}{K_a}-1} + \frac{\Delta\left(\dfrac{K_c}{K_a}\right)}{\Delta E}\frac{C_\Phi}{\left(\dfrac{K_c}{K_a}-1\right)^2} \tag{6}$$

$$\frac{\Delta C_a}{\Delta E} = -\frac{\Delta C_\Phi}{\Delta E}\frac{1}{\dfrac{K_c}{K_a}-1} - \frac{\Delta\left(\dfrac{K_a}{K_c}\right)}{\Delta E}\frac{C_\Phi}{\left(1-\dfrac{K_a}{K_c}\right)^2} \tag{7}$$

Of course, eqs 5 and 7 lead to

$$\frac{\Delta C_c}{\Delta E} - \frac{\Delta C_a}{\Delta E} = -\frac{\Delta C_\Phi}{\Delta E} \tag{8}$$

As for monocharged anions and cations,

$$\frac{K_a}{K_c} = \frac{K_{a_0}}{K_{c_0}}\exp\left[\frac{-2F}{RT}E\right] \tag{9}$$

Therefore,

$$\frac{\Delta\left(\dfrac{K_a}{K_c}\right)}{\Delta E} = \frac{-2F}{RT}\frac{K_a}{K_c} \tag{10}$$

Moreover

$$\frac{\Delta C_\Phi}{\Delta E} = \frac{\Delta C_\Phi}{\Delta t}\frac{\Delta t}{\Delta E} \tag{11}$$

that is,

$$\frac{\Delta C_\Phi}{\Delta E} = \frac{I}{d_{film}vF} \tag{12}$$

where I is the current density, d is the film thickness, and v is the potential sweep rate.

Hence,

$$\frac{\Delta C_c}{\Delta E} = -\frac{I}{d_{film}vF}\frac{1}{1-\dfrac{K_a}{K_c}} + \frac{2F}{RT}\frac{K_a}{K_c}\frac{C_\Phi}{\left(1-\dfrac{K_a}{K_c}\right)^2} \tag{13}$$

$$\frac{\Delta C_a}{\Delta E} = -\frac{I}{d_{film}vF}\frac{1}{\dfrac{K_c}{K_a}-1} + \frac{2F}{RT}\frac{K_a}{K_c}\frac{C_\Phi}{\left(1-\dfrac{K_a}{K_c}\right)^2} \tag{14}$$

Limiting cases are as follows: (i) For $K_a \gg K_c$,

$$\frac{\Delta C_c}{\Delta E} = \frac{K_c}{K_a}\left(\frac{I}{d_{film}vF} + \frac{2F}{RT}C_\Phi\right) \tag{15}$$

$$\frac{\Delta C_a}{\Delta E} = \frac{I}{d_{film}vF} + \frac{2F}{RT}\frac{K_c}{K_a}C_\Phi \tag{16}$$

then, $\Delta C_c/\Delta E \approx 0$ and $\Delta C_a/\Delta E \approx I/(d_{film}vF)$, cation movement is negligible, and anions enter the electroactive film for anodic current during charge compensation. (ii) For $K_a \ll K_c$,

$$\frac{\Delta C_a}{\Delta E} = \frac{K_a}{K_c}\left(-\frac{I}{d_{film}vF} + \frac{2F}{RT}C_\Phi\right) \tag{17}$$

$$\frac{\Delta C_c}{\Delta E} = -\frac{I}{d_{film}vF} + \frac{2F}{RT}\frac{K_a}{K_c}C_\Phi \tag{18}$$

then, $\Delta C_a/\Delta E \approx 0$ and $\Delta C_c/\Delta E \approx -I/(d_{film}vF)$, anion movement is negligible, and cations leave the electroactive film for anodic current during charge compensation.

More generally, if K_a and K_c are such as $K_a/K_c = 1 + \chi$, where $\chi > 0$ if $K_a > K_c$ and $-1 < \chi < 0$ if $K_a < K_c$, then

$$\frac{\Delta C_c}{\Delta E} = \frac{I}{d_{film}vF}\frac{1}{\chi} + \frac{2F}{RT}\frac{C_\Phi}{\chi^2}(1+\chi) \tag{19}$$

$$\frac{\Delta C_a}{\Delta E} = \frac{I}{d_{film}vF}\frac{1+\chi}{\chi} + \frac{2F}{RT}\frac{C_\Phi}{\chi^2}(1+\chi) \tag{20}$$

Between the limiting cases, it is possible to discuss according to the values of χ (for an anodic current, $I > 0$) the following: (1) For $\chi > 0$, $\Delta C_c/\Delta E$ and $\Delta C_a/\Delta E > 0$; the two species are inserted in the polymer. (2) For $\chi < 0$,

$$-\frac{2F}{RT}\frac{C_\Phi}{\dfrac{I}{d_{film}vF}+\dfrac{2F}{RT}C_\Phi} < \chi < 0, \quad \frac{\Delta C_c}{\Delta E} \text{ and } \frac{\Delta C_a}{\Delta E} > 0$$

the two species are inserted in the polymer.

It should be noted that

$$-\frac{2F}{RT}\frac{C_\Phi}{\dfrac{I}{d_{film}vF}+\dfrac{2F}{RT}C_\Phi}$$

is the root of the equation $\Delta C_c/\Delta E = 0$.

$$-\frac{2F}{RT}\frac{d_{film}vF}{I}C_\Phi < \chi < -\frac{2F}{RT}\frac{C_\Phi}{\dfrac{I}{d_{film}vF}+\dfrac{2F}{RT}C_\Phi}, \quad \frac{\Delta C_c}{\Delta E} < 0,$$

$$\text{and } \frac{\Delta C_a}{\Delta E} > 0$$

the anions are inserted in the polymer and the cations are expelled. This is the case of polypyrrole in the experimental conditions studied in this work.

It should be noted that

$$-\frac{2F}{RT}\frac{d_{film}vF}{I}C_\Phi$$

is the root of the equation $\Delta C_a/\Delta E = 0$.

$$-1 < \chi < -\frac{2F}{RT}\frac{d_{film}vF}{I}C_\Phi, \quad \frac{\Delta C_c}{\Delta E} \text{ and } \frac{\Delta C_a}{\Delta E} < 0$$

the two species are expelled from the polymer.

Therefore, depending on the relative values of the partition coefficient of the cations and anions in regard to the polymer, they can be inserted or expelled from the polymer when it is oxidized. For polyaniline, it was shown that anions are

predominantly inserted and cations may be either inserted or expelled following the acid in which the oxidation occurs.[39]

For material like Prussian Blue (see paper I[13]), where anionic sites prevail in the film, the cations mainly compensate the charge during the redox process. Electroneutrality in the polymer leads to

$$C_c - C_\Phi - C_a = 0$$

then

$$C_c = -K_c \frac{C_\Phi}{K_c - K_a} \quad \text{and} \quad C_a = -K_a \frac{C_\Phi}{K_c - K_a}$$

$$\frac{\Delta C_\Phi}{\Delta E} = -\frac{I}{d_{film} v F} \tag{21}$$

Hence,

$$\frac{\Delta C_c}{\Delta E} = \frac{I}{d_{film} v F} \frac{1}{1 - \frac{K_a}{K_c}} - \frac{2F}{RT} \frac{K_a}{K_c} \frac{C_\Phi}{\left(1 - \frac{K_a}{K_c}\right)^2} \tag{22}$$

$$\frac{\Delta C_a}{\Delta E} = \frac{I}{d_{film} v F} \frac{1}{\frac{K_c}{K_a} - 1} - \frac{2F}{RT} \frac{K_a}{K_c} \frac{C_\Phi}{\left(1 - \frac{K_a}{K_c}\right)^2} \tag{23}$$

Like above, if K_a and K_c are such as $K_a/K_c = 1 + \chi$, where $\chi > 0$ if $K_a > K_c$ and $-1 < \chi < 0$ if $K_a < K_c$, then

$$\frac{\Delta C_c}{\Delta E} = -\frac{I}{d_{film} v F} \frac{1}{\chi} - \frac{2F}{RT} \frac{C_\Phi}{\chi^2} (1 + \chi) \tag{24}$$

$$\frac{\Delta C_a}{\Delta E} = -\frac{I}{d_{film} v F} \frac{1 + \chi}{\chi} - \frac{2F}{RT} \frac{C_\Phi}{\chi^2} (1 + \chi) \tag{25}$$

(1) For $\chi > 0$, $\Delta C_c/\Delta E$ and $\Delta C_a/\Delta E < 0$; the two species are expelled from the polymer. (2) For $\chi < 0$,

$$-\frac{2F}{RT} \frac{C_\Phi}{\frac{I}{d_{film} v F} + \frac{2F}{RT} C_\Phi} < \chi < 0, \quad \frac{\Delta C_c}{\Delta E} \quad \text{and} \quad \frac{\Delta C_a}{\Delta E} < 0$$

the two species are expelled from the polymer.

$$-\frac{2F}{RT} \frac{d_{film} v F}{I} C_\Phi < \chi < -\frac{2F}{RT} \frac{C_\Phi}{\frac{I}{d_{film} v F} + \frac{2F}{RT} C_\Phi}, \quad \frac{\Delta C_c}{\Delta E} > 0$$

$$\text{and} \quad \frac{\Delta C_a}{\Delta E} < 0$$

the anions are expelled from the polymer and the cations are inserted.

$$-1 < \chi < -\frac{2F}{RT} \frac{d_{film} v F}{I} C_\Phi, \quad \frac{\Delta C_c}{\Delta E} \quad \text{and} \quad \frac{\Delta C_a}{\Delta E} > 0$$

the two species are inserted in the polymer

Now, the limiting cases are rapidly examined: For $K_a \gg K_c$, $\Delta C_c/\Delta E \approx 0$ and $\Delta C_a/\Delta E \approx -I/(d_{film} v F)$, cation movement is negligible, and anions leave the electroactive film for anodic current during charge compensation. For $K_a \ll K_c$, $\Delta C_a/\Delta E \approx 0$ and $\Delta C_c/\Delta E \approx I/(d_{film} v F)$, anion movement is negligible, and

cations enter the electroactive film for anodic current during charge compensation. This is the case of Prussian Blue (paper I[13]).

Therefore, like for cationic sites in the polymer, depending on the relative values of the partition coefficient of the cations and anions in regard to the polymer, they can be inserted or expelled from the polymer when it is oxidized.

Concerning the solvent, at least, two causes can be invoked to explain its movement. Either, as any change in ionic concentration changes the activity of the solvent, to maintain its activity, the solvent has to move from or into the polymer. Second, steric problems may arise.

The first cause can be explored by considering a partition coefficient defined such as $K_s = A_s/A_{s_{sol}}$ for the solvent. Because $A_{s_{sol}}$ is water activity in the aqueous phase, it is a constant, which implies that A_s has to be also a constant in the polymer in a first approximation.[58,59] However, when cations, anions, or both leave or enter the polymer, the activity of the solvent is changed as $A_i = C_i 10^{-z_i^2 F_I^{1/2}/(2(1+F_I^{1/2}))}$ where $F_I = {}^1/_2 \Sigma_i z_i^2 C_i$ ($F_I < 0.2$), and therefore, the activity of each species i is changed by

$$\frac{\Delta A_i}{A_i} = \frac{\Delta C_i}{C_i} - \frac{z_i^2 \Delta F_I}{4\sqrt{F_I}(1 + \sqrt{F_I})^2} \tag{26}$$

where

$$\Delta F_I = \frac{1}{2} \sum_i z_i^2 \Delta C_i \tag{27}$$

For one monovalent anion or one monovalent cation, one has

$$\Delta F_I = \frac{1}{2}(\Delta C_c + \Delta C_a) \tag{28}$$

Then, to maintain its activity in the polymer ($\Delta A_s = 0$), the solvent should need to have

$$\frac{\Delta C_s}{C_s} = \frac{\frac{1}{2}(\Delta C_c + \Delta C_a)}{4\sqrt{F_I}(1 + \sqrt{F_I})^2} \tag{29}$$

where for a positive potential change (oxidation) $\Delta C_c < 0$ and $\Delta C_a > 0$ as cations are expelled and anions are inserted. As

$$\frac{\Delta C_c}{\Delta E} - \frac{\Delta C_a}{\Delta E} = -\frac{\Delta C_\Phi}{\Delta E} \tag{30}$$

As shown above, for positive sites $\Delta C_\Phi/\Delta E > 0$, and then $\Delta C_c/\Delta E < \Delta C_a/\Delta E$. Therefore, the concentration change should be such as $\Delta C_s > 0$. However, experiments show that solvent is expelled in these conditions. This demonstrates that the activity of the solvent does not remain constant for switching of the polymer between oxidation states.[59]

Another possibility of solvent movement is mechanical constraints (called volume constraint in ref 27) due to space factor problems leading to solvent expulsion when ions are inserted. This is supported by experimental results obtained on polyaniline, which is another conducting polymer, where the maximum of the absolute derivative of the solvent expulsion isotherm is proportional to the molar mass of anions when various salts with the same cation are tested.[39] From eq 5 of paper I,[13] this result shows that the maximum concentration of the expelled solvent $C_{s_{max}}$ is proportional to the molar mass, that is, approximately to the size, of the inserted anions.
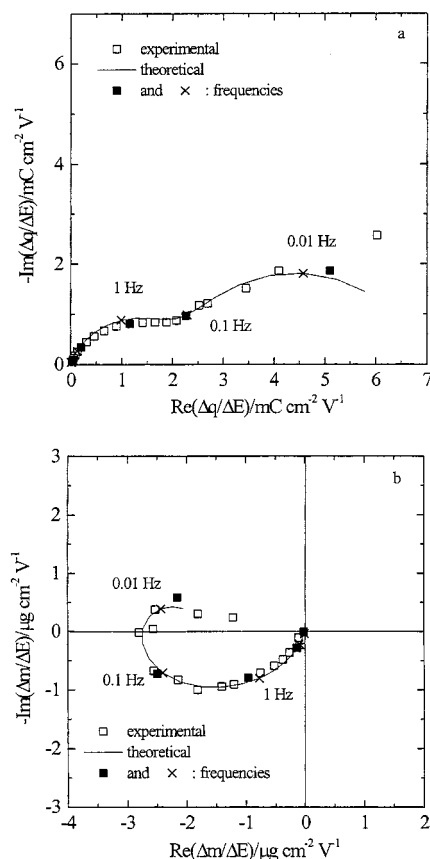
Figure 7. Examples of calculated transfer functions, (a) $(\Delta q/\Delta E)(\omega)$ and (b) $(\Delta m/\Delta E)(\omega)$, taking into account a constant phase element (CPE) with the following parameters used for the calculation: $\alpha_a = 0.65$, $\alpha_c = 0.65$, $\alpha_s = 0.85$, and for the other parameters the same values as those in Figure 2.

Therefore, when bigger anions are inserted in the polymer, more solvent is expelled as volume is limited in the polymer matrix.

Finally, like in paper I, a remark can be made concerning the adequacy of the model with the experimental results. As shown in Figures 2 and 3, the calculated quantities from the model have semicircular shapes whereas the experimental results have depressed semicircular loops. Using a constant phase element (CPE) instead of a first-order time constant can eliminate this discrepancy in the equivalent circuit:

$$\frac{\Delta C_i}{\Delta E}(\omega) = \frac{-G_i}{(j\omega)^{\alpha_i} d_{film} + K_i} \quad \text{instead of}$$

$$\frac{\Delta C_i}{\Delta E}(\omega) = \frac{-G_i}{j\omega d_{film} + K_i}$$

Figure 7a,b shows examples of calculated quantities $(\Delta q/\Delta E)$-(ω) and $(\Delta m/\Delta E)(\omega)$, taking into account a constant phase element (CPE) with $\alpha_a = 0.65$, $\alpha_c = 0.65$, and $\alpha_s = 0.85$. Like in paper I, this CPE can be due to a nonuniformity of the thickness of the polymer layer.

Conclusion

Ac-electrogravimetry allows the anions, cations, and solvent transfer at the polymer/electrolyte interface to be separated. The time constant of their relaxation can be determined. The derivative of the insertion/expulsion isotherm and, consequently, the isotherms of the exchanged species can be obtained. The quantity of free solvent can be differentiated from the solvent

bonded to ions for solvation. The hydration number of the solvated cation is determined. Moreover, these results show the great interest of this approach compared with the classical QCM technique: at -0.550 V vs SCE, three species were involved, while at 0.300 V vs SCE, only one ionic species is active. Therefore, an anodic sweep between these two potential values cannot permit discrimination of these changes even when the scan rate is modified.

List of symbols

z_i: charge number for each ion.

i: chemical species, cation, anion, or solvent; c = cation, a = anion, and s = solvent.

J_i: flux of the species i (cation, anion, or solvent) in mol cm^{-2} s^{-1}.

x: distance from the metal/film interface, cm.

Δm: mass change per surface unit in the film, g cm^{-2}.

Δq: charge change per surface unit in the film, C cm^{-2}.

m_c, m_a, m_s: cation atomic mass, anion atomic mass, solvent molar mass, g mol^{-1}.

n: number of solvent molecules accompanying cations.

$\Delta\xi_c$, $\Delta\xi_a$, $\Delta\xi_s$: number of species in moles exchanged between the solution and the film per surface unit, mol cm^{-2}.

F: Faraday number, 96 486 C mol^{-1}.

k_i, k_i': kinetic constant for the species i insertion or expulsion, cm s^{-1}.

C_i: concentration of the species i in the film, mol cm^{-3}.

d_{film}: film thickness, μm.

$C_{i_{max}}$: maximum concentration of the sites available for insertion of the i species, mol cm^{-3}.

$C_{i_{min}}$: minimum concentration of the sites occupied by the species i in the host film, mol cm^{-3}.

$C_{i_{sol}}$: concentration of species i in the solution, mol cm^{-3}.

E: applied potential to the electrochemical system, V.

b_i, b_i': tafel constant for the species i, V^{-1}.

ω: pulsation of the perturbation sine wave signal, rad s^{-1}, where $\omega = 2\pi f$.

K_i: flux sensitivity over concentration of the species i, cm s^{-1}.

G_i: flux sensitivity over potential of the species i, mol s^{-1} cm^{-2} V^{-1}.

I_F: Faradaic current density, A cm^{-2}.

$C_{interface}$: interfacial capacitance, F cm^{-2}.

Δ"parameter": change of a measured parameter under a small amplitude potential perturbation.

$(\Delta E/\Delta I)(\omega)$: electrochemical impedance, Ω cm^2.

$(\Delta m/\Delta E)(\omega)$: electrogravimetric transfer function, g cm^{-2} V^{-1}.

$(\Delta q/\Delta E)(\omega)$: electric charge/potential transfer function, C cm^{-2} V^{-1}.

$(\Delta m/\Delta q)(\omega)$: mass/electric charge-transfer function, g mol^{-1}.

$(\Delta m_{cs}/\Delta E)(\omega)$: partial electrogravimetric transfer function for cation and solvent, g cm^{-2} V^{-1}.

$(\Delta m_{as}/\Delta E)(\omega)$: partial electrogravimetric transfer function for anion and solvent, g cm^{-2} V^{-1}.

$f_{microbalance}$: microbalance frequency, Hz.

$(\Delta m/\Delta V)(\omega)$: electrogravimetric transfer function without correction of the ohmic drop, g cm^{-2} V^{-1}.

$(\Delta V/\Delta I)(\omega)$: electrochemical impedance without correction of the ohmic drop, Ω cm^2.

R_{el}: electrolyte resistance, Ω cm^2.

α_i: constant phase element for the species i.

k_i'': apparent kinetic constant for the species i insertion or expulsion, mol cm^{-2} s^{-1}.

Electroactive Thin Films: Polypyrrole

J. Phys. Chem. B, Vol. 106, No. 12, 2002 **3201**

K_i: generalized partition coefficient for the species i.

α_{t_i}: transfer coefficient for species i.

C_Φ: concentration of the sites (cationic or anionic) in the film, mol cm^{-3}.

v: potential sweep rate, V s^{-1}.

χ: ratio between K_a and K_c expressed by: $\chi = 1 - K_a/K_c$.

A_i: activity of the species i, mol^{-1} cm^{-3}.

F_I: ionic strength in the solution.

References and Notes

(1) Dinh, H. N.; Vanysek, P.; Birss, V. I. *J. Electrochem. Soc*. **1999**, *146*, 3324.

(2) Jureviciute, I.; Bruckenstein, S.; Hillman, A. R. *J. Electroanal. Chem*. **2000**, *488*, 73.

(3) Zotti, G.; Cattarin, S.; Comisso, N. *J. Electroanal. Chem*. **1988**, *239*, 387.

(4) Nunziante, P.; Pistoia, G. *Electrochim. Acta* **1989**, *34*, 223.

(5) Duic, L. J.; Mandic, Z.; Kovacicek, F. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 105.

(6) Disilvestro, J.; Scheifele, W. *J. Mater. Chem.* **1993**, *3*, 263.

(7) Tang, H.; Kitani, A.; Schiotani, M. *Electrochim. Acta* **1996**, *41*, 1561.

(8) Chidsey, C. E. D.; Murray, R. W. *J. Phys. Chem.* **1986**, *90*, 1479.

(9) Hillman, A. R.; Loveday, D. C.; Swann, M. J.; Bruckenstein, S.; Wilde, C. P. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2047.

(10) Varela, H.; Torresi, R. M. *J. Electrochem. Soc*. **2000**, *147*, 665.

(11) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 192.

(12) Hillman, A. R. In *Electrochemical Science and Technology of Polymers*; Linford, R., Ed.; Elsevier: London, 1987; Vol. 1, p 103.

(13) Gabrielli, C.; Garcia Jareno, J.; Keddam, M.; Perrot, H.; Vicente, F. *J. Phys. Chem. B* **2002**, *106*, 3182.

(14) Orata, D.; Buttry, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 3574.

(15) Bruckenstein, S.; Wilde, C. P.; Shay, M.; Hillman, A. R.; Loveday, D. C. *J. Electroanal. Chem.* **1989**, *258*, 457.

(16) Torresi, R. M.; Cordoba de Torresi, S. I.; Gabrielli, C.; Keddam, M.; Takenouti, H. *Synth. Met.* **1993**, *61*, 291.

(17) Matencio, T.; Vieil, E. *Synth. Met.* **1991**, *44*, 349.

(18) Vieil, E.; Meerholtz, K.; Matencio, T.; Heinze, J. *J. Electroanal. Chem*. **1994**, *368*, 183.

(19) El Rhazi, M.; Lopez, C.; Deslouis, C.; Musiani, M. M.; Tribollet, B.; Vieil, E. *Synth. Met.* **1996**, *78*, 59.

(20) Miras, M. C.; Barbero, C.; Kotz, R.; Haas, O.; Schmid, V. M. *J. Electroanal. Chem.* **1992**, *338*, 279.

(21) Barbero, C.; Miras, M. C.; Kotz, R.; Haas, O. *J. Electroanal. Chem.* **1997**, *437*, 191.

(22) Barbero, C.; Miras, M. C.; Kotz, R.; Haas, O. *Solid State Ionics* **1993**, *60*, 167.

(23) Barbero, C.; Miras, M. C.; Haas, O.; Kotz, R. *J. Electrochem. Soc.* **1991**, *138*, 669.

(24) Henderson, M. J.; French, H.; Hillman, A. R.; Vieil, E. *Electrochem. Solid State Lett.* **1999**, *2*, 631.

(25) French, H. M.; Henderson, M. J.; Hillman, A. R.; Vieil, E. *J. Electroanal. Chem*. **2001**, *500*, 192.

(26) Dinh, H. N.; Birss, V. I. *J. Electroanal. Chem.* **1998**, *443*, 63.

(27) Bruckenstein, S.; Brzezinska, K.; Hillman, A. R. *Electrochim. Acta* **2000**, *45*, 3801.

(28) Glarum, S. H.; Marshall, J. H. *J. Electrochem. Soc.* **1987**, *134*, 142.

(29) Hunter, T. B.; Tyler, P. S.; Smyrl, W. H.; White, H. S. *J. Electrochem. Soc.* **1987**, *134*, 2198.

(30) Gabrielli, C.; Haas, O.; Takenouti, H. *J. Appl. Electrochem.* **1987**, *17*, 82.

(31) Lang, G.; Inzelt, G. *Electrochim. Acta* **1999**, *44*, 2037.

(32) Vorotyntsev, M. A.; Daikhin, L. I.; Levi, M. D. *J. Electroanal. Chem.* **1994**, *364*, 37.

(33) Rossberg, K.; Paasch, G.; Dunsch, L.; Ludwig, S. *J. Electroanal. Chem.* **1998**, *443*, 49.

(34) Gabrielli, C.; Takenouti, H.; Haas, O.; Tsukada, A. *J. Electroanal. Chem.* **1991**, *302*, 59.

(35) Albery, W. J.; Elliott, C. M.; Mount, A. R. *J. Electroanal. Chem.* **1990**, *288*, 15.

(36) Mathias, M. F.; Haas, O. *J. Phys. Chem.* **1992**, *96*, 3175.

(37) Cordoba Torresi, S.; Gabrielli, C.; Keddam, M.; Takenouti, H.; Torresi, R. *J. Electroanal. Chem.* **1990**, *290*, 269.

(38) Gabrielli, C.; Keddam, M.; Perrot, H.; Pham, M. C.; Torresi, R. *Electrochim. Acta* **1999**, *44*, 4217.

(39) Gabrielli, C.; Keddam, M.; Nadi, N.; Perrot, H. *J. Electroanal. Chem.* **2000**, *485*, 101.

(40) Gabrielli, C.; Garcia Jareno, J.; Perrot, H. *Models Chem.* **2000**, *137*, 269.

(41) Yang, H.; Kwak, J. *J. Phys. Chem. B* **1997**, *101*, 774.

(42) Yang, H.; Kwak, J. *J. Phys. Chem. B* **1997**, *101*, 4656.

(43) Yang, H.; Kwak, J. *J. Phys. Chem. B* **1998**, *102*, 1982.

(44) Yang, H.; Lee, H.; Kim, Y. T.; Kwak, J. *J. Electrochem. Soc.* **2000**, *147*, 4239.

(45) Maia, G.; Torresi, R. M.; Ticianelli, E. A.; Nart, F. C. *J. Phys. Chem.* **1996**, *100*, 15910.

(46) Inzelt, G. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 90.

(47) Deronzier, A.; Moutet, J. C. *Coord. Chem. Rev.* **1996**, *147*, 339.

(48) Wang, L. X.; Li, X. G.; Yang, Y. L. *React. Funct. Polym.* **2001**, *47*, 125.

(49) Diaz, A. F.; Rubinson, J. F.; Mark, H. B. *Adv. Polym. Sci.* **1988**, *84*, 113.

(50) Scharifker, B. R.; Garcia-Pastoriza, E.; Marino, W. *J. Electroanal. Chem.* **1991**, *300*, 85.

(51) Peres, R. C. D.; Pernault, J. M.; De Paoli, M. A. *J. Polym. Sci.* **1991**, *29*, 225.

(52) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.

(53) Garcia-Jareno, J. J.; Gabrielli, C.; Perrot, H. *Electrochem. Commun.* **2000**, *2*, 195.

(54) Inzelt, G.; Kertesz, V.; Nybäck, A. N. *J. Solid State Electrochem.* **1999**, *3*, 251.

(55) Grande, H.; Otero, T. F. *J. Phys. Chem. B* **1998**, *102*, 7535.

(56) Otero, T. F.; Grande, H.; Rodriguez, J. *J. Phys. Chem. B* **1997**, *101*, 8525.

(57) Peres, R. C. D.; Paoli, M. A.; Torresi, R. M. *Synth. Met.* **1992**, *48*, 259.

(58) Bruckenstein, S.; Hillman, A. R. *J. Phys. Chem.* **1988**, *92*, 4837.

(59) Bruckenstein, S.; Hillman, A. R. *J. Phys. Chem.* **1991**, *95*, 10748.