

Effect of the Solvent and the Anion on the Doping/Dedoping Behavior of Poly(3,4-ethylenedioxythiophene) Films Studied with the Electrochemical Quartz Microbalance

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The doping/dedoping behavior of poly(3,4-ethylenedioxythiophene) (PEDT) in acetonitrile (lithium, sodium, and tetrabutyl perchlorate) and aqueous electrolytes (lithium and sodium perchlorate, sodium nitrate, sulfate, citrate, and toluenesulfonate) was investigated using the electrochemical quartz crystal microbalance (EQCM) technique. No significant cation exchange was observed. For the investigated anions (except sulfate), the calculated exchanged molar mass could be explained by the reversible replacement of solvent by anions during oxidation. The special behavior of sulfate that carries water into the film was explained by the high charge-to-volume ratio of this anion.

Introduction

It is well known that conducting polymer films can act as ion-exchange membranes during reversible oxidation and reduction. Upon oxidation, positive charges are formed in the polymer backbone. To satisfy the condition of electroneutrality, anions are incorporated or cations are ejected (doping reaction). Often, this ion transfer is accompanied by the exchange of solvent molecules.^{1–6}

Among a variety of factors, the wetting behavior of the polymer film in the investigated solvent determines the kinetics of the ion exchange. Poly(3,4-ethylenedioxythiophene) (PEDT) shows good redox activity in aqueous systems because of its hydrophilic surface imparted by the ether substituents in the 3 and 4 positions of the thiophene ring.⁷ Conducting polymer films prepared from other thiophene derivatives, such as the alkyl substituted, show much more sluggish redox behavior in water^{8,9} because of their hydrophobic surface properties. Furthermore, because the 3 and 4 positions of 3,4-ethylenedioxythiophene are blocked by substituents the polymerization reaction mainly occurs via the 2 and 5 positions, and cross linking is almost absent. Another important feature for electrochemical investigations (and applications) in aqueous media is the low oxidation potential of PEDT (0.21 V versus Ag/AgCl)¹⁰ that is well below the decomposition potential of water (approximately 1 V versus Ag/AgCl).

It has been shown that the electrochemical quartz crystal microbalance (EQCM) is well suited to the investigation of the electropolymerization^{11,12} and redox cycling^{13–15} of conducting polymers. The oscillating quartz crystal acts as an electromechanical transducer that translates mechanical impedances into electrical impedances.¹⁶ In the simplest case, the mechanical impedance is a surface mass load, $\Delta m/A$ (where A is the mass-sensitive area). The presence of this surface mass load causes a decrease in the resonance frequency of the quartz crystal, Δf ,

compared to the resonance frequency of the unloaded crystal, f_0 (eq 1).¹⁷

$$\Delta f = -\frac{2f_0^2}{Z_{M,Q}} \frac{\Delta m}{A} = -C_{SB} \frac{\Delta m}{A} \quad (1)$$

$Z_{M,Q}$ is the mechanical impedance of the quartz crystal ($8.849 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ for a 10-MHz AT quartz), and C_{SB} is the Sauerbrey constant ($226.01 \text{ Hz cm}^2 \mu\text{g}^{-1}$).

Real layers, such as polymer films, often cannot be described as thin, rigid layers. In these cases, the expression for the mechanical impedance contains the shear modulus of the polymer.^{18–21} The situation becomes more complicated if the surface roughness of the layer is on the order of magnitude of the penetration depth of the shear wave in the liquid (100–200 nm). For such cases, some models have been proposed that take into consideration the surface roughness parameters, such as the correlation lengths of the surface topography.^{22,23} As a result of these more complicated mechanical impedances, the resonance frequency shift of the quartz crystal becomes a complex quantity, $\Delta f^* = \Delta f + i\Delta w/2$ ($i^2 = -1$). This means that besides the frequency decrease, Δf , a damping increase, Δw , occurs. In this relation, the damping has the same unit as the frequency (Hz) and can be identified as the fwhm (full width at half-maximum) of the resonance curve of the quartz crystal. The complex frequency shift can be measured using measuring techniques based on an electric impedance analysis of the quartz near its resonance frequency.^{24–26} Recently, it has been shown that a semiquantitative characterization of the shear modulus and the surface roughness of thin layers is possible with this approach.²⁷

The combination of hydrophilic properties, relatively well defined chemical structure, and low redox potential of the polymer makes PEDT a promising material for gravimetric sensor applications in aqueous media. However, it is known that the preparation conditions of conducting polymers strongly influence the morphology²⁸ and the mechanical properties of

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TABLE 1: Apparent Molar Mass (M_{app} , Equation 2) and Number of Transferred Solvent Molecules (α , Equation 3) for the Doping/Dedoping Process of PEDT Films

	ClO_4^-	ClO_4^-	NO_3^-	TS	citrate	SO_4^{2-}
diameter/nm	0.45	0.45	0.33	0.74	0.98	0.32
solvent ^a	AN (0.34)	water (0.17)	water (0.17)	water (0.17)	water (0.17)	water (0.17)
$M_{app}/(\text{g mol}^{-1})$ from slope of m/Q plot	62.1 ± 4.9	60.0 ± 5.2	45.1 ± 4.4	84.8 ± 4.9	169.1 ± 4.5	130.5 ± 6.2
α	-1	-2	-1	-5	-3	+2
average $M_{app}/(\text{g mol}^{-1})$ (from dm/dQ)	66.2	59.8	44.8	85.0	169.0	130.5

^a Values in parentheses give the approximate diameter of the solvent molecules.

the polymer layer.²⁷ These factors are important for gravimetric sensor applications of conducting polymers in liquids.²⁹ Given the practical importance of PEDT for such applications, the aim of this work was to characterize the doping/dedoping behavior of thin PEDT layers in the “classical” solvent acetonitrile and in aqueous solutions. Special focus was given to polyvalent anions.

Experimental Section

All chemicals were analytical grade. The monomer 3,4-ethylenedioxythiophene (EDT, Bayer) was distilled prior to use. Acetonitrile (AN, Aldrich) was dried over molecular sieves (3 Å). Solutions were purged with argon (99.998%) during the experiments.

The quartz crystals used for the investigations were polished, 10-MHz AT-cut crystals with Au electrodes (ca. 100 nm) on a chromium adhesion layer (ca. 5 nm) provided by KVG (Neckarbischofsheim, Germany). The potential of the Au electrode (electrochemically active area 22.135 mm²) facing the solution was controlled with an EG&G 263A potentiostat, and the other electrode faced the air. The potentials were measured versus an aqueous Ag/AgCl/KCl(sat.) electrode with an electrolyte bridge that contained the solution under study. In the following text, all potentials refer to this reference electrode. The counter electrode was a Pt foil. The electrical admittance curve of the quartz was measured with a network analyzer (model R3753BH, Advantest, Tokyo). Approximately every 500 ms one data set could be acquired, consisting of the resonance frequency f , the fwhm w (damping of the quartz), the current, the potential, and the charge. Further details concerning the experimental setup are described elsewhere.^{26,27}

The polymer films were potentiostatically deposited at 1.1 V on the Au electrode of the quartz in acetonitrile containing 0.1 M EDT and 0.1 M lithium perchlorate (Fluka). The deposition was stopped when the resonance frequency had decreased by ca. 10 kHz.

After the preparation, the films were washed carefully with acetonitrile and cycled in monomer-free 0.1 M LiClO₄/AN with a scan rate of 10 mV/s between -0.4 and 1.1 V until a stable cyclic voltammogram (CV) was obtained. This doping/dedoping behavior in AN was compared with CV experiments (10 mV/s) in 0.1 M aqueous solutions of LiClO₄, NaClO₄, NaNO₃, sodium toluenesulfonate (TS), sodium citrate, and Na₂SO₄ between -0.4 and 0.8 V.

Scanning electron microscopy (SEM) investigations were performed with a Zeiss DSM 982 Gemini microscope (Carl Zeiss, Oberkochen, Germany).

Results and Discussion

The deposition of poly(3,4-ethylenedioxythiophene) films (PEDT) from acetonitrile caused a damping shift $\Delta w \approx 2.5$ kHz

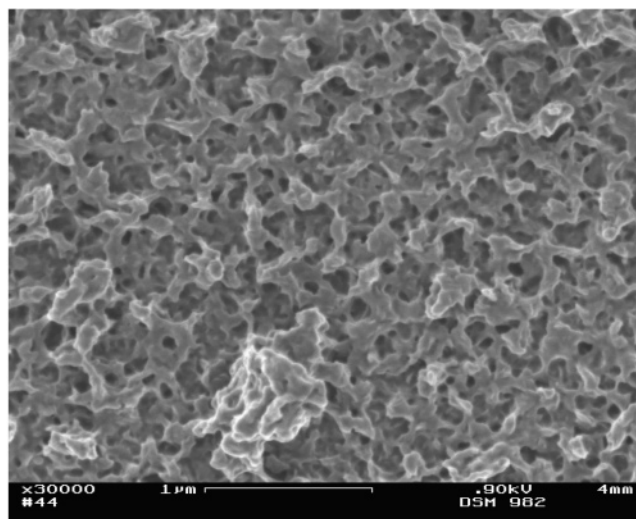


Figure 1. SEM micrograph of a PEDT film prepared from 0.1 M EDT and 0.1 M LiClO₄/AN at 1.1 V vs Ag/AgCl saturated KCl.

(frequency shift, $\Delta f \approx -10$ kHz, see Experimental Section). From these data, the real mass density of the polymer film can be calculated by using a model for viscoelastic and rough films:²⁷ $m = 25.69 \mu\text{g cm}^{-2}$. Assuming a density of $\rho = 1.5 \text{ g cm}^{-3}$, this would correspond to a smooth layer of ca. 170 nm thickness. Note, however, that the film is not smooth as indicated by the damping increase. SEM micrographs of the dried films showed a spongelike morphology with a large inner surface (Figure 1).

The doping behavior was studied for anions of different sizes (Table 1): perchlorate (the same anion as in the polymerization) with a diameter of about 0.45 nm, nitrate (0.33 nm), TS (0.74 nm), sulfate (0.32 nm), and citrate (0.98 nm). The dimensions of the anions and the solvent molecules were estimated using the commercial software ChemBats3D Pro 7.0 Chem Office 2002.

During the redox cycling (i.e., doping/dedoping) at 10 mV/s, the EQCM indicated only small damping changes, typically $\Delta w \approx 50$ Hz. The resonance frequency decreased during oxidation, indicating that the mass increased due to the doping reaction and increased during dedoping. Because of the small damping changes, the frequency changes Δf could be directly related to mass changes Δm using eq 1. The almost constant damping behavior is in contrast to observations of other conducting polymers³⁰ where the viscoelastic properties of the film (indicated by damping changes) change strongly when anions are incorporated. This is another advantage of PEDT because it facilitates the signal evaluation.

From the ratio of the mass change to the passed electrical charge $\Delta m/\Delta Q$, the apparent exchanged molar mass M_{app} can be calculated using eq 2.

$$M_{\text{app}} = zF \frac{\Delta m}{\Delta Q} \quad (2)$$

where z is the charge of the anion and F is the Faraday constant (96 484.56 C mol⁻¹).

The thus-calculated value M_{app} is a sum signal representing the difference in the molar mass of the incorporated and the ejected species (eq 3).

$$M_{\text{app}} = M_{\text{anion}} + \alpha M_{\text{solv}} \quad (3)$$

where M_{anion} and M_{solv} are the molar masses of the anion and the solvent, respectively, and α describes the number solvent molecules transferred per anion.

One might argue that eq 3 should contain a third term to model the exchange of cations. It is known from the literature that this is true for a variety of polymer films.^{1,3,4} For PEDT films synthesized and cycled in tetrafluoroborate, a mixed ion transfer has been reported, and even the relatively large tetrabutylammonium (TBA) cation was incorporated.³¹ Blanchard et al. found that the porosity of PEDT films and the reproducibility of the doping/dedoping reaction depend on the anion used for synthesis.³² They found “the best results in term of current density and time of discharge in the presence of lithium hexafluorophosphate and lithium perchlorate”. Therefore, one could assume that cation exchange is absent (at least in the potential range between -0.8 to 0.8 V) in the case of PEDT films that were synthesized in perchlorate solutions because of their fast doping/dedoping kinetics. To confirm this hypothesis, a comparative study of the doping/dedoping behavior in 0.1 M acetonitrile solutions of lithium, sodium, and TBA perchlorate was performed. The mass/charge balance (M_{app} , eq 2) was identical in all three electrolytes (Figure 2). The curvature of the plot in Figure 2 indicates that M_{app} (which is the slope of this curve) shows a significant potential dependence. This will be discussed below in more detail. Within the potential range of 0.2–0.6 V, one perchlorate ion is replaced by one molecule of acetonitrile. Therefore, we can exclude the effect of cation exchange within this potential range, and the apparent exchanged molar mass is not influenced by the ejection of cations during oxidation.

Because we measure M_{app} (eq 2) and we know M_{anion} and M_{solv} , we can easily calculate α from eq 3. For all investigated systems (except sulfate), a negative value of α was obtained, which means the anion replaces some solvent molecules during oxidation (Table 1).

The mass/charge balance in eq 2 was determined as an integral value using linear regression in the m versus Q plots between 0.2 and 0.6 V versus Ag/AgCl. In this case, M_{app} represents an average value for the corresponding potential range. Alternatively, we used the derivative dm/dQ and thus obtained a potential-dependent value of M_{app} (Figures 3–6). Numerical calculation of the derivative dm/dQ easily produces very noisy M_{app} data. To avoid this, an evaluation procedure based on the LINEST function (returns statistics that describe a linear trend matching known data points by fitting a straight line using the least-squares method) of Microsoft Excel was used. The key feature is a sliding linear regression over a number of data points.

It must be borne in mind that the anion/solvent ratios given in Table 1 represent average values in the potential range of 0.2–0.6 V. The solvent-exchange behavior is in agreement with the different dimensions of the investigated anions. The relatively small perchlorate anion (0.45 nm) replaces ca. two water molecules, whereas toluenesulfonate (TS, 0.78 nm)

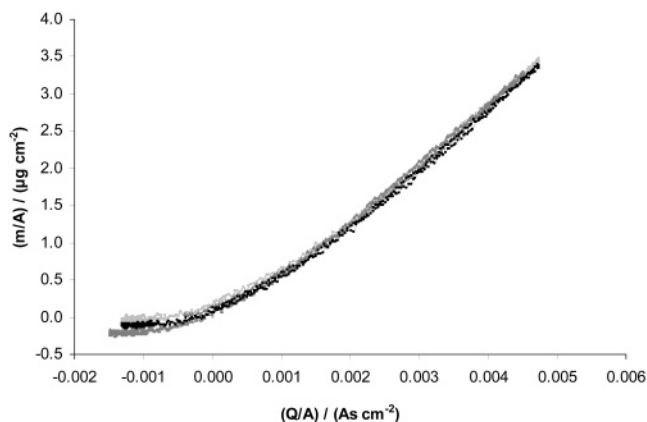


Figure 2. Comparison of the mass/charge balance for PEDT films in acetonitrile containing 0.1 M lithium (Δ), sodium (\blacksquare), and TBA (\circ) perchlorate.

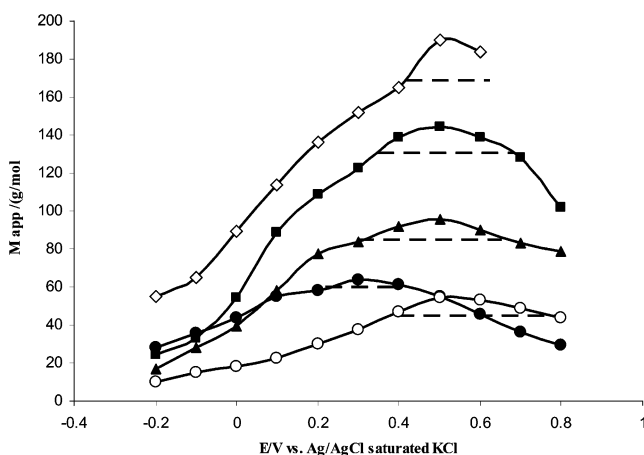


Figure 3. Apparent exchanged molar mass during the oxidation process in aqueous solution determined via the first derivative dm/dQ in comparison with the apparent exchanged molar mass calculated via the slope (---): (●) perchlorate, (■) sulfate, (○) nitrate, (◇) citrate, and (▲) toluene sulfonate.

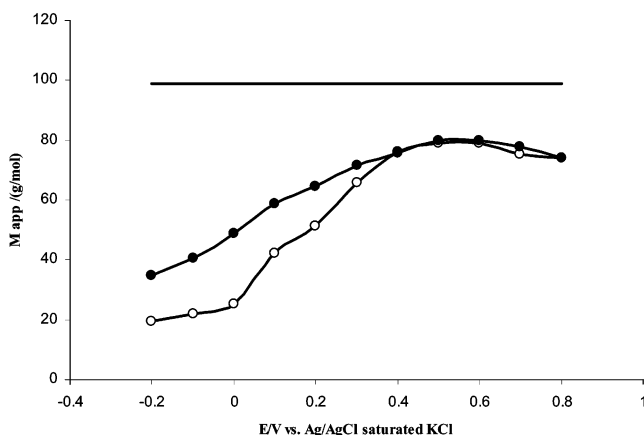


Figure 4. Apparent exchanged molar mass during redox cycling of PEDT in a solution of acetonitrile and 0.1 M LiClO₄ (fifth scan, potential range -0.8 to 0.8 V) with a scan rate of 10 mV/s calculated for selected potentials from the first derivative dm/dQ for the oxidation process (●) and the reduction process (○). The solid line (—) indicates the molar mass of perchlorate.

replaces five molecules. The results for TS are in good agreement with results from Efimov et al.,⁶ who found $M_{\text{app}} = 78 \text{ g mol}^{-1}$ in an aqueous solution of sodium TS. As in our

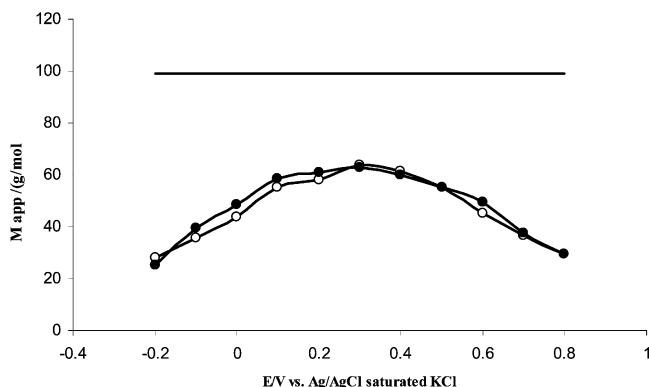


Figure 5. Apparent exchanged molar mass during redox cycling of PEDT in an aqueous solution of 0.1 M LiClO₄ (fifth scan, potential range -0.4 to 0.8 V) with a scan rate of 10 mV/s calculated for selected potentials from the first derivative dm/dQ for the oxidation process (●) and the reduction process (○). The solid line (—) indicates the molar mass of perchlorate.

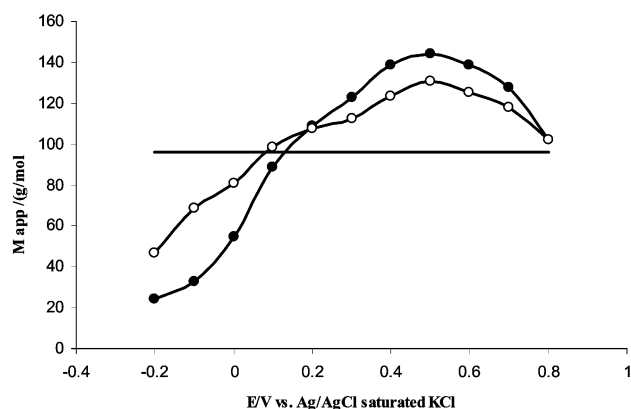


Figure 6. Apparent exchanged molar mass during redox cycling of PEDT in an aqueous solution of 0.1 M Na₂SO₄ (fifth scan, potential range -0.4 to 0.8 V) with a scan rate of 10 mV/s calculated for selected potentials from the first derivative dm/dQ for the oxidation process (●) and the reduction process (○). The solid line (—) indicates the molar mass of sulfate.

case, this value was explained by the replacement of five water molecules by one TS molecule.

The role of the charge density of the doping anion becomes obvious when comparing the results of sulfate and citrate. Sulfate is a relatively small, divalent anion and therefore bears a high charge density and a strongly bound hydration shell. As a consequence, it shows contrary doping behavior in comparison to that of all other investigated anions. When sulfate is incorporated, it does not replace water but inserts two more water molecules into the polymer film (Table 1). Citrate, although trivalent but with sizable dimensions (0.98 nm) and therefore with a comparably low charge density, replaces approximately three water molecules (Table 1). For perchlorate, the behavior in water is comparable to the behavior in acetonitrile (Table 1). In water, one perchlorate replaces two solvent molecules; in acetonitrile, one solvent molecule is expelled per anion. This behavior is in accordance with the larger size of acetonitrile compared to that of water.

It is evident that the apparent molar masses obtained from the slope of the m/Q charts (Table 1) should be the average values of those numerically calculated from the derivative dm/dQ (Figures 3–6). To illustrate this, the average of the potential-dependent M_{app} values between 0.2 and 0.6 V has been included in Table 1. Both values show excellent agreement.

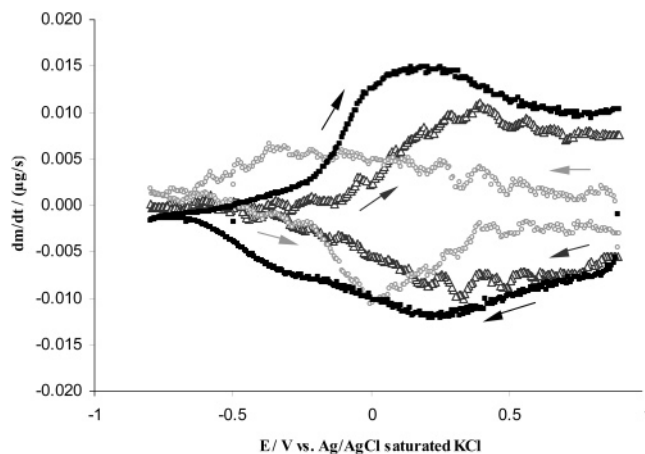


Figure 7. Comparison of the mass fluxes during redox cycling (10 mV/s) of PEDT in a solution of acetonitrile and 0.1 M TBAClO₄ (fifth scan). Arrows indicate the direction of the potential scan. (Δ) $dm[\text{film}]/dt$, (○) $dm[\text{acetonitrile}]/dt$, and (■) $dm[\text{perchlorate}]/dt$.

Figures 4–6 show that the apparent molar mass incorporated during the oxidation process is fully expelled in the reduction process. This demonstrates the reversibility of the process for perchlorate in acetonitrile (Figure 4) as well as perchlorate (Figure 5) and sulfate (Figure 6) in aqueous solution under our experimental conditions.

The numerical procedure outlined above was also used to calculate the total mass flux $dm[\text{film}]/dt$ from the EQCM data. Assuming that all passed charge leads to the creation of redox centers and thus the incorporation of anions, the mass flux of the anions $dm[\text{anion}]/dt$ can be calculated from eq 4.

$$\frac{dm[\text{anion}]}{dt} = I \frac{M}{zF} \quad (4)$$

where I is the current and M and z are the molar mass and the valence of the anion, respectively.

Once one has obtained $dm[\text{anion}]/dt$ and $dm[\text{film}]/dt$, the mass flux of solvent can be calculated from eq 5.

$$\frac{dm[\text{film}]}{dt} = \frac{dm[\text{anion}]}{dt} + \frac{dm[\text{solvent}]}{dt} \quad (5)$$

Figures 7–9 show the thus-calculated mass fluxes during the redox cycling of PEDT films for the systems perchlorate/AN (Figure 7), perchlorate/water (Figure 8), and sulfate/water (Figure 9). For perchlorate in acetonitrile, the apparent exchanged molar mass shows a maximum at 0.5 V that corresponds to ca. 80% of the molar mass of the anion (Figure 4). From Figure 7, one sees that at 0.5 V the mass fluxes of the anion (■) and of AN (○) are 0.012 μg/s and -0.003 μg/s, respectively. These mass fluxes correspond to the molar fluxes of 1.2×10^{-4} μmol/s (anion) and -6.5×10^{-5} μmol/s (AN), which means that two anions replace one solvent molecule. Because the average ratio for anion to solvent exchange is 1 (α value, Table 1), the anion inclusion is obviously speeding up at higher potentials. In the case of perchlorate/water, the maximum of M_{app} appears at 0.3 V and corresponds to 60% of 99 g mol⁻¹ (Figure 5). The anion and solvent fluxes at this potential can be obtained from Figure 8: 1.0×10^{-4} μmol/s (anion, □) and -2.2×10^{-4} μmol/s (water, ○). Thus, one perchlorate replaces two water molecules at 0.3 V. For sulfate/water, the maximum of M_{app} is reached at 0.5 V, but here the value of M_{app} exceeds the molar mass of the anion by ca. 40%

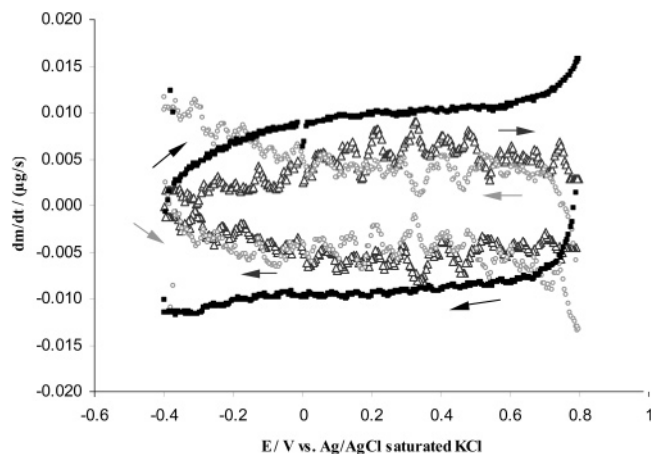


Figure 8. Comparison of the mass fluxes during redox cycling (10 mV/s) of PEDT in an aqueous solution of 0.1 M LiClO_4 (fifth scan). Arrows indicate the direction of the potential scan. (Δ) $dm[\text{film}]/dt$, (\circ) $dm[\text{water}]/dt$, and (\blacksquare) $dm[\text{perchlorate}]/dt$.

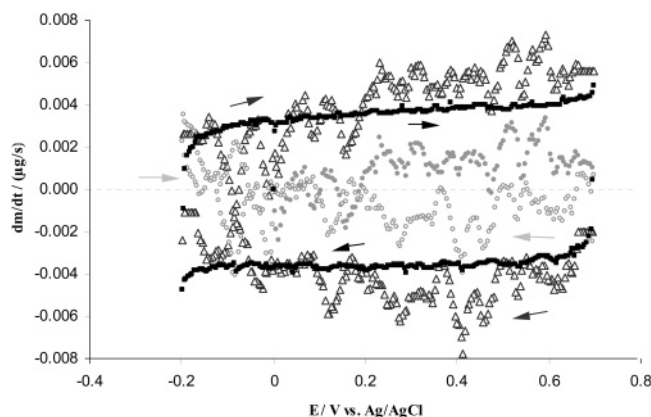


Figure 9. Comparison of the mass fluxes during redox cycling (10 mV/s) of PEDT in an aqueous solution of 0.1 M Na_2SO_4 (fifth scan). Arrows indicate the direction of the potential scan. (Δ) $dm[\text{film}]/dt$, (\circ) $dm[\text{water}]/dt$, and (\blacksquare) $dm[\text{sulfate}]/dt$.

(Figure 6). As discussed above, this special behavior is caused by the high charge density of the sulfate anion, which causes the transfer of water together with the anion ($\alpha = +2$, Table 1). In Figure 9, it can be seen that for the anodic scan the mass fluxes of the solvent (\circ) and the anion (\blacksquare) are both positive. The result is a value of M_{app} that exceeds the molar mass of the anion.

When the experiments were performed at higher scan rates, the maximum of M_{app} was shifted to more cathodic potentials. For example, for the system perchlorate in acetonitrile the maximum occurs at 0.5 V for 10 mV/s (Figure 4). For a scan rate of 100 mV/s, it is reached at 0.3 V. The obvious differences in the potential dependence of the mass fluxes of the anions and the solvent lead to the conclusion that the time constants of the exchange reactions are different.³³ The exchange of the anions is driven by the electric potential and the condition of electroneutrality, whereas the solvent flux will be mainly determined by differences in the chemical potential (diffusion).^{34,35} Thus, it can be assumed that the inclusion of the anions will occur faster than the ejection of the solvent, especially at high potentials. This is in agreement with our experimental data and with the results of AC electrogravimetry studies of polypyrrole.³

In aqueous solutions of all of the investigated anions (except perchlorate), the maximum of M_{app} appears at ca. 0.5 V (Figure 3). The maximum of M_{app} for perchlorate is shifted by ca. 0.2 V to more cathodic values. Because the films were synthesized from 0.1 M perchlorate in acetonitrile, this finding can be explained with selectivity for the anion used for the polymerization of the polymer film. This result might be the basis for the development of a sensor with an increased sensitivity toward selected anions, as already described for polypyrrole.³⁶

Conclusions

The EQCM investigations of PEDT films in acetonitrile and in aqueous solutions of different anions indicate a reversible exchange of anions and solvent during redox cycling (doping/dedoping). No significant cation transfer was observed. The amount of exchanged solvent is in good agreement with the different dimensions of the scrutinized anions. Investigations of the polyvalent anions sulfate and citrate indicated that the solvent-exchange behavior depends not only on the dimensions but also on the charge density of the anion. This information can be used for specific tailoring of sensor films. Furthermore, we could demonstrate that the apparent exchanged molar mass as well as the solvent and the anion fluxes depend on the potential. This is caused by the different kinetics of anions and solvent transfer.

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