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Csaba Visy · Csaba Janáky · Emese Kriván

Solvation/desolvation during the redox transformation of poly(3-methylthiophene)

Abstract Solvation/desolvation effects were studied during the redox transformation of poly(3-methylthiophene) by electrochemical quartz crystal microbalance technique. The effect was demonstrated by studying the phenomenon in different solvents, and comparing the results after a solution change. From the data obtained with the same film transferred between nitrobenzene and acetonitrile in both directions, the solvation effect was directly evidenced, and the virtual molar mass of the moving species in and from the same film was determined to illustrate semi-quantitatively the effect of the solvation.

Keywords Polythiophene · EQCM · Redox transformation · solvatation/desolvation

Introduction

The changes in the electrical conductivity and in the coupled physical properties upon the redox transformation of the conjugated polymers have been generally interpreted on the basis of the polaron/bipolaron model [1, 2]. In polythiophenes the concentration of the ESR-active polaron was found to be rather small [3], and the splitting of the voltammetric current peak indicating a two-step electrochemical process was widely observed only during the reduction [4].

C. Visy (✉) · C. Janáky · E. Kriván
Institute of Physical Chemistry,
University of Szeged, Hungary
E-mail: visy@chem.u-szeged.hu
Fax: +36-62-544652

Although the bipolaron form was assumed to be the main charge carrier [3, 5, 6], evidence was found for the temporary existence of the paramagnetic intermediate [7].

As the generation of charge carriers had to be compensated, soon after the first simple electrochemical studies, fundamental combined methods were applied to follow the achievement of the role of electroneutrality. In situ methods, completing the electrochemical measurements on conducting polymers, may deliver very important extra information about the phenomena coupled with the redox transformation of the film. Data obtained with these methods are very important, and their contribution to a better understanding of the charging/discharging process of polythiophenes is fundamental. The most direct and persuasive of those methods was the combined radiotracer technique, using labelled anions. In a series of papers Horányi et al. [8–11] used this method successfully to remove the doubts: the redox transformations are accompanied by ionic movements, so the presence of such dopants is not the cause of the increase in the electric conductance, but is the consequence of the electrochemical generation of charge carriers along the chains.

The insufficiency of the original polaron/bipolaron model for the interpretation of the totality of the experimental results was experimentally demonstrated soon afterwards. The formation of species through interchain interactions—called π-dimers and π-stacks, or σ-dimers—has been suggested, and as an alternative to bipolarons the diamagnetic behaviour could be explained [12–16] by the coupling of two polarons.

Besides the successfully applied laser beam deflection (mirage effect) technique [17, 18], another very informative combined method is the electrochemical quartz crystal microbalance (EQCM) technique, which may deliver more complete information about the process, including mass changes caused by ionic and non-ionic movements [19–23]. On this basis the conformational changes observed with different films could be inserted into the mechanistic views, and the redox transforma-

tion was satisfactorily described by the original and extended multiple cube model.

In a recent paper it has been demonstrated that the time consuming, slow chemical step—which is necessary for the accomplishment of the transformation into the conducting state after the charge transfer process—seems to be the desolvation of the film [24]. The conformational changes [19] delayed with respect to the charge transfer, were considered to be the result of the solvent removal endowing the layer with a different dielectric constant and therefore a different capacitance. Thus, the desolvation plays the key role in the transformation into the conducting state, being the essential step for the achievement of the so-called quasi-metallic state. Its importance after the end of the polymerisation in an open circuit was demonstrated [25], as well. On this basis it was assumed that after the removal of the solvent, the charged layer might possess a much larger dielectric constant than the uncharged one, stuffed with solvent molecules. This may be the result of the overall process involving a transition between non-conducting (solvated) and conducting (desolvated) phases. It has also been shown that the detection of a "mysterious" extra charge connects the different observations. A pre-oxidation can make either anodic or cathodic extra charge "available," or the effect may remain hidden from the second or further scans, and the redox transformation is symmetric and reversible within a certain potential range. The extra charge is not "created," it has to be already accumulated in the layer earlier, during either some pre-treatment or even at the end of the polymerisation, and it merely becomes available and detectable. The appearance and even the sign of this extra charge strongly depend on the "history" of the films.

The main goal of the present work was to evidence the desolvation directly. Thus, we studied the effect of the solvent *change* on the redox transformation of the same film by the EQCM technique. Since the desolvation is influenced by the electric field [26], the aim of the present work was also to study the effect of the increase in the potential window, changed gradually in the anodic direction. In order to elucidate the effect of the slow, non-electrochemical step, the process was also investigated at different sweep rates. As for the solvent change, the film was electropolymerised in one solution, studied in the monomer-free solution prepared with the same solvent, then washed with and studied in another solution containing the same ions at an identical concentration. In this paper, the effect of the change between nitrobenzene (NB) and acetonitrile (AN) was investigated. The solvent change was done in both directions, from NB to AN and from AN to NB. This way, the solvent effect could be separated into two parts: on the one hand the behaviour of the same, single film was compared in two solvents, on the other hand the behaviour of films polymerised in different solvents were compared in the same solvent.

Experimental

The EQCM measurements were performed using a quartz crystal resonator and analyser EQCM type 5510 (Poland). The crystals ($f_0 = 8.9$ MHz and 10 MHz) were Pt coated and had a surface area of $A = 0.196$ cm^2 ($r = 0.25$ cm). Data in Figs. 1–3 were measured by using the quartz crystal of 8.9 MHz. Viscoelastic effects were controlled by measuring the resistance of the electrode, as described in [24]. The EQCM system was calibrated by electrochemical silver deposition using the standard procedure, and the value of -0.86 ng/Hz calibration constant was obtained for the crystal $f_0 = 10$ MHz. The electrochemical measurements were carried out on a potentiostat/galvanostat (model PGSTAT 10, AUTO-LAB) using its programme package. A Ag/AgCl microelectrode was used as reference.

Nitrobenzene, 3-methylthiophene MT and tetrabutylammonium-hexafluoro-phosphate Bu$_4$NPF$_6$ (purchased all from Aldrich) were used as received, acetonitrile AN (Aldrich) was dried over activated alumina and kept under inert atmosphere. The water content of the solutions were controlled by coulometric Karl Fischer titration, and was kept below 50 ppm. The cell and solutions were deaerated by nitrogen. Poly(3-methylthiophene) (PMT) was prepared galvanostatically at a current density of 2.5 mA/cm^2 up to a maximum 100 mC/cm^2 of total charge. In the case of the EQCM measurements in connection with the solvent change the charge density was restricted to 50 mC/cm^2 to avoid viscoelastic effects [27]. The polymerisation solution contained 0.1 M of the monomer 3-methylthiophene and 0.1 M Bu$_4$PF$_6$ in AN or NB solution. After the polymerisation step the solution was changed for further studies to a monomer-free solution of Bu$_4$NPF$_6$. During the special measurements, the solution was exchanged for the appropriate other solvent, containing Bu$_4$NPF$_6$ in the same concentration.
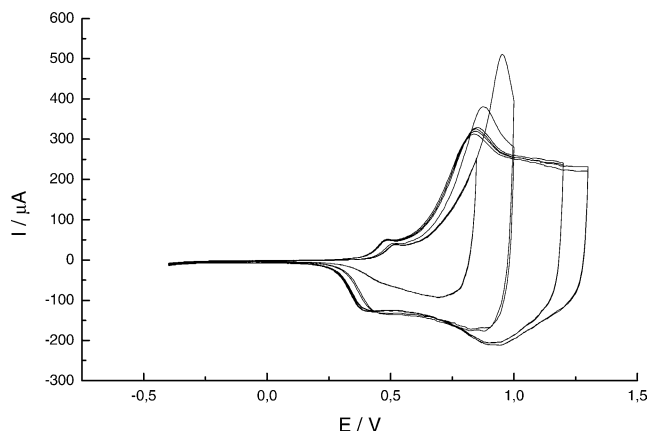

Fig. 1 Voltammetric curves registered with a PMT film prepared and studied in AN solution at $v = 10$ mV/s scan rate. The potential window was gradually increased in the anodic direction after each double scan
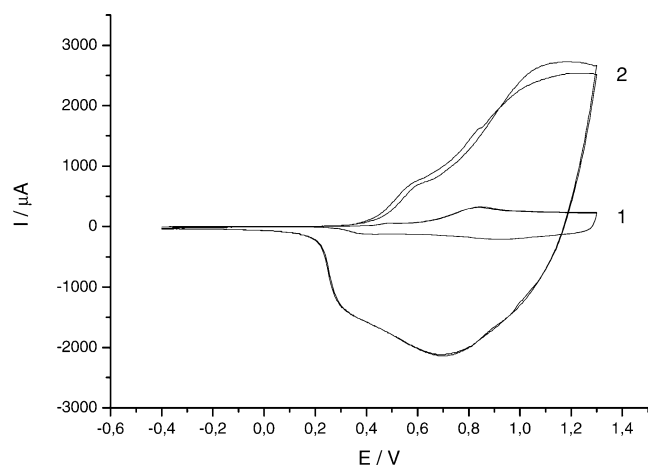
Fig. 2 Comparison of the double potential – current curves registered in AN in the extended potential range at different scan rates. (*1*) v = 10 ; (*2*) 100 mV/s

Results and discussion

In the first section of the measurements the effect of the increase in the potential window was studied by chang-

Fig. 3 Charge values integrated along the double scans at 10 mV/s (*1*) and 100 mV/s (*2*) scan rates. Parts show the curves run to different anodic endpoints: **a** 0.85 V; **b** 1.0 V; **c** 1.2 V; **d** 1.3 V
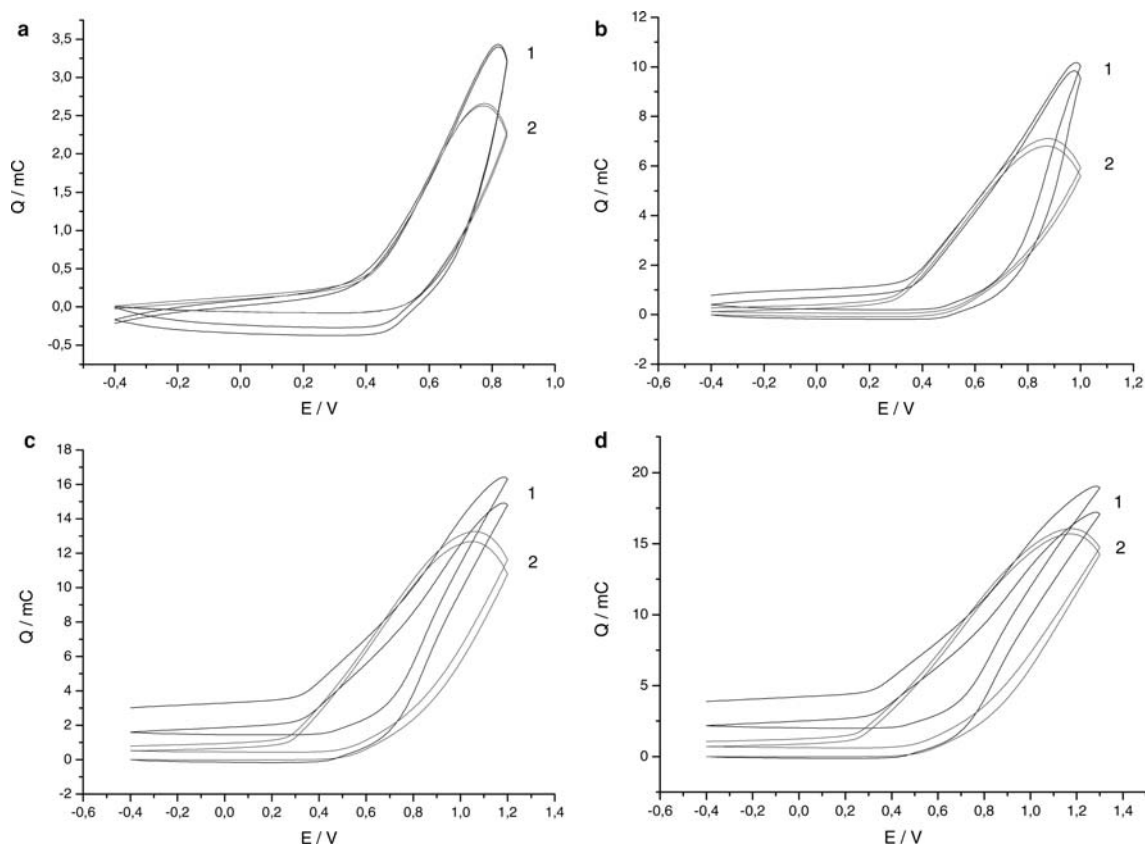
ing it gradually in the anodic direction during subsequent voltammetric scans. Figure 1 shows that the increase in the anodic turning point at slow scan rate results in a transition in the layer: without sweeping beyond the oxidation peak the current on the double scans reaches smaller values. When the anodic end of the scans is over the peak potential, a current increase can be seen on the next voltammogram, and the oxidation is easier thereafter. After this transition the current peak becomes stationary, and the double scans run on the same pathway. This observation can be explained by the frequently reported morphological change [19, 20].

As presented in the introduction, the chemical step necessary for the accomplishment of the transformation into the conducting state after the charge transfer process, is time consuming. In order to get information about the time scale of this step, the effect of the scan rate (10, 25, 50 and 100 mV/s) was studied after the previously described stabilisation of the voltammetric behaviour in Fig. 1. The voltammetric curves at the two extreme sweep rates are compared in Fig. 2. It can be clearly seen that the memory effect can be traced during fast subsequent scans, while the two current curves totally cover each other at a slow rate. The effect of the scan rate can be demonstrated when the charge values—calculated during the voltammetric transformation—are compared at the different scan rates. The results are summarised in Fig. 3a–d, as a function of the potential of the anodic endpoint. As the maximum is always larger at 10 mV/s, the oxidation is more complete

at a slow scan rate. If we focus on the final value of the charge Q_e at the end of the double sweeps, we see that this Q_e is not equal to zero, as it would be if the transformation were totally reversible. In other words, Q_e represents the "extra charge" [24]. This extra charge is larger—in all cases from *a* to *d*—at the end of the scan at $v = 10$ mV/s, i.e. when the perturbation is slow, and enough time is ensured for the slow chemical process to occur. Moreover, the sign of Q_e changes with the anodic end of the potential window: within the potential range up to 850 mV Q_e is negative, but it becomes gradually more and more positive by the increase in the extent of the oxidation. The results clearly demonstrate that the extra positive charge decreases with the scan rate, thus a time consuming process stands in the background.

In our work we determined again the molar mass of the moving species. From the slope of the mass change vs. the charge curve this molar mass is 59.7 g/mol, which value is much smaller than the molar mass of PF_6^- ions ($M_r = 145$). This observation is in accordance with the conclusions in [24], namely that the oxidation is coupled with solvent removal from the film. The "lack of mass" is equivalent with the simultaneous removal of two AN molecules. It is known that in certain cases cation movement can take place as well [28]. However, while small cations such as Li^+, may interfer in AN, bulky tetrabutyl-ammonium cations are too large to enter the film. In [29] the penetration of these cations into the polythiophene film during the trial of cathodic doping was experimentally excluded. In order to demonstrate that our frequency measurements were not influenced by viscoelasticity, we present the mass change vs. time data (Fig. 4) during the constant current polymerisation. As the slope of the curve is practically constant throughout the whole process, the development and involvement of viscoelastic effects can be excluded. At the same time the data make it possible to calculate the "molar mass" of one monomeric unit doped and compensated in its charge. Applying the usually accepted approximation
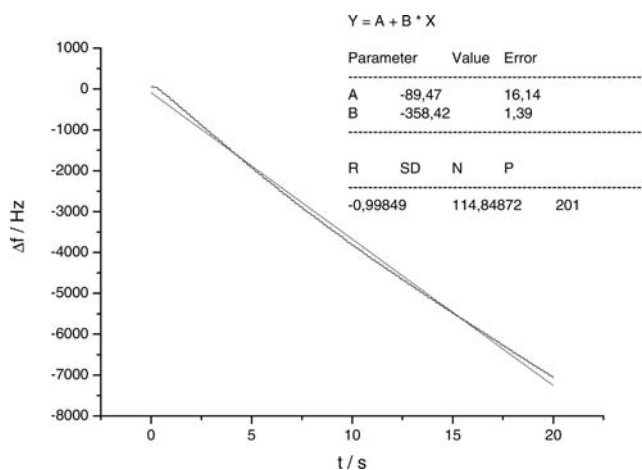
that the oxidation level at the end of the polymerisation is equal to that at the end of the redox transformation, the doping level $y = 0.23$ (close to the generally found 0.25) was obtained. Using this value the molar mass of one unit is 135 g/mol, which is slightly larger than the theoretical one: 129 g/mol. On this basis it can be assumed that during the polymerisation some other species, probably solvent, may incorporate into the film. That is in accordance with the data reported recently for polypyrrole/DS films [25], where the deprotonation and desolvation during the open circuit relaxation following the electropolymerisation was demonstrated.

In order to evidence directly the solvation/desolvation of the film, the mass changes during the redox transformation of the polymer was measured in different solvents. By a solution change with the ion content in the same concentration, we were able to compare the behaviour of the same, single film in different solvents. First a film was electropolymerised in NB. Figure 5 shows the voltammetric curves recorded in monomer free NB solution, while in Fig. 6 the frequency change of the quartz crystal electrode during the redox transformation of the film studied at a scan rate of 100 mV/s is presented. Figure 6 shows that the film exhibits anion exchanger properties: the frequency decreases during the oxidation because of the anion penetration. The curve shows that the oxidation causes a monotonous mass increase, indicating anion incorporation. The insertion of the anions starts in parallel with the current increase, and their removal becomes fast at the end of the reduction of the film. According to recent observations the involvement of the cations occurs at the end of the reduction [30]. If so, the effect of this interference should cause a smaller slope at the cathodic end, which is certainly not the case in Fig. 6. The transformation of the measured data are presented in Fig. 7, and from the slope the virtual molar mass of the moving species was calculated. The value of 103 g/mol is again smaller than the molar mass of the anion.
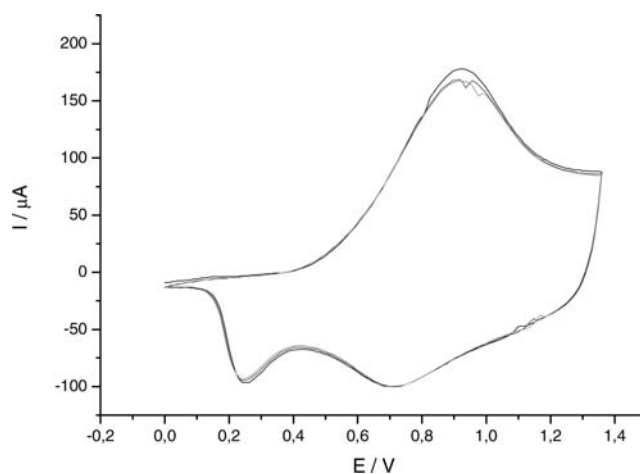

Fig. 4 EQCM data registered during the galvanostatic polymerisation

Fig. 5 Voltammetric curves of the film prepared in NB and studied in its monomer free solution at 100 mV/s scan rate
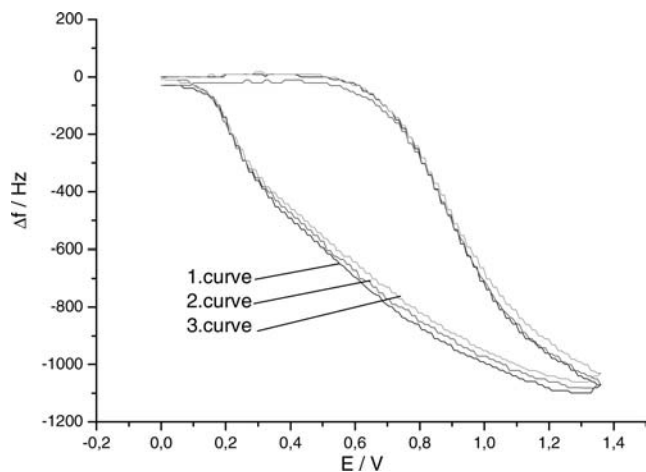
Fig. 6 Frequency change – potential curves registered with the film in NB during the triple potential scan at 100 mV/s rate
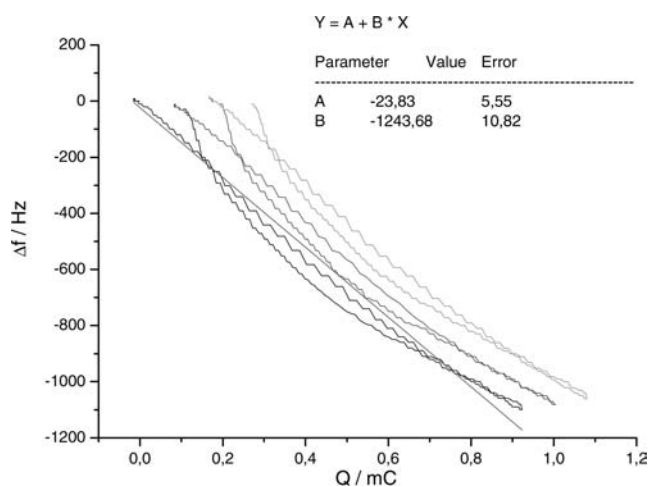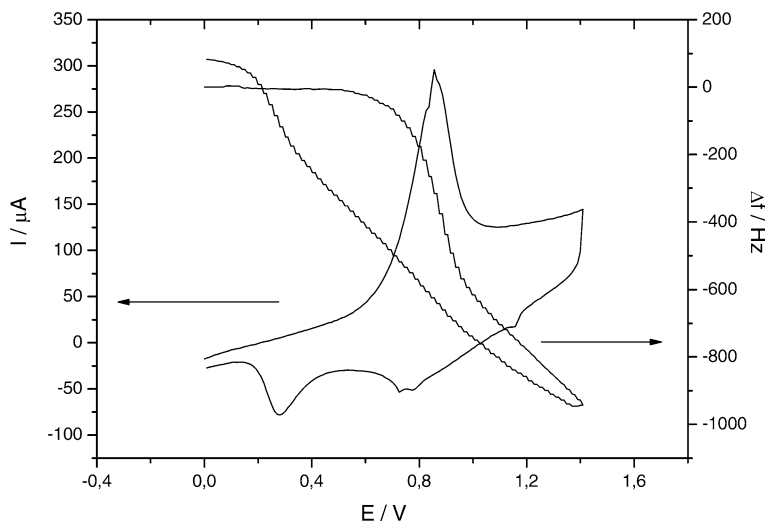

Fig. 7 Transformation of the data in Figs. 5, 6 in function of the charge. The insert shows the result of the linear fitting

If the scan rate was decreased to 25 mV/s and 10 mV/s, the values obtained from the slopes for the molar mass of the adsorbed material were about the same (119 and 113, respectively).

In order to see the effect of the solvent change, the NB solution in the cell was exchanged, and the further experiments were performed in Bu_4NPF_6/AN solution. In Fig. 8 we present the voltammetric curves recorded in AN together with the frequency changes after the solution change. The voltammetric curve is shifted into the direction of the positive currents, resulting in an extra positive charge during the redox cycle in AN. Previous results showed that during the redox transformation of polythiophene films an extra reduction charge could be measured when the cycling was stopped, and the potential was held at even a small negative current flow, before performing the rest of the cathodic scan [26]. During the occurrence of this strange phenomenon one had to keep in mind that the extra reduction charge can not be "created," it has to be accumulated in the film earlier. This accumulation can be traced in Fig. 8. as the asymmetry of the voltammetric curve, and it has to be the consequence of the solvation of the film in AN.

Figure 9 presents the frequency change of the film prepared in NB but studied in AN as a function of the charge. It can be seen that the positive shift in the current resulted in a large irreversibility. At the same time the extent of the mass change is similar (~90%) to that measured in NB before the solvent change. Furthermore, it has to be emphasized that the mass change is reversible, so the "electrochemistry" of the process should also be reversible. From the slope of the oxidation section of this curve a value of 75 g/mol is obtained, which is again much smaller than the theoretical value. We may come to the conclusion that solvation in the new solvent (AN) caused the appearance of the extra charge, and resulted in the decrease of the slope, i.e. the decrease in the virtual molar mass of the moving species.

In Fig. 10 the stabilised current – potential curves are compared with the ones registered in NB with the same
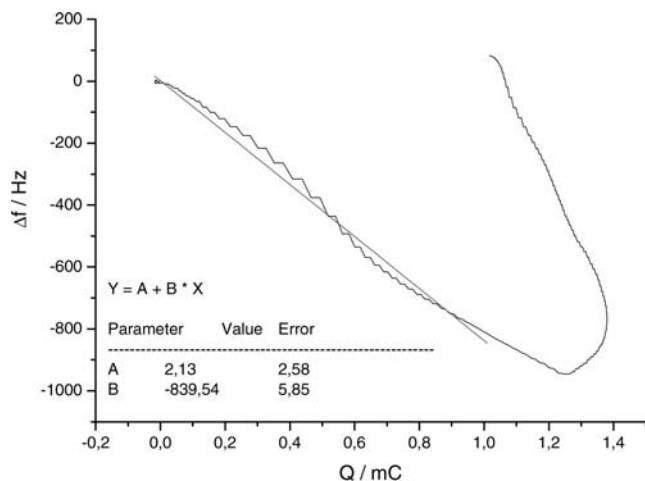
Fig. 8 Voltammetric curve and the coupled frequency changes registered with the film (prepared in NB) during the cycling in AN soon after the solution change. The scan rate is 100 mV/s

Fig. 9 Transformed EQCM data after the solution change for AN in Fig. 8 in function of the charge. The insert shows the result of the linear fitting

Fig. 11 Development of the stabilisation of the shape of the curve in NB after a solution change from AN at a sweep rate of 10 mV/s. For comparison the figure shows the voltammograms in NB at the same scan rate. The solvents used during the preparation of the films are indicated

film. The differences between the two cases are striking, and they have to be associated with the presence of different solvents, as it was the only changed parameter.

In order to see the effect of the solvent change more in detail, the same procedure was repeated using the two solvents in the opposite order. The film was polymerised in AN, and after a solvent change the redox transformation was studied in NB. In Fig. 11 the voltammetric curves after the solvent change can be followed. The current – potential curves taken at 10 mV/s sweep rate keep changing, indicating that after the solvent change the resolution in NB is slow. The same figure shows the current – potential curves of a film prepared and studied in NB at the same scan rate. This way we can see the usually reported solvent effect on the structure of the film during the electropolymerisation: the later shape of the voltammetric curves greatly depends on the solvent used during the formation, assumingly due to the
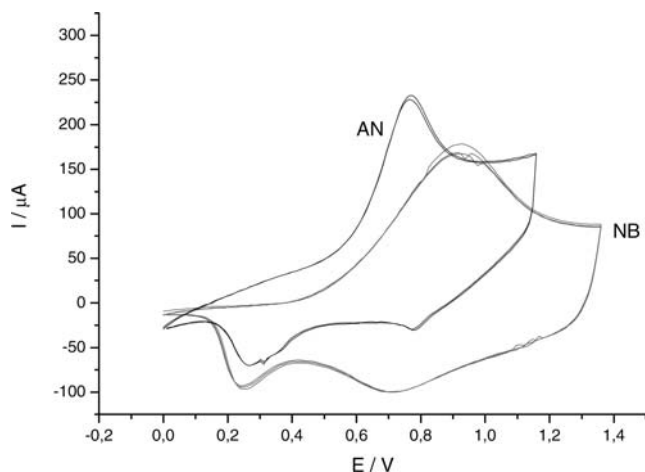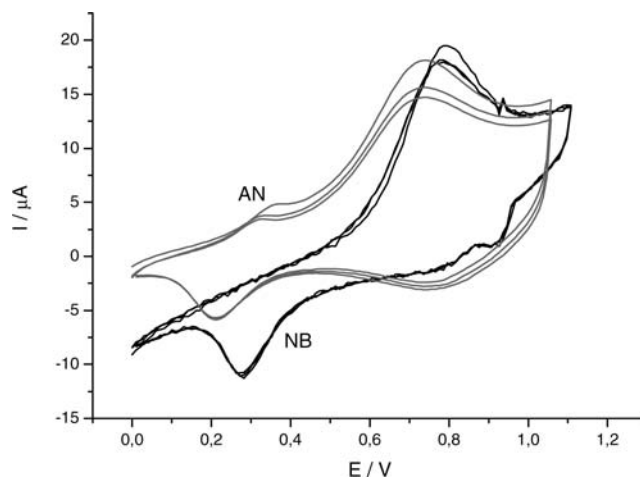
different structure formation of the polymers. Thus, we could separate the effect of the solvent into two parts: Fig. 10 presents the effect of the resolution of one identical film in the original (NB) and the new solvent (AN), while Fig. 11 shows the effects of different solvents used during the synthesis, on the behaviour of the film when studied afterwards in the same solution.

Conclusions

During the studies on the redox transformation of PMT films we could see that the electrochemical process is coupled with mass changes, but these mass changes do not reflect simply the movement of the anions. Instead, the results reveal a "lack" of mass change, so that some species, leaving the film, compensate the mass increase originating from the anion incorporation during the oxidation. This effect is influenced by the actual solvent. For example, in the case of acetonitrile the difference in mass is equivalent with about two moles of AN. With the experiments on solution change we could demonstrate that a similar value was obtained in AN after the solution change with a film deposited from NB (in Fig. 9). Thus, the solvation/desolvation effect of AN is independent of whether the film was prepared in AN or NB. In NB the lack of mass is 26–42 g/mol, suggesting that only 0.2–0.35 NB molecule leaves the layer in parallel with the incorporation of one anion. We note that the exact values of the lack of mass are not really important, but they can be used for a semi-quantitative characterisation of the solvation effect.

The solvent change in both cases results in asymmetry on the voltammograms, and leads to the appearance of extra charges. The EQCM results indicate the solvent movement during the redox transformation of the film, and confirm the solvent removal from the layer during

Fig. 10 Stabilised voltammetric curves in different solvents (AN and NB) registered with the same film prepared in NB. The scan rate is $v = 100$ mV/s

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the oxidation process. After the solvent change the film becomes solvated by the new solvent during the reduction. Thus, the large extra charge observed in connection with the scannings (e.g. in Figs. 8, 9.) should originate from the resolvation in the new solvent. The amount of this extra charge depends on the character of the solvent and on the sweep rate applied during the scan, hence on the time available. Since the mass curves preserve their reversible character during a cycle, we conclude that the extra charge is capacitive.

Finally, we could separate the solvent effect into two parts: we evidenced again the role of solvent in the determination of the structure during the polymerisation, but we could demonstrate that the behaviour of the same film is different in different solvents. This may lead to the conclusion that the layer is being resolvated after the solvent change during the redox cycles. Further studies are in progress in this direction.

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