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A comparison of redox processes for polypyrrole/dodecylsulfate films in aqueous and non-aqueous media

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Abstract Polypyrrole/dodecylsulfate (PPy/DDS) films were synthesized in aqueous and ethanolic solutions and investigated in aqueous, ethanolic, methanolic and acetonitrile solutions by cyclic voltammetry (CV). The amounts of anions and cations in the films before and after electrochemical treatment were determined by electron probe microanalysis (EPMA); the film morphology was studied by scanning electron microscopy (SEM). The results prove that the mobility of bulky DDS^- ions in PPy increases in the order: water < acetonitrile < ethanol < methanol. It was found that dopant DDS^- ions can be easily removed from PPy matrix swollen in alcohols or acetonitrile by electrochemical reduction or by soaking in electrolyte solutions of these solvents. The influence of electrochemical treatment on the change of doping level in aqueous solution is essentially less and depends on the cations in the test solution. Although the electroneutrality of PPy/DDS films during redox cycling is realized mainly by movement of the cations in aqueous solution and by movement of the anions in organic solvents, nevertheless the participation of anions in aqueous and cations in organic solvents is also established. The redox properties of PPy/DDS are more dependent on the solvent of the test solutions than of the synthesis solutions.

Key words Polypyrrole · Dodecylsulfate · Alcohols · Cyclic voltammetry · Electron probe microanalysis

Introduction

The redox properties of polypyrrole/large organic anion films have been mainly studied in aqueous electrolyte solutions. Among these films are polypyrrole (PPy) doped with dodecylsulfate (DDS) [1, 2, 3, 4, 5, 6, 7, 8], dodecylbenzenesulfonate [1, 9, 10, 11], naphthalene-(di)sulfonates [1, 10, 12, 13] or polymeric anions like poly(vinylsulfonate) or poly(styrenesulfonate) [1, 14, 15]. Research on the electroactivity of these PPy-modified electrodes in non-aqueous solutions is in most cases limited to the use of acetonitrile (AN) or propylene carbonate (PC) [4, 12, 15, 16, 17], although in some cases some other solvents have been investigated [15]. The properties of PPy are influenced by the solvent used for the synthesis or the electrochemical treatment as well as by solvent vapours. As an example, a tendency has been observed in case of PPy films with small dopants that the conductivity is increased when using solvents with a higher nucleophilicity, i.e., with higher donor numbers (DN), probably owing to a better defined structure of the polymer [18]. Further, it was observed that there is an increase in current efficiency of pyrrole polymerization with increasing solvent DN [19]. In addition, the solvent affects the doping level and mechanical properties of PPy films [4, 20], the diffusion coefficients [21, 22], the redox activity, the charge storage ability and the shape of the cyclic voltammetry (CV) curves [4, 15, 16, 23, 24, 25, 26]. As stated above, such solvent effects are also observed when solvent vapours interact with the polymer film. It has been found previously that, in the case of PPy, the swelling ability of solvent vapours decreases in the order $\text{CH}_2\text{Cl}_2 > \text{CH}_3\text{OH} > \text{H}_2\text{O}$ [27]. In addition, for the first four members of the homologous series of *n*-alcohols, a tendency for facilitation of the penetration of the PPy by alcohol molecules was observed with decreasing molecular size of the alcohol [27]. The positive correlation between the dielectric constant (ϵ) of the solvent and the conductivity of PPy also indicates the importance of the nature of the solvent in

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polymer-solvent (vapour) interactions [27]. The electrical parameters of the solvents such as their dielectric constant and their dipole moment (μ) also influence the properties of PPy in the case of interaction of the PPy matrix with the liquid solvent [25].

Besides the quite numerous papers on the properties of PPy/DDS films in conjunction with aqueous solutions only, some reports refer to the redox behaviour when non-aqueous solvents are used. AN and PC have been used both as solvents for synthesis as well as for electrochemical measurements [4, 17, 26]. The use of AN instead of water as the solvent in electrodeposition of PPy/DDS leads to films with higher electrical conductivity, density and mechanical strength, as well as to better smoothness and compactness of the film [4]. As in the case of PPy/polymeric anion films, the migration of solution cations accompanies redox process in both aqueous and AN solutions [14, 16]; then upon reduction-reoxidation of PPy/DDS films the cation diffusion is dominant only in aqueous solution. In AN a large quantity of the bulky DDS^- leaves the polymer film during electrochemical reduction [4, 26]. Similar to aqueous solutions, it is assumed that the reduction of PPy/DDS films proceeds also in PC electrolyte solutions based on a cation compensation mechanism [17]. Although it has been found for aqueous solutions that, besides the cation migration also the anionic species participate in the redox process [3, 6, 28], it has been mainly believed that conservation occurs of the original dopant DDS^- in the film [2, 3, 4, 5, 6, 7, 26]. Only a few reports [3, 5, 29] indicate that there is a possibility of DDS^- movement into or out of the film during electrochemical cycling. However, quantitative analysis of this process is meagre or missing. Therefore, our attention was focused on the electrochemical characterization of the redox behaviour of a PPy/DDS film in aqueous, AN, ethanolic (ET) and methanolic (ME) electrolyte solutions, especially with the aim of obtaining quantitative information about changes in film composition during various treatments in order to understand the role of the solvent.

Experimental

The PPy/DDS films for electrochemical measurements and electron probe microanalysis (EPMA) were prepared by galvanostatic electropolymerization ($i=2 \text{ mA/cm}^2$) of pyrrole in aqueous solution containing 0.1 M pyrrole and 0.1 M NaDDS or in ethanolic solution containing 0.1 M pyrrole and, owing to a more limited solubility, 0.05 M NaDDS. Some syntheses were carried out in aqueous solutions of 0.1 M pyrrole and 0.05 M or 0.15 M NaDDS. The working electrodes were Pt wires (0.1 cm^2), the counter electrode was a Pt ring or wire and the reference electrode was a saturated Ag/AgCl electrode. Common electrochemical cells were used in all experiments. The film thickness was calculated based on the assumption of a charge density of 0.2 C/cm^2 per $1 \mu\text{m}$ [2] and the thickness was varied from 2 to $3 \mu\text{m}$ in the case of CV measurements; it was $3 \mu\text{m}$ for EPMA.

Electrochemical measurements were performed in 0.1–0.15 M chloride and perchlorate solutions saturated with argon. The initial potential of CV measurements was 0.4 V, at which the films are in

the oxidized and conductive state but where they are not yet undergoing any overoxidation. The electrolyte cations have been varied by size, charge and nature. Pyrrole (Aldrich) was distilled in vacuum and stored refrigerated. Methanol (Merck) and ethanol were distilled over CaO and acetonitrile was dried with molecular sieves (4 \AA) and distilled. Bidistilled water was used throughout to prepare the aqueous solutions. NaDDS was recrystallized; the other salts of analytical and reagent grade were used as received.

The composition of the PPy films was determined by EPMA using JSM-35CF (JEOL, Japan) equipment supplied with two crystal spectrometers and with an energy dispersive spectrometer AN 10/55S (Link Systems, Oxford Instruments, UK). The analysis was performed with an energy of 10 keV that guaranteed information collection from the entire film thickness ($3 \mu\text{m}$). During the analysis the electron probe was defocused ($\phi \approx 10 \mu\text{m}$) and the specimen was linearly scanned relative to the fixed probe. Thus a lower dose density of primary electron irradiation and a wider area of the analysis were achieved. The K_α lines were used as analytical X-ray lines for the determination of the content of S, Cl, Na and Mg, and L_α lines for determination of Cs. Freshly cleaved single-crystal pieces of NaCl for the analysis of Cl and Na, CsCl for the analysis of Cs, a conductive single crystal of ZnS for the analysis of S and metallic Mg were used as standards. The scanning electron micrographs were obtained using the JSM-35CF scanning electron microscope (SEM) in secondary electron image mode with 20 keV primary electron energy. Before EPMA and SEM analyses the investigated films were soaked in bidistilled water for 5 min to remove ions weakly adsorbed on the polymer matrix as well as excess electrolyte from the PPy pores.

Results and discussion

The properties of PPy/DDS in aqueous solutions

On the basis of voltammograms of PPy/DDS films that were synthesized from aqueous solutions of 0.1 M pyrrole and 0.15 M NaDDS, and studied in 0.15 M chloride aqueous solutions (see Fig. 1A), a correlation between cathodic peak potential (E_{pc}) and ionic potential (qr^{-1}) was derived (Fig. 1B). It has been observed before [7] that the CV parameters depend on the charge, radius and nature of the electrolyte cation used. The ionic potential of the cation, i.e., the ratio of charge to ionic radius, thus refers to two important characteristics of ions. Figure 1B suggests a certain tendency of $E_{\text{pc},1}$ to shift towards more positive potentials with increasing ionic potentials. This means that the cations with a smaller Pauling radius can more easily penetrate the film. Hence it can be concluded that owing to the structural peculiarity and the hydrophobicity of the film, the incorporation of at least partially dehydrated cations takes place during the first reduction cycle. Similar conclusions have been made previously [8]. Also there is an obvious tendency that the incorporation of doubly charged cations during the first cycle begins at more positive potentials than in the case of singly charged ions [Fig. 1A(a, c)]. This may be caused by their smaller Pauling radius and stronger electrostatic interaction between M^{2+} and PPy/DDS^- . As the second (and following) cycles essentially differ from the first one by shape and sharpness of the reduction peak, the $E_{\text{pc},2}$ vs. qr^{-1} dependence must be taken with caution. However, a weak tendency exists for $E_{\text{pc},2}$ to shift towards

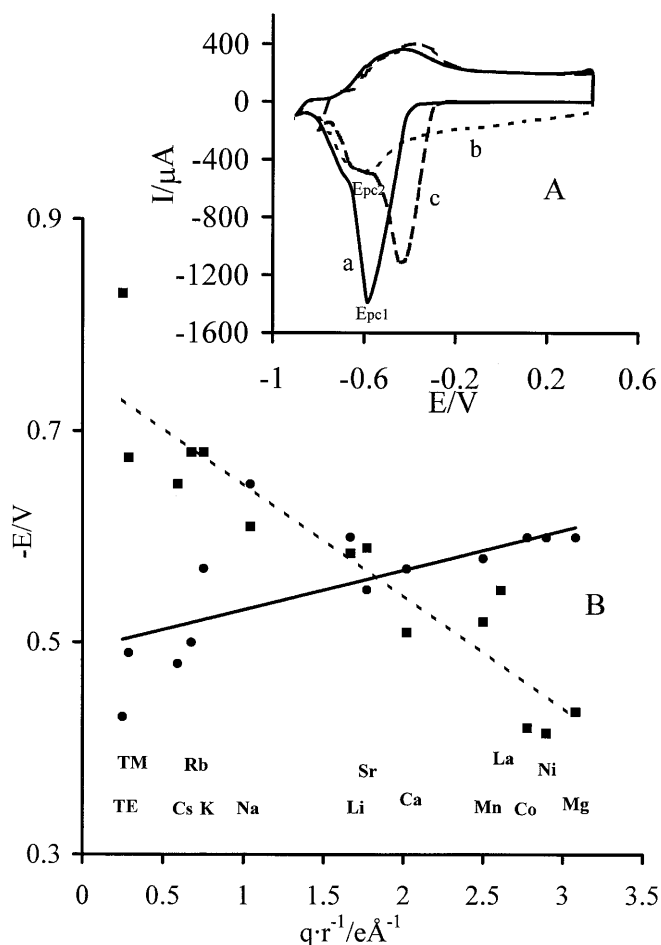


Fig. 1 A The CV curves of PPy/DDS films (2 μm) in 0.15 M chloride aqueous solutions: LiCl (a, b); MgCl_2 (c). The first cycles (a, c); the second cycle (b). Sweep rate 50 mV s^{-1} . B Plot of $E_{\text{pc},1}$ (■) and $E_{\text{pc},2}$ (●) vs. ionic potential (qr^{-1}) of the cation. The E_{pc} values are from CV curves of 2 μm PPy/DDS films in 0.15 M chloride aqueous solutions with different cations. Sweep rate 50 mV s^{-1} . TM, tetramethylammonium ion; TE, tetraethylammonium ion. The oxidation number is 3 (La) or 2 (Mn, Co, Ni)

more negative potentials with increasing ionic potentials for the second cycle (Fig. 1B). This seems unreasonable from an electrostatic viewpoint. However, this kind of dependence probably indicates that the radii of the hydrated ions must be taken into account, as the ions with higher qr^{-1} values generally possess greater effective radii due to their hydration sphere. Obviously, within the first redox cycle the essential structural changes of the PPy/DDS film take place, enabling ions to insert into the polymer matrix with their entire or partial hydration sphere. The same conclusions regarding the changes of the film morphology caused by the interaction of the polymer with ions have been made also in the case of PPy films with small dopants [30]. This concerns also the need to take into account the solvent flux during the redox cycles.

However, in order to decide about a possible immobility of the DDS^- ions originally incorporated into the PPy matrix, there still needs more detailed studies when this is attempted to be derived from the dependence of the electrochemical behaviour of PPy/DDS film on parameters of the electrolyte cations. To solve this problem the electrochemical cycling of PPy/DDS films (3 μm , electrodeposited from solution of 0.1 M pyrrole and 0.1 M NaDDS) was studied in aqueous solutions of 0.1 M NaClO_4 inside a potential interval of 0.4 V and -1.0 V. The EPMA data presented in Table 1A show that the doping level (f), expressed as a mole ratio of anion per pyrrole unit of the freshly synthesized film, diminishes approximately by 16% during the first cycle and by 32% and 52% during 10 and 100 cycles. This means that in each cycle between the 2nd and the 10th, $f(\text{DDS}^-)$ decreases by approximately 2%, and by roughly 0.3% between the 11th and 100th cycles. During the first redox cycle a decrease of both $f(\text{DDS}^-)$ and $f(\text{total})$ [where $f(\text{total}) = \sum f(\text{anions}) - \sum f(\text{cations})$] takes place, and in the following cycles mainly $f(\text{DDS}^-)$ diminishes, while $f(\text{total})$ remains constant [$f(\text{total}) \approx 0.23\text{--}0.24$] owing to partial replacing of DDS^- by ClO_4^- . The relatively large decrease of DDS^-

Table 1 The influence of various electrochemical treatments on the PPy/DDS films composition in aqueous test solutions

PPy/DDS from aqueous (AQ) solution		Mol ratio of incorporated ions to pyrrole unit (f)				
		DDS^-	ClO_4^- or Cl^-	Na^+	Cs^+	Mg^{2+}
A	Untreated	0.31	–	0	–	–
	Soaked in bidistilled water for 1 h	0.30	–	0	–	–
	Soaked in bidistilled water for 24 h	0.25	–	0	–	–
	Soaked in 0.1 M NaClO_4 (AQ) for 1 h	0.30	0.005	0	–	–
	Soaked in 0.1 M NaClO_4 (AQ) for 24 h	0.25	0.008	0	–	–
	Cycled in 0.1 M NaClO_4 (AQ); 1 cycle	0.26	0.01	0.02	–	–
	Cycled in 0.1 M NaClO_4 (AQ); 10 cycles	0.21	0.04	0.01	–	–
	Cycled in 0.1 M NaClO_4 (AQ); 100 cycles	0.15	0.1	0.02	–	–
B	Reduced in 0.1 M NaCl (AQ) at $E = -0.68$ V for 5 s	0.24	0	0.12	–	–
	Reduced in 0.1 M NaCl (AQ) at $E = -0.68$ V for 1 min	0.23	0	0.11	–	–
	Reduced in 0.1 M NaCl (AQ) at $E = -0.82$ V for 1 min	0.19	0	0.09	–	–
	Reduced in 0.1 M CsCl (AQ) at $E = -0.82$ V for 1 min	0.25	0	–	0.16	–
	Reduced in 0.1 M MgCl_2 (AQ) at $E = -0.82$ V for 1 min	0.20	0	–	–	0.10
	Reduced in 0.1 M BTEACl (AQ) at $E = -0.82$ V for 1 min	0.28	0	–	–	–

content in the film during first cycle (ca. 16%) compared with the corresponding value for cycles 2–10 (ca. 2% for each cycle), and also the fact that the charges of the first and second reduction cycles are close ($Q_{C,1} \approx Q_{C,2}$), allows us to suppose that a certain part of DDS^- ions originally included in the PPy film are not dopant ions. The different types of DDS^- dopant ions (conventionally shallowly trapped and deeply trapped) are present in PPy films doped with DDS, as in the case of PPy films with small inorganic dopant ions [31, 32]. It should be mentioned that the shallowly trapped ions are neither the weakly adsorbed ones nor originate from the electrolyte in polymer pores as both were removed by thorough leaching in water (see Experimental section). They are DDS^- ions more weakly bonded with the matrix or more easily accessible. The leaching of DDS^- from a PPy membrane occurs not only by applying an external electric field but also by soaking the film in electrolyte solution (NaClO_4) or even in a pure solvent, e.g. water. Approximately the same value of $f(\text{total})$ was reached after 24 h soaking as in the case of one electrochemical cycle (see Table 1A). Some decrease of $f(\text{total})$ during soaking may only be apparent as it is possible that some part of the DDS^- ions is replaced by OH^- ions [33] not determined by EPMA in this work. Further, a possible irreversible overoxidation must be taken into account [34].

It has been accepted that during electrochemical reduction the electroneutrality of the PPy/DDS film is guaranteed by the incorporation of cations from the electrolyte into the film. To characterize the relationship between the two processes, i.e., pseudo cation doping and release of bulky DDS^- ions during reduction, the PPy/DDS films were reduced at cathodic potentials near $E_{\text{pc}} = -0.68$ V and at a more negative potential of $E = -0.82$ V during 5 s or 1 min, followed by analysing the films by EPMA. Table 1B again shows, besides the insertion of cations into the film, the migration of bulky DDS^- out of the film. In this respect, our results differ from the conclusions made by Ko et al. [4], according to which the concentration of sulfur in the film, prepared under conditions not very different to ours, did not change even after 24 h reduction in aqueous solution. Our data show that the doping degree with regard to DDS^- is approximately twice higher than $f(\text{cation})$, indicating that the reduction of the film is incomplete even at quite a high cathodic potential ($E = -0.82$ V). In Ko et al. [4] the slight decrease of electrical conductivity of the film after film reduction (only by one order or two) also refers to the incomplete character of the reduction process. Moreover, in solutions of bulky cations, e.g. tetrabutylammonium (TBA) or benzyltriethylammonium (BTEA), the cations practically cannot be incorporated into the film during the first reduction cycle (see diminutive reduction current in Fig. 2) and the film remains in the oxidized state also at cathodic potentials. These CV results are in accordance with the EPMA data (Table 1B), which suggest that after the film reduction in the solution of 0.1 M BTEACl at -0.82 V

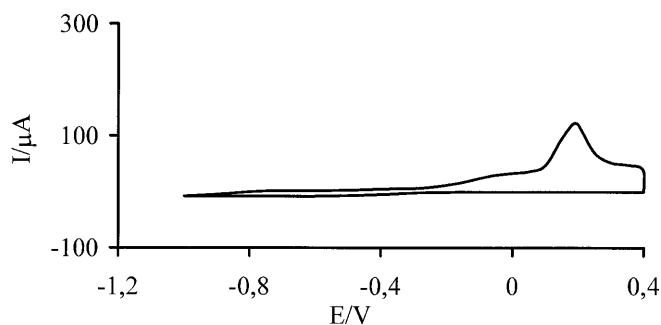


Fig. 2 The CV curve of PPy/DDS film (2 μm) in 0.15 M benzyltriethylammonium chloride aqueous solution. Sweep rate 50 mV s^{-1}

for 1 min, the $f(\text{total})$ designating the degree of film oxidation remains 2.8–3.1 times higher than in the solution of small metal ions. It also becomes evident that the release of the “accessible part” of the doping DDS^- ions in electrochemical reduction preferentially proceeds only after the incorporation of electrolyte cations into the film.

The properties of PPy/DDS in non-aqueous solutions

In Fig. 3a–c the CV curves of PPy/DDS films recorded in 0.1 M NaClO_4 solution in ME, ET and AN are presented. For comparison, the CV curves in aqueous solution are given in Fig. 3d. Opposite to the behaviour of a PPy/DDS film in aqueous solutions, where there exists in the first cycle a large potential interval without a noticeable reduction current with a following quite narrow potential interval for the incorporation of cations into the film (peak widths at half-height, $\Delta H^{1/2}_{\text{pc},1}$, are between 120 and 180 mV for metal cations in Cl^- solutions or ca. 250 mV in ClO_4^- solution), the film reduction in non-aqueous solutions starts immediately at the initial potential of 0.4 V and proceeds within a wide potential interval. As seen from Fig. 3, the shapes of the CV curves in ME and ET media resemble those obtained during redox cycles of common PPy films with small anions in aqueous solution (i.e. anion exchangers). This indicates that during the first cycle an essentially large part of DDS^- releases from the matrix, and during the following oxidation the anionic species of the test solution will be incorporated into the polymer. The formal redox potential (E_f) of a PPy/DDS film remains within -0.25 to -0.20 V during first 10 cycles in ME and AN; in ET the E_f varied within -0.32 to -0.26 V. These E_f values are more positive than the corresponding values for PPy/DDS in aqueous solutions (with E_f around -0.50 V); however, they are more negative than in the case of PPy films with small anions such as ClO_4^- , NO_3^- , Cl^- or Br^- , with E_f around 0 V or higher. It must be mentioned that this comparison of potential values is very approximate as it does not consider the differences of potential drop on the boundary between the aqueous

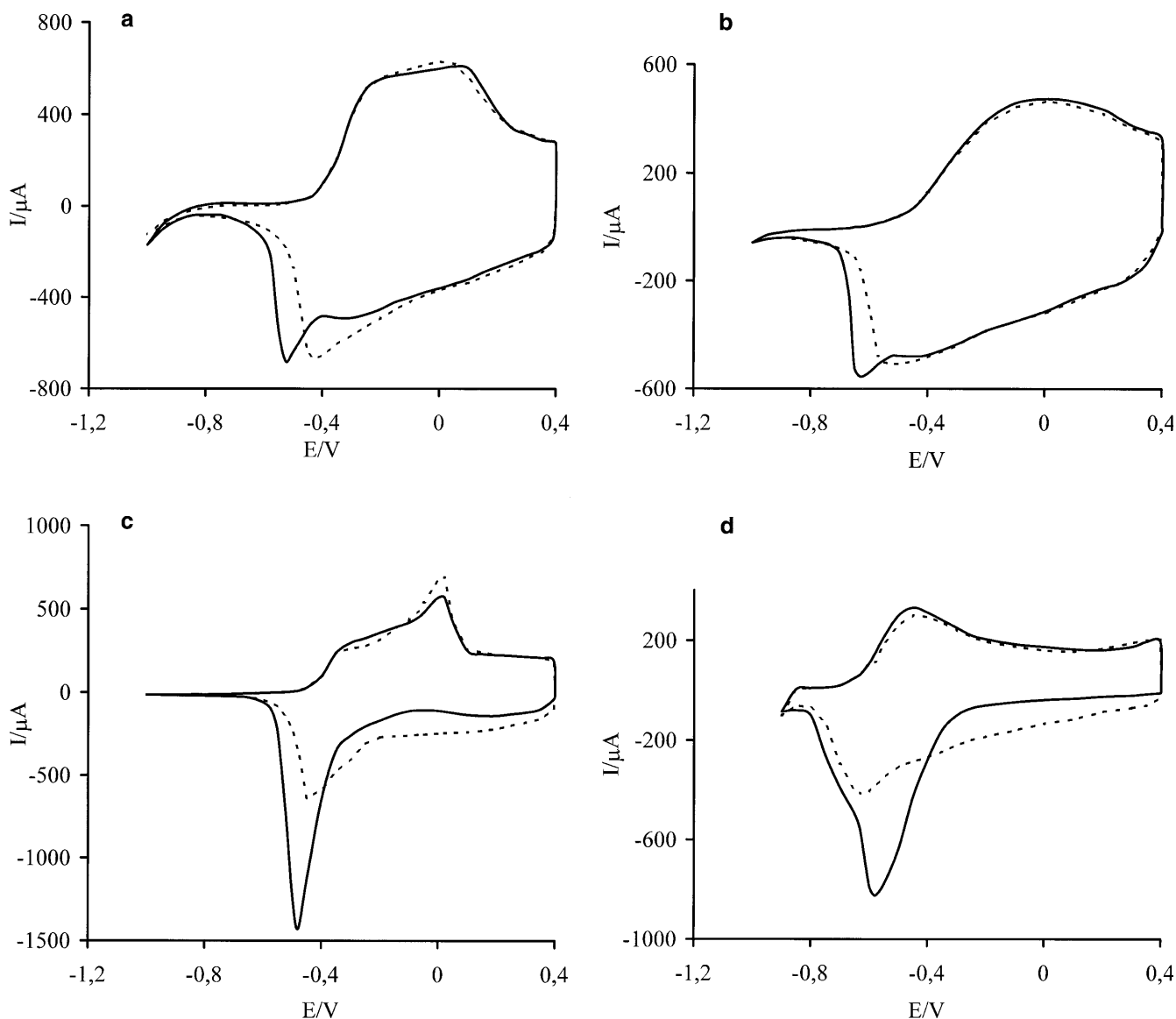


Fig. 3 The CV curves of PPy/DDS films synthesized in aqueous solution and cycled in 0.1 M NaClO₄ solutions with different solvents: **a** methanol; **b** ethanol; **c** acetonitrile; **d** water. The first (—) and the second (---) cycles. Sweep rate 50 mV s⁻¹. The film thickness is 3 μm (**a**, **b**) or 2 μm (**c**, **d**)

reference electrode/non-aqueous solution. The E_{pc} values characterizing the DDS⁻ ion releasing from the matrix in alcoholic solutions are, despite the size of the surfactant ion, close to those obtained for PPy/ClO₄ films in alcohols [25]. Similar also are the shapes of the CV curves. The reason for this obviously consists of a good swelling ability in methanol and ethanol.

From Fig. 3c it is evident that in AN solution the first reduction cycle of a PPy/DDS film differs from those obtained in alcoholic solutions and resembles more the reduction curve in aqueous media. The small reduction charge in the “anionic area” (0.4 to -0.2 V) and the following narrow peak indicate that a pseudo cation doping (cation incorporation) process dominates. These considerations are confirmed by EPMA data (Table 2A).

While one redox cycle from 0.4 V to -1.0 V and back to 0.4 V in a solution of 0.1 M NaClO₄ in ME diminished the $f(\text{DDS}^-)$ approximately 100 times and in ET approximately 5 times, the decrease in AN solution was only 50%. Also, the presence of a small amount of electrolyte cations (Na⁺) not expelled after reoxidation, compensating a part of DDS⁻ in the film, is established after a redox cycle in AN. From these results it is evident that the mobility of anions in PPy/DDS films increases in the order AN < ET < ME. The same order is found to be valid from the results of different PPy/DDS film treatments, including electrochemical reduction and film soaking into solutions (Table 2A). The most complete depletion of the polymer from DDS⁻ occurred in ME solution already after its reduction at a potential of -0.51 V (close to $E_{pc,1}$) during 1 min, which was deduced from not detecting any DDS⁻ anions in the film. The same result was obtained after an analogous treatment at -0.82 V. The identical treatment of PPy/DDS film in ET solution at -0.82 V also resulted in $f(\text{DDS}^-) = 0$.

Table 2 The influence of organic solvents in the composition of the test or synthesis solutions on the properties of PPy/DDS films

PPy film		Molar ratio of incorporated ions to pyrrole unit (<i>f</i>)		
		DDS ⁻	ClO ₄ ⁻	Na ⁺
A	PPy/DDS from aqueous (AQ) solution			
	Soaked in 0.1 M NaClO ₄ (ME) for 1 h	0.006	0.19	0
	Soaked in 0.1 M NaClO ₄ (ET) for 1 h	0.01	0.20	0
	Soaked in 0.1 M NaClO ₄ (AN) for 1 h	0.09	0.13	0
	Cycled in 0.1 M NaClO ₄ (ME); 1 cycle	0.003	0.20	0
	Cycled in 0.1 M NaClO ₄ (ET); 1 cycle	0.06	0.18	0
	Cycled in 0.1 M NaClO ₄ (AN); 1 cycle	0.15	0.10	0.02
	Reduced in 0.1 M NaClO ₄ (ME) at <i>E</i> = -0.51 V for 1 min	0	0.015	0
	Reduced in 0.1 M NaClO ₄ (ME) at <i>E</i> = -0.82 V for 1 min	0	0.014	0
	Reduced in 0.1 M NaClO ₄ (ET) at <i>E</i> = -0.51 V for 5 s	0.1	0.02	0.06
	Reduced in 0.1 M NaClO ₄ (ET) at <i>E</i> = -0.53 V for 1 min	0.01	0.02	0
	Reduced in 0.1 M NaClO ₄ (ET) at <i>E</i> = -0.82 V for 1 min	0	0.012	0.006
	B	PPy/DDS from ET solution		
Untreated		0.27	–	0
Cycled in 0.1 M NaClO ₄ (AQ); 1 cycle		0.21	0.04	0.05
Cycled in 0.1 M NaClO ₄ (ET); 1 cycle		0.04	0.09	0
Cycled in 0.1 M NaClO ₄ (AN); 1 cycle		0.09	0.08	0.01

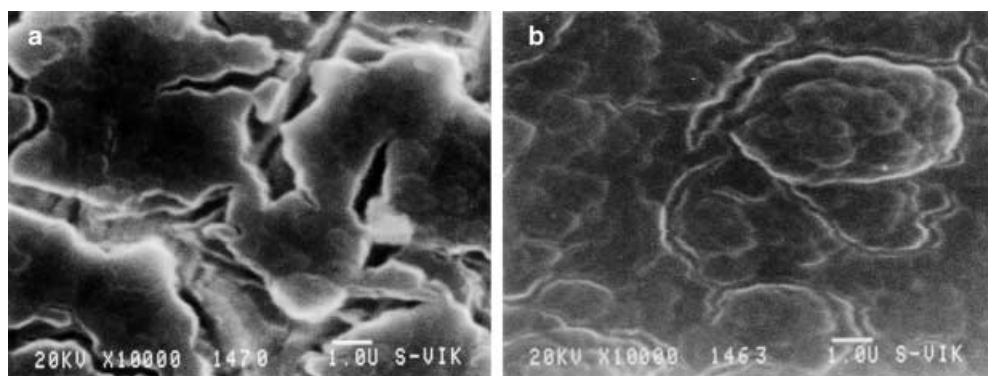
When the film was reduced at -0.53 V for 1 min, the $f(\text{DDS}^-)$ value decreased considerably, i.e. about 30 times. The experiments of anion exchange processes in different organic bathing media show once again that the replacement of the bulky DDS^- ions by ClO_4^- proceeds more easily in ME and ET solutions. After 1 h exposition time, $f(\text{DDS}^-)$ decreased ~52 times (in ME) and ~31 times (in ET) in comparison with $f(\text{DDS}^-)$ of untreated film and the residual $f(\text{DDS}^-)$ was only 3% (in ME) and ~5% (in ET) of $f(\text{total})$. In AN media the $f(\text{DDS}^-)$ value decreased ~3.5 times, forming ~41% of $f(\text{total})$. For aqueous solutions the latter value was ~98%. It must be noted that after 1 h soaking of the PPy/DDS film in 0.1 M NaClO₄ aqueous solution, $f(\text{total})$ was nearly the same as f of a freshly prepared film, whereas film exposure to organic electrolyte solutions for 1 h caused a decrease of $f(\text{total})$ by 1.4–1.6 times (cf. Tables 1A and 2A).

The stronger interaction between organic solvents and a PPy/DDS film (compared with interaction with H₂O) also follows from strong solvent effects, such as lack of break-in phenomena and greater film permeability to bulky ions [35], in potential scans from the rest

potential (0.4 V) towards negative potentials, and is also found in potential scans in the positive direction (overoxidation). The results of a positive potential scan on the mechanical behaviour of the film are presented in Fig. 4. This figure shows that if in 0.1 M NaClO₄ aqueous solution the PPy/DDS film is overoxidized for 1 min at 1.0 V, this results in a mechanical breaking of the film (a) whereas in a corresponding ET solution the DDS^- ions can leave the film more easily (b). From all these results there follows that the swelling ability of PPy films in the solvents used increases in the order water < AN < ET < ME.

Although the EPMA data collected after reduction of the polymer in ME or ET for 1 min show, in contrast to aqueous solutions, the complete or almost complete absence of cations in the film, a comparison of the concentration of dopant/pseudodopant ions after film reduction for different durations (5 s and 1 min) in ET near -0.5 V (Table 2A) indicates that the cations participate in this process. The diminishing of both $f(\text{DDS}^-)$ and $f(\text{Na}^+)$ with time allows us to suppose that dopant DDS^- ions (or part of them) are released from the PPy matrix during the electrochemical reduction by the help

Fig. 4 SEM microphotographs of PPy/DDS films (3 μm, prepared in 0.1 M pyrrole and 0.1 M NaDDS aqueous solution) after overoxidation in 0.1 M NaClO₄ for 1 min at 1.0 V: **a** aqueous solution; **b** ethanolic solution



of cations previously incorporated into the film from the electrolyte.

Our results have not yet revealed a clear relationship between solvent swelling ability and such essential physicochemical solvent parameters as dipole moment, polarizability or electron donating/accepting properties (DN/AN) [36, 37]. Yet a certain dependence of polymer-solvent interaction strength (swelling degree) on solvent parameters, such as the dielectric constant (ϵ) and surface tension (γ) [36], has been found. Solvents with a low ϵ , e.g. ET (25.3), ME (33.0) or AN (36.6), enable the interaction between polymer polarons/bipolarons and solvent on a larger spatial scale than the solvents with a high ϵ , e.g. H₂O (80.1). In this way the solvent with a low ϵ has been found to increase the charge storage ability of PPy/ClO₄ films [25]. The solvents with a low γ (mN m⁻¹), e.g. ET (22.0), ME (22.1) or AN (28.7), probably favour the ion transport process in the polymer more than H₂O (72.0).

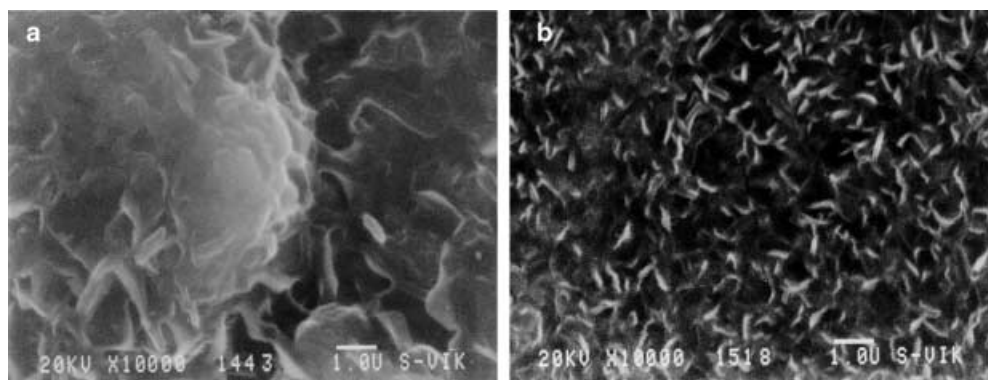
The properties of PPy/DDS synthesized in ethanolic solutions

Figure 5a shows the surface morphology of an untreated PPy/DDS (ET) film. By comparison with the film from aqueous media (Fig. 5b), whose surface is uniform and smooth, the basically smooth surface of the former is covered with small bumps. During electropolymerization in ET solution at the same current density as in aqueous solutions ($i = 2$ mA/cm²), the synthesis potential is 250–350 mV higher than in aqueous media. The voltammograms of PPy/DDS films synthesized in ET solution and measured in ET, AN and aqueous electrolyte solutions are presented in Fig. 6a–c. Using an equivalent amount of charge during the film synthesis, the film formed in ET solution shows in all investigated media (water, AN, ET) reduction charges 1.4–1.7 times smaller than the films prepared in aqueous solution and measured in corresponding media. This is probably caused by part of the electropolymerization charge being consumed by side reactions, which become more pronounced with potential increase and also depend on solvent because of an increased solubility of the intermediate oligomers. A comparison of the shapes of CV

curves taken for PPy/DDS films synthesized in ET and aqueous media and measured in ET solution (cf. Fig. 6a and Fig. 3b) reveal many similarities. Only the peak separation ΔE is found to be somewhat smaller for films from ET solution. Similar also are the changes in film composition during a redox cycle from 0.4 V to –1.0 V and back to 0.4 V in 0.1 M NaClO₄ ET solution. The $f(\text{DDS}^-)$ values of the original dopant of the film prepared in ET decreased ca. 6.8 times after the above-mentioned electrochemical treatment. For the film from aqueous solution, this number was 5.2 times (cf. Table 2B and A). To some extent, larger differences result in AN solution. In the case of films prepared in aqueous solution and cycled in 0.1 M NaClO₄ (AN), there existed a high narrow reduction peak for the first cycle that probably corresponded to cation incorporation into the film. The reduction peak for the films from ET synthesis solution, however, is smaller and is shifted to positive potentials. In addition, this peak diminishes or disappears during the next cycles. The shape of the voltammograms after the first or a couple of redox cycles resembles the one of a “common” PPy/ClO₄ film, indicating that by its structure the PPy/DDS film from ET preparation media is better adaptable to new dopant than the film from aqueous media. The doping degree of the original dopant reduces after the first redox cycle in AN by 3 times. This is, similar to films grown in aqueous solutions, less than in ET.

As seen from Fig. 6c, the behaviour of a PPy/DDS film synthesized in ET and measured in aqueous media is rather similar to one prepared in aqueous media, i.e. there exists a potential region where redox processes practically do not occur and there is a subsequent narrow reduction peak corresponding mainly to cation incursion into the film. A low mobility of DDS⁻ ions in this case is evidenced from the EPMA data (Table 2B), according to which $f(\text{DDS}^-)$ decreased ~ 1.3 times, i.e. close to the corresponding value for films from aqueous solutions (~ 1.2 times). The results obtained confirm that the redox properties of PPy/DDS films are influenced more by the solvent for the electrochemical treatment than by the media in which the synthesis was performed. The structure of the PPy/DDS film obtained in ET media seems to favour the dedopation/redopation of the polymer swollen in organic media.

Fig. 5 SEM microphotographs of PPy/DDS films (3 μm) synthesized from: **a** ethanolic solution; **b** aqueous solution



Conclusions

Electrochemical (CV) and anion-exchange experiments, and also EPMA results, show significant differences in

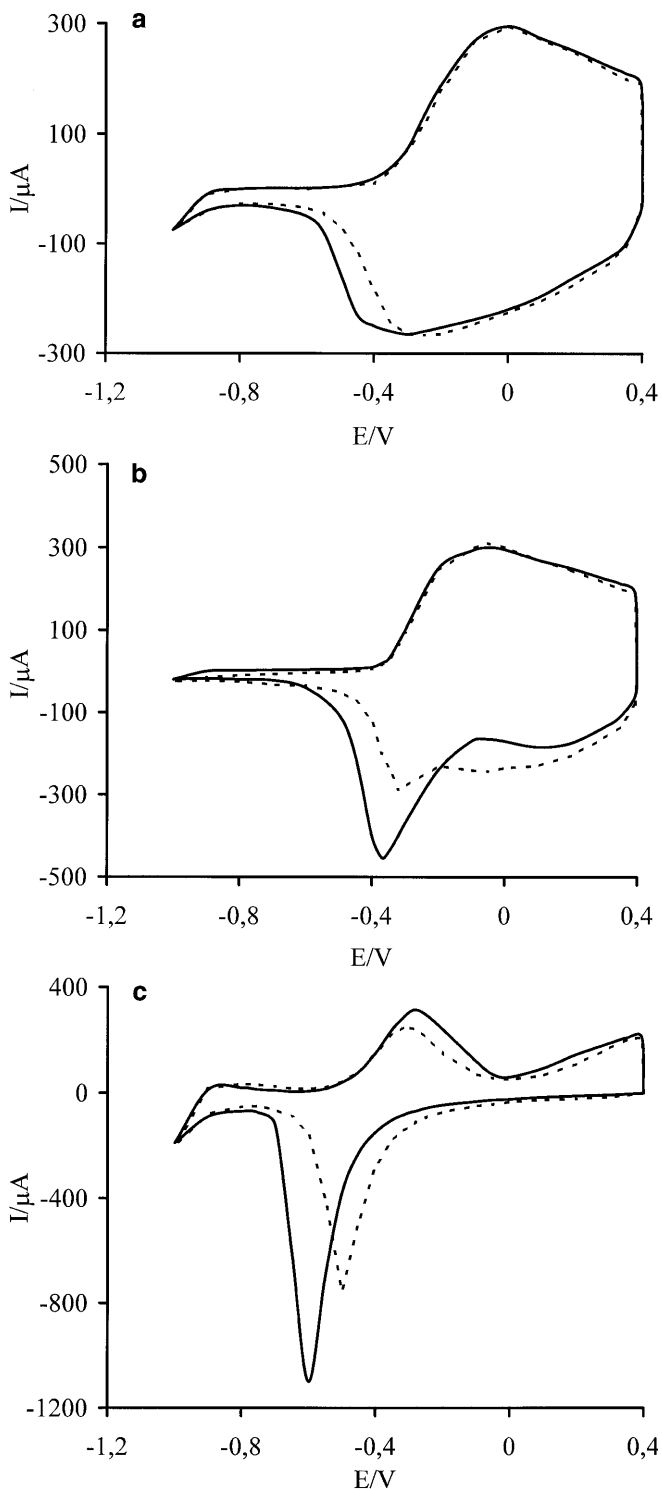


Fig. 6 The CV curves of PPy/DDS films synthesized in ethanolic solution and cycled in 0.1 M NaClO₄: **a** ethanolic solution; **b** acetonitrile solution; **c** aqueous solution. The first (—) and the second (---) cycles. Sweep rate 50 mV s⁻¹

the redox behaviour of PPy/DDS films in aqueous and organic media. The influence of the solvent on the electrochemical properties of polymers is much stronger when the solvent is used in redox cycling than its influence in electropolymerization. The quantitative experimental data on the chemical composition of the films after various treatments indicate that the original dopant ions (DDS⁻) are not irreversibly trapped in the matrix for any of the studied media. The swelling ability of solvents increases in the order water < AN < ET < ME. Whereas in organic solutions the bulky DDS⁻ ions are easily removed from the matrix by applying constant reduction potentials, by redox cycling or by self-diffusion, for the process in aqueous solutions the DDS⁻ ions bound to the matrix are found to be always present in the film. During redox cycling in aqueous solutions the electroneutrality of the film is maintained by cation inclusion/exclusion, although this process is accompanied by partial replacement of original DDS⁻ ions by electrolyte anions. The participation of cations of the test solution in the redox processes of PPy/DDS is observed also in the case of organic solvents.

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