



# Effect of hydroxypropyl- $\beta$ -cyclodextrin on the electrochemical oxidation and polymerization of 3,4-ethylenedioxythiophene

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## Abstract

The electrochemical oxidation of 3,4-ethylenedioxythiophene (EDOT) on platinum is studied in electrolyte solutions containing hydroxypropyl- $\beta$ -cyclodextrin (HP- $\beta$ -CD). HP- $\beta$ -CD is found to increase the solubility of EDOT up to a concentration of 0.026 M in aqueous solutions. Addition of HP- $\beta$ -CD (0.1 M) produces a slight red shift of the EDOT main absorption band from 254.9 to 257.7 nm and an increase of the HP- $\beta$ -CD concentration decreases the absorption coefficient,  $\epsilon_{\max}$  to  $6150 \text{ l mol}^{-1} \text{ cm}^{-1}$  in the UV–vis region, indicating complex formation. The cyclic voltammetric response of EDOT in 0.1 M aqueous  $\text{LiClO}_4$  solutions consists of an ill-defined wave ( $P_1$ ) and an adsorption peak ( $P_2$ ). Contrary to the case of oxidation in acetonitrile medium, a post-peak is observed in the voltammograms of EDOT electro-oxidation in aqueous  $\text{LiClO}_4$  solutions due to the adsorption of the oxidized EDOT species. A gradual reduction of the peak current of  $P_2$  with increasing [HP- $\beta$ -CD] and its total disappearance at high [HP- $\beta$ -CD] suggest complex formation between HP- $\beta$ -CD and  $\text{EDOT}^{*+}$  and also the peak  $P_2$  to be due to adsorption of  $\text{EDOT}^{*+}$  species. The experiments intended to show the effect of ‘pre-adsorbed’ HP- $\beta$ -CD on EDOT oxidation led to the conclusion that adsorbed HP- $\beta$ -CD also solubilizes EDOT at the electrode surface. The CV behaviour of EDOT in HP- $\beta$ -CD is discussed in comparison with that in sodium dodecylsulfate micellar solutions. Addition of increasing amounts of HP- $\beta$ -CD shifts  $P_1$  positively and  $P_2$  negatively while also suppressing  $P_2$  totally and reducing the peak current of  $P_1$  to a significant extent. At a higher concentration of HP- $\beta$ -CD, viz. 0.05 M, a peak appears at 1.29 V as a result of the above two opposing effects of CD on the peak potentials of  $P_1$  and  $P_2$ . This resultant peak ( $P_{\text{composite}}$ ) is more positive relative to the position of  $P_1$  observed in the absence of HP- $\beta$ -CD. The positive shift of the peak and peak current reduction indicate that EDOT (or an oxidized EDOT species) possibly interacts with the outer nucleophilic part of HP- $\beta$ -CD. The electro-oxidation processes occurring at  $P_1$  and  $P_2$  are explained using an oligomeric approach, in which the electrochemical reactions are coupled to chemical reactions or adsorption of the oxidized species. Potential cycling of the platinum electrode in solutions containing 0.026 M EDOT + 0.05 M HP- $\beta$ -CD + 0.1 M  $\text{LiClO}_4$  between  $-0.5$  and  $1.2$  V yields an adherent and smooth polymer film of poly(ethylenedioxythiophene), as shown in the SEM examination. In situ resistance measurements carried out with the polymer films in the electroactive region show a minimum resistance in the potential range of  $0.3$ – $0.4$  V. Even the electrochemically-reduced films are found to possess some residual electrical conductivity. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Ethylenedioxythiophene;  $\beta$ -Cyclodextrin; Solubilization; Adsorption; Electropolymerization

## 1. Introduction

There is a widespread realization that polymerization in organized media provides an exciting possibility of controlling polymer microstructures [1]. We have earlier reported electropolymerization of benzene in oil-in-water type microemulsions [2–4] to yield freestanding

films of poly(*para*phenylene and of aniline in water-in-oil microemulsions [5,6]. Apart from increased solubility of the monomers in aqueous media, several interesting microstructures were evident when monomers were electropolymerized in such organized media [7,8]. Subsequently, this approach was applied to the electropolymerization of thiophene monomers in aqueous media by Sakmeche et al. [9] using anionic micelles. Interestingly, electropolymerization becomes possible at oxidation potentials lower than those ob-

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served in non-aqueous media. The anionic micelles appear to shift the oxidation of the monomer to lower potentials, while also shifting the oxidative dissolution of the substrate metals such as zinc, iron, etc. [10,11]. In their recent work, Lagrost et al. [12,13] have reported a host–guest complexation strategy for electrodeposition of processable polythiophene composites from aqueous medium, using  $\beta$ -cyclodextrin as the host.

Cyclodextrins have been widely studied, mainly due to their ability to form inclusion compounds/complexes with various molecules. These cyclic oligosaccharides have a hydrophobic (cavity) interior and a hydrophilic outer side, and therefore can form inclusion compounds with hydrophobic species in aqueous media. Because  $\beta$ -cyclodextrin is rather poorly soluble in water (0.02 M), a more soluble (up to 0.7 M) substituted  $\beta$ -cyclodextrin, HP- $\beta$ -CD is employed in the present work. Adsorption of CD is also known to occur on substrates such as platinum [14,15], gold [16] and mercury from their solutions [17,18]. Thiophene structures are very weakly soluble in water and undergo oxidation at high positive potentials. Among the polythiophene derivatives, PEDOT [19], which can be electrosynthesized either in organic [20] or in aqueous media in the presence of sodium polystyrenesulfonate [21] or polyoxyethylene-10-laurylether [22], has the advantage of providing very stable and highly conductive films [23]. PEDOT exhibits remarkable electrochromic properties [24] and has recently been used in the development of electroluminescent diodes [25], preparation of anti-static, transparent films [26] used as catalyst supports for proton exchange fuel cell [27], and in electrochemical capacitors [28].

The electro-oxidation of EDOT was studied in non-aqueous and aqueous media [7,20,22,24]. In acetonitrile medium, EDOT oxidation exhibits only one irreversible peak at 1.38 V versus saturated calomel reference electrode (SCE) whereas in the aqueous  $\text{LiClO}_4$  solutions, a peak at 1.34 V ( $P_2$ ), preceded by an ill-defined wave ( $P_1$ ) at 1.05 V versus SCE, was observed. Based on the results of the peak current versus scan rate dependence, Sakmeche et al. [7] concluded that the peak ( $P_2$ ) was due to the diffusion-controlled oxidation of EDOT at the electrode surface and the wave ( $P_1$ ) to be due to the adsorption of the oxidized species of EDOT. The surfactant, sodium dodecylsulfate, above its critical micelle concentration (cmc) was found to electrocatalyze the EDOT oxidation like the case of polystyrenesulfonate [29]. It was shown that the films generated have properties and structures similar to those formed in organic media. In this report, we present the voltammetric results of the electrooxidation of EDOT and its polymerization in the presence and absence of HP- $\beta$ -CD in aqueous  $\text{LiClO}_4$  solutions.

## 2. Experimental

All the chemicals of analytical grade were used without further purification. 3,4-Ethylenedioxythiophene (Baytron M) and HP- $\beta$ -CD (Cavitron 8205; degree of substitution = 3–8) were used as received. All solutions were prepared using Milli-Q water of 18-M $\Omega$  impedance. A three-electrode cell assembled with a Pt counter electrode, a SCE and a Pt disc working electrode (WE) (2 mm diameter) was used. All cyclic voltammetric experiments were carried out with a potentiostat (PINE, Model AFRDE5 Bipotentiostat) coupled to an X–Y–t recorder (Rikadenki RW-201T). The working Pt electrode was pre-polished using emery papers of 3/0, 4/0 and 5/0 grades and alumina paste, rinsed in acetone and then subjected to ultrasonic cleaning in Milli-Q water prior to each experiment.

The in situ resistance measurements on the polymer films were performed according to the method described in Ref. [30]. Briefly, an insulated Pt wire probe was positioned close to the WE, so that when PEDOT film of sufficient thickness was deposited on the WE, the probe tip was just embedded in the PEDOT film. This probe was used to monitor the surface potential of the PEDOT film during potentiostatic polarization. Polymerization was carried out in a solution containing 0.1 M  $\text{LiClO}_4$  + 0.05 M HP- $\beta$ -CD + 0.026 M EDOT. After a sufficient thickness of the PEDOT film was formed on the WE, it was shifted to a three-electrode cell assembly containing only 0.1 M  $\text{LiClO}_4$  solution. Then, the PEDOT film was cycled in 0.1 M  $\text{LiClO}_4$  solution between –0.4 and 1.2 V till a stabilized CV response was obtained. The voltage drop across the PEDOT film due to its resistance was measured between the WE and the Pt wire probe. The resistance of the polymer film is given by  $V/I$ .

The morphology of the polymer films deposited on the Pt substrates was examined using a computer-controlled SEM (Hitachi Model H-3000).

The UV–vis spectra were recorded with a HITACHI U-3400 UV–vis NIR double beam spectrophotometer. The spectra were recorded for EDOT monomer with and without HP- $\beta$ -CD and also for the PEDOT films in their oxidized and reduced states.

## 3. Results and discussion

### 3.1. Solubility of EDOT and UV–vis absorption spectra

The solubility of EDOT in aqueous solutions containing HP- $\beta$ -CD is determined to be 0.026 M whereas its solubility in water is only 0.014 M at 25 °C (Fig. 1). Fig. 2 shows the effect of the concentration of HP- $\beta$ -CD on the UV–vis absorption of EDOT in 0.1 M

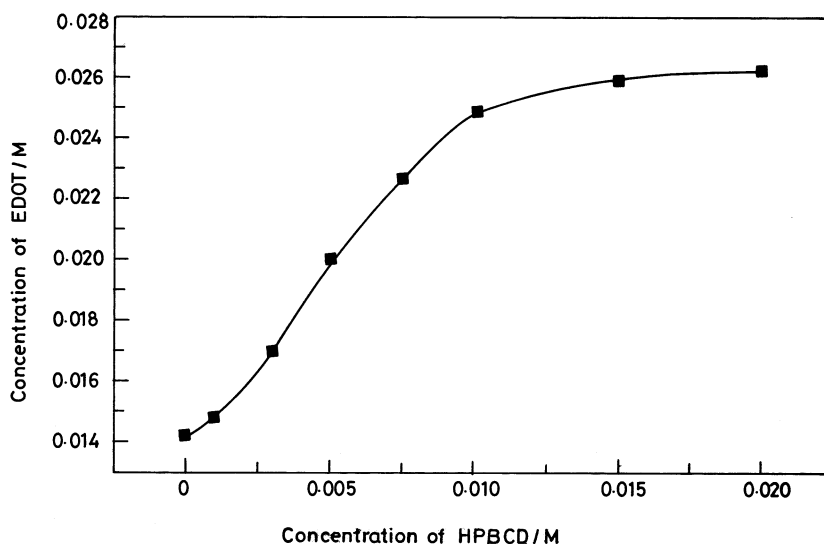


Fig. 1. Solubilization of EDOT in aqueous solution containing HP-β-CD.

aqueous  $\text{LiClO}_4$ . In the absence of HP-β-CD, the spectrum shows an absorption at 254.9 nm and a shoulder at 224.6 nm. Addition of 0.1 M HP-β-CD to the aqueous solutions of EDOT does not modify the general spectral features but produces a red shift of the main band of EDOT spectra from 254.9 to 257.7 nm. In addition, an increase of HP-β-CD concentration decreases the  $\epsilon_{\text{max}}$  value from 8010 to 6150  $\text{l mol}^{-1} \text{cm}^{-1}$ . This decrease was previously observed in the case of other organic compounds that can be attributed to the change of the medium dielectric constant caused by the increase of the amount of amphiphile in the aqueous solution [31]. The absorption band at 254.9 nm can be attributed to  $\pi$ - $\pi^*$  electronic transition. This

weak red shift indicates EDOT complex formation with HP-β-CD. In fact, aqueous solutions of 0.01 M EDOT can easily be prepared with 0.1 M HP-β-CD, indicating the formation of an inclusion complex between EDOT and HP-β-CD.

### 3.2. Voltammetric behaviour of EDOT oxidation in aqueous $\text{LiClO}_4$ solutions

Fig. 3 shows the effect of addition of HP-β-CD on the voltammetric behaviour of 0.001 M EDOT in 0.1 M aqueous  $\text{LiClO}_4$  at a platinum WE. An irreversible wave ( $P_1$ ) and an irreversible peak ( $P_2$ ) are observed in a solution free from HP-β-CD (Fig. 3; curve 1) at 0.98 and 1.32 V versus SCE, respectively. This response is same as that reported by Sakmeche et al. [7]. Fig. 3 (curves 2–6) shows the effect of addition of HP-β-CD on the voltammetric behaviour of 0.001 M EDOT in 0.1 M aqueous  $\text{LiClO}_4$  at a platinum WE. Whereas EDOT undergoes oxidation at 1.38 V versus SCE in acetonitrile, its oxidation potential is 1.26 V in water in the presence of a twofold excess of HP-β-CD. This potential shift could be explained by a greater stabilization of the cation-radical in aqueous medium. It should be noted that the interpretation of the CV behaviour of EDOT is central to the understanding of the effect of HP-β-CD on its oxidation. The plots of  $\log I_p$  versus  $\log v$  yield slope values of 0.45 and 0.27 for  $P_1$  and  $P_2$ , respectively (Fig. 4). Earlier, Sakmeche et al. [7] assigned: (i)  $P_1$  to the adsorption of oxidized EDOT species at the platinum electrode; and (ii)  $P_2$  to the oxidation of EDOT species diffusing to the electrode based on the analysis of the  $I_p$ - $v^n$  plots. Unfortunately, these authors did not present the above plots in their publication making it difficult to re-analyze the data,

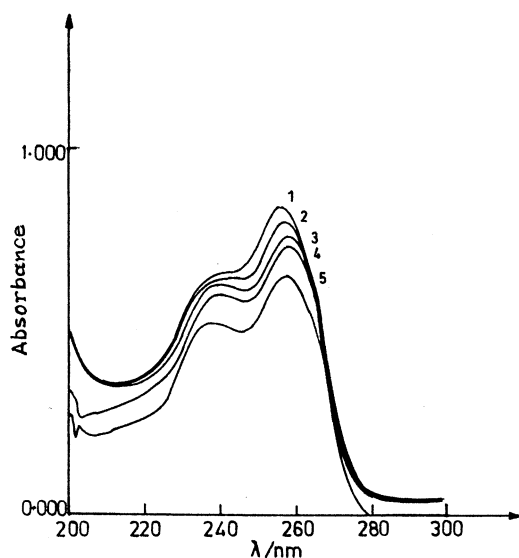


Fig. 2. Effect of HP-β-CD concentration on UV-vis absorption of EDOT ( $1 \times 10^{-4}$  M) in 0.1 M  $\text{LiClO}_4$  aqueous solution containing: (1) 0.0 M; (2) 0.01 M; (3) 0.025 M; (4) 0.2, 0.05 M; and (5) 0.1 M HP-β-CD.

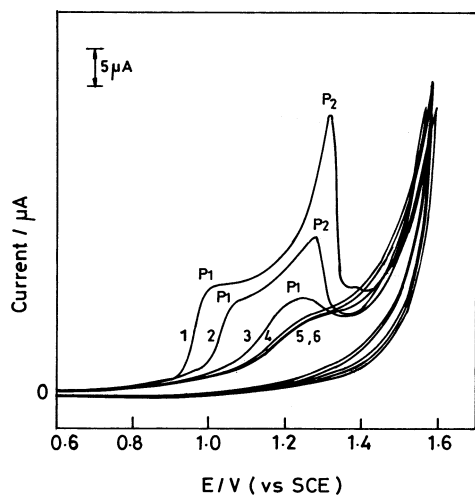


Fig. 3. Cyclic voltammograms of EDOT ( $1 \times 10^{-3}$  M) oxidation obtained on a platinum electrode in aqueous 0.1 M  $\text{LiClO}_4$  solutions containing: (1) 0.0 M; (2) 0.01 M; (3) 0.025 M; (4) 0.05 M; (5) 0.075 M; and (6) 0.1 M HP- $\beta$ -CD; scan rate:  $50 \text{ mV s}^{-1}$ .

in our study are found to be different. A slope value of  $\sim 0.5$  indicates that the process is diffusion controlled, whereas an  $n$  value of 0.27 different from the usual 0.5 or 1.0 indicates otherwise. This is likely for electrode processes that are associated with electrochemical processes involving coupled chemical reactions [32,33] in which adsorption of electroactive species can be one of several steps (Sections 3.2 and 3.3). In addition, with increasing scan rate, the sharpness of peak  $P_2$  (full-width-half-maximum,  $\Delta E_{1/2}$ ) decreases and the peak current ratio ( $I_{p,P_2}/I_{p,P_1}$ ) of  $P_2$  to  $P_1$  decreases from a value of 3.16–1.89 [33]. Hence, from the above analysis, it can be deduced that  $P_2$  is an adsorption peak while  $P_1$  is diffusion-controlled. In the first step ( $P_1$ ), EDOT is oxidized to yield a radical cation, and the oxidized (monomeric or oligomeric) species ( $\text{EDOT}^{*+}$ ) adsorbs in the potential range of  $P_2$ . (All the studies on electropolymerization of thiophenes and pyrroles have hitherto involved the use of non-aqueous media such as acetonitrile, methylene chloride and propylene carbonate. The solubility and/or stabilization of radical cations of dimers or oligomers in these solvents is expected to be high compared to that in aqueous medium, considering the difference in their dielectric constants. Further, their concentration increases with increased applied positive potential.) Hence, it can be expected that this insolubility can lead to their adsorption on the electrode surface (a possible role of HP- $\beta$ -CD in solubilizing and stabilizing the radical cations of dimers or oligomers is discussed in the following). Then, the polymerization process occurs in the adsorbed state [34].

It has now been established [35–38], using the oligomeric approach that the dimerization of the monomers and oligomers involve coupling between the electrogenerated cation radicals (radical–cation coupling) leading to the precipitation of the polymer film at the electrode surface. Studies [37] have revealed that the elimination of protons after the coupling of the radical cations is slow. In this case, a charged  $\sigma$ -complex exists as a short-lived intermediate. In the case of pyrrole or thiophene oligomerization (dimer–tetramer), the deprotonation step is significantly slower than the radical–radical coupling step, indicating that the stability of the  $\sigma$ -dimer increases as a function of chain length. This provides a reason for the neutral or oxidized dimer/oligomer to adsorb on the electrode surface in the second step ( $P_2$ ).

### 3.3. Voltammetric behaviour of EDOT oxidation in aqueous $\text{LiClO}_4 + \text{HP-}\beta\text{-CD}$ solutions

The addition of HP- $\beta$ -CD in increasing concentrations brings about the following changes in the CV behaviour of EDOT oxidation (Fig. 3): (a)  $P_1$  shifts to more positive potential ( $\sim 100 \text{ mV}$ ); while (b)  $P_2$  shifts

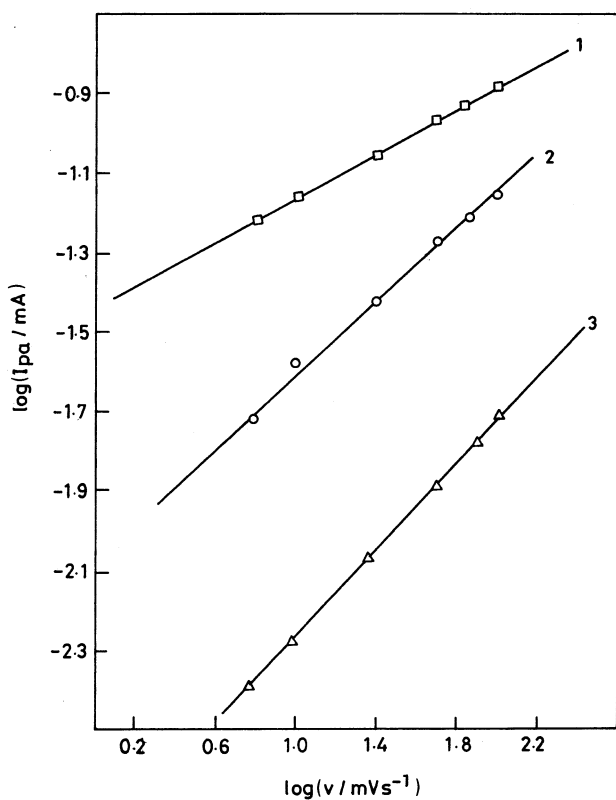


Fig. 4. Scan rate dependence of peak current of  $P_1$ ,  $P_2$  and  $P_{\text{composite}}$ : (1)  $P_2$ ; and (2)  $P_1$  without HP- $\beta$ -CD; and (3)  $P_{\text{composite}}$  in the presence of 0.1 M HP- $\beta$ -CD (voltammetric conditions as in Fig. 3).

although the electrocatalytic effect of SDS on the peaks due to EDOT oxidation is significant. However, our results based on the analysis of the  $I_p - \nu^n$  data are contrary to those of Sakmeche et al. [7] in that the slope values of the  $\log I_p$  versus  $\log \nu$  plots (Fig. 4) obtained

to less positive potentials (by  $\sim 40$  mV) with  $[\text{HP-}\beta\text{-CD}] = 0.01$  M (care was taken to compensate for the solution resistance that may arise due to the addition of HP- $\beta$ -CD). As can be found from Fig. 3,  $P_1$  shifts more rapidly than  $P_2$  resulting in the merger of both  $P_1$  and  $P_2$  to yield an ill-defined composite peak. The resultant composite voltammogram (Fig. 3; curves 5–6) now consists of only one drawn-out peak ( $P_{\text{composite}}$ ) corresponding to  $P_1$ , appearing at a more positive potential (1.29 V) relative to the position of the peak ( $P_1$ ) observed in the absence of HP- $\beta$ -CD. This may indicate that EDOT is more difficult to oxidize when it is bound to HP- $\beta$ -CD (from a thermodynamic point of view), since dissociation of the complex precedes the actual electrochemical process. When the scan rate is varied between 0.1 and 1.0  $\text{V s}^{-1}$ , broadening of the anodic wave is observed with increasing  $[\text{HP-}\beta\text{-CD}]$  (figure not shown) and a plot of  $\log I_{p,P_{\text{composite}}}$  versus  $\log \nu$  yields a slope value of  $\sim 0.5$  showing the process to be diffusion-controlled (Fig. 4; plot 3). Besides, a substantial reduction of the anodic peak current is observed upon the addition of HP- $\beta$ -CD. This is generally observed in this type of host–guest association [39]. The decrease is caused by the fact that much of the EDOT exists as the more slowly diffusing inclusion complex [39,40] since no noticeable increase in the solution viscosity is expected over the range of 0.01–0.1 M  $[\text{HP-}\beta\text{-CD}]$ . A larger decrease in the peak current occurs for the lower  $[\text{HP-}\beta\text{-CD}]$  (up to 0.025 M). With increasing  $[\text{HP-}\beta\text{-CD}]$ , the peak current continues to decrease but tends to approach a limiting value beyond 0.05 M. This means that most of the EDOT molecules are bound to HP- $\beta$ -CD and the peak current tends to be governed by the diffusion of the complex. A likely consequence of the presence of HP- $\beta$ -CD in solution is that the (monomeric or oligomeric) radical cations are stabilized and solubilized at the same time to yield soluble oligomers in solution. These will diffuse to the electrode surface for further oxidation to form finally a polymer

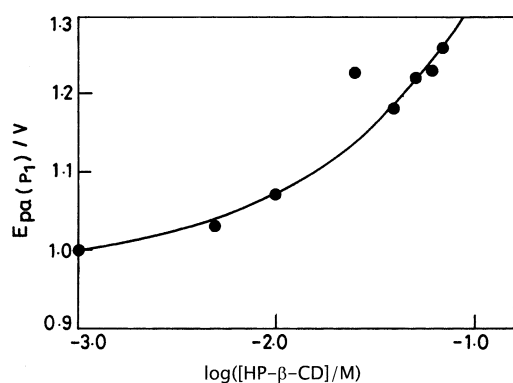
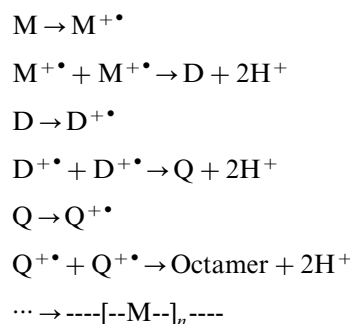


Fig. 5. Plot of positive peak potential ( $P_1$ )\* versus  $\log[\text{HP-}\beta\text{-CD}]$  (\*for details of the behaviour of the peak,  $P_1$ , refer to discussion in Sections 3.2 and 3.3).

film via oligomerization steps. The oligomerization in solution preferably occurs via consecutive ‘dimerization’ steps (involving a number of chemical and electrochemical (ECE) steps) leading from a dimer (D) to a tetramer (Q) and then finally to a polymer. The precipitation of the polymer occurs by coupling of oligomers in solution, according to the following mechanism (monomer,  $M = \text{EDOT}$ ):



In addition, the plot (Fig. 5) of oxidation peak potential versus  $[\text{HP-}\beta\text{-CD}]$  is a curve and can be viewed as consisting of two segments. This may suggest the presence of more than one species undergoing electro-oxidation in the presence of HP- $\beta$ -CD. Incidentally,

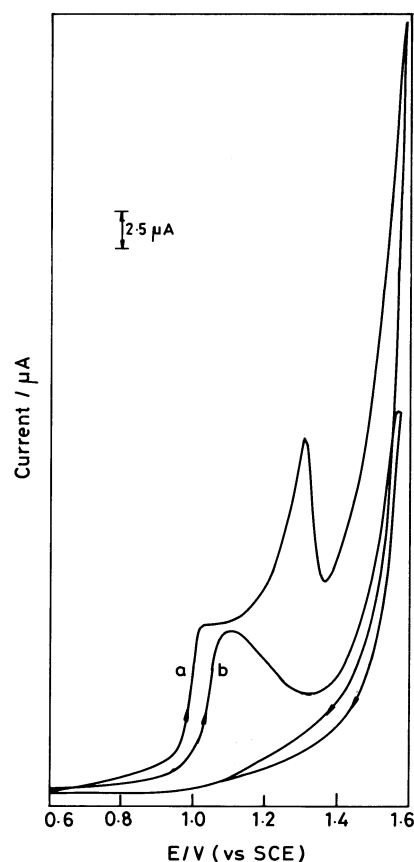


Fig. 6. Cyclic voltammograms of EDOT ( $1 \times 10^{-3}$  M) obtained in aqueous solutions containing 0.1 M  $\text{LiClO}_4$  on a platinum electrode before (a) and after (b) dipping in 0.1 M HP- $\beta$ -CD; scan rate: 50  $\text{V s}^{-1}$ .

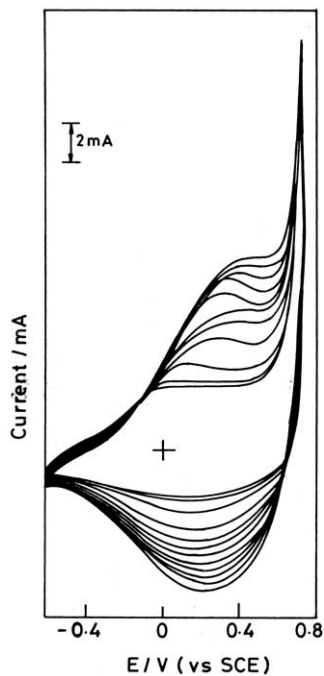


Fig. 7. Cyclic voltammetry (CV) of PEDOT film growth in aqueous solution containing 0.1 M LiClO<sub>4</sub> and 0.01 M EDOT on a platinum electrode; scan rate: 50 mV s<sup>-1</sup>.

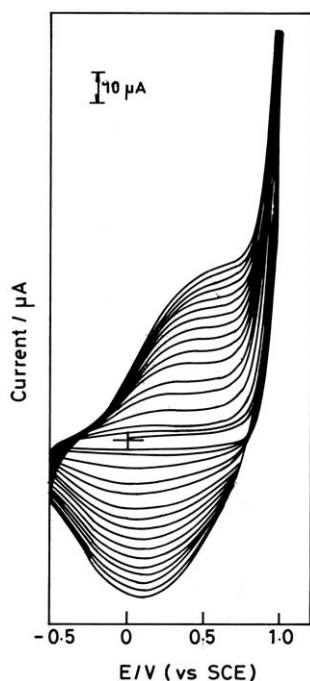


Fig. 8. CV of PEDOT film growth in aqueous solution containing 0.1 M LiClO<sub>4</sub> and 0.026 M EDOT + 0.05 M HP-β-CD on a platinum electrode; scan rate: 50 mV s<sup>-1</sup>.

Lagrost et al. [12] have recently reported an interesting observation of the formation of sexithiophene when bithiophene was electro-oxidized in HP-β-CD solutions. It may be worthwhile examining if such plots are any

indication for the formation of intermediate oligomers. In the light of these observations, we conjecture that using the oligomeric approach [37], it will be interesting to study the possibility of synthesizing individual oligomers of EDOT by a judicious choice of addition agents.

In order to probe the effect of the adsorption of HP-β-CD on the electro-oxidation of EDOT on platinum and to distinguish between the effects in its dissolved and adsorbed states the following experiments were carried out. After keeping the electrode at open circuit in 0.1 M LiClO<sub>4</sub> + 0.1 M HP-β-CD for about 2 h, the electrode was transferred to another cell containing 1 mM EDOT in 0.1 M LiClO<sub>4</sub> aqueous solution and voltammograms recorded at a scan rate of 50 mV s<sup>-1</sup> (Fig. 6). For comparison, another voltammogram for a platinum electrode in 0.1 M LiClO<sub>4</sub> + 1 mM EDOT + 0.025 M HP-β-CD in the same solution (Fig. 3, curve 1) is presented. These two voltammograms are qualitatively identical in their characteristic features such as shift in the oxidation potential of EDOT and suppression of P<sub>1</sub> (Fig. 3; curves 2–6). The adsorption peak (P<sub>2</sub>) is absent in the voltammogram for platinum electrode with pre-adsorbed HP-β-CD. Contact of the electrode with a HP-β-CD solution for an extended period of time is found to cause a shift in the oxidation potential by ~200 mV. This experiment provides conclusive proof for the adsorption of HP-β-CD prior to, or co-adsorption with EDOT electro-oxidation, leading to a catalytic effect as is shown by a reduction in the oxidation potential of P<sub>2</sub>, though the shift is very small (~40 mV) (Fig. 3). Such adsorbed layers of β-CD have been reported to influence the rates of catalytic reactions [14] as in the case of hemi-micelles on the electrode surface [41]. Based on the above observations, we propose a model for the oxidation of EDOT in HP-β-CD solutions in which the latter exists as adsorbed layers on the electrode surface [14–17]. An aqueous solution of HP-β-CD above a critical concentration constitutes a complex mobile-phase modifier. These solutions are microscopically heterogeneous and amphiphilic. Adsorbed layers are stabilized when the concentration increases. It is reasonable to assume that HP-β-CD may behave like the usual surfactants acting as suppressors for arising due to adsorption.

At this juncture, the effect of HP-β-CD on EDOT electrooxidation may be contrasted with that of the surfactant, sodium dodecylsulfate wherein a catalytic effect was observed [7]. In the latter case, an increase in the anodic current and a negative shift in the positive peak potential were observed. In the present work, HP-β-CD does not exert any overall 'catalytic' effect, but there certainly seems to be some interaction of EDOT<sup>•+</sup> with the outer nucleophilic part of HP-β-CD. Our future work will focus on: (a) identifying the possible intermediates during the above processes and

their effect on the polymer characteristics (e.g. thiophenes and pyrroles); and (b) classifying the addition agents as catalytic for electro-oxidation of monomers.

### 3.4. Electropolymerization of EDOT

Cyclic potential sweep voltammetry was carried out between  $-0.5$  and  $1.2$  V versus SCE in solutions of  $0.01$  M EDOT +  $0.1$  M LiClO<sub>4</sub> (Fig. 7) and  $0.026$  M EDOT +  $0.1$  M LiClO<sub>4</sub> +  $0.05$  M HP- $\beta$ -CD (Fig. 8) at a scan rate of  $50$  mV s<sup>-1</sup>. The current starts rising at  $0.078$  V. An increase of anodic and cathodic current values during successive cycles and a rapid growth of anodic current at  $0.78$  V indicate the growth of an electroactive polymer film on the electrode surface. On electrooxidation, a radical cation of EDOT is produced which is transformed to a polymeric species via several follow-up reactions (Sections 3.2 and 3.3).

In a possible model for the electrochemical formation of PEDOT, the EDOT monomer is considered to be

preferentially dissolved into the adsorbed layer of HP- $\beta$ -CD because of the hydrophobic nature of EDOT monomer. In effect, an efficient supply of EDOT monomer for the generation of radical cations must occur during the electropolymerization process. The nucleation [8] of the PEDOT is supposed to start at the defect of the adsorbed layer.

A homogeneous and smooth adherent film is observed under SEM (Fig. 9) whereas the deposit obtained from cyclodextrin-free solutions is found to be powdery. Incidentally, the PEDOT films synthesized from HP- $\beta$ -CD solutions after reduction at  $-0.3$  V (for about 2 h) are found to be dispersible in organic solvents such as DMF, DMSO and THF under sonication. This dispersibility arises possibly due to the association of the reduced polymer with HP- $\beta$ -CD, as in the case of polybithiophene [40]. It is likely that small amounts of HP- $\beta$ -CD may be present in the polymer film. In fact, the presence of HP- $\beta$ -CD was detected by Lagrost et al. [42] in thicker films of polybithiophene in

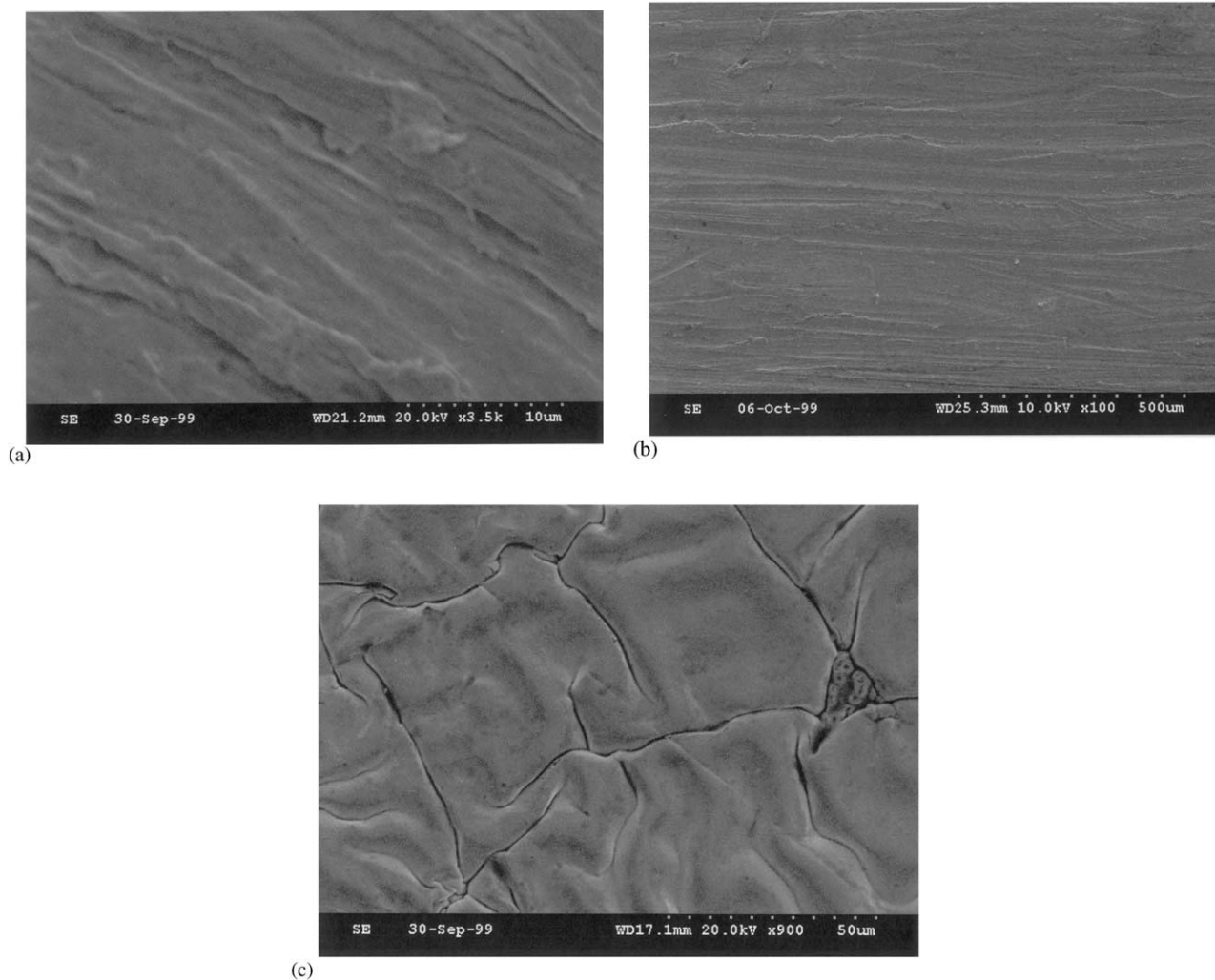


Fig. 9. SEM of PEDOT films deposited by potential cycling from: (a)  $0.1$  M LiClO<sub>4</sub> +  $0.01$  M EDOT; (b)  $0.1$  M LiClO<sub>4</sub> +  $0.026$  M EDOT +  $0.05$  M HP- $\beta$ -CD; and (c)  $0.1$  M LiClO<sub>4</sub> in acetonitrile.

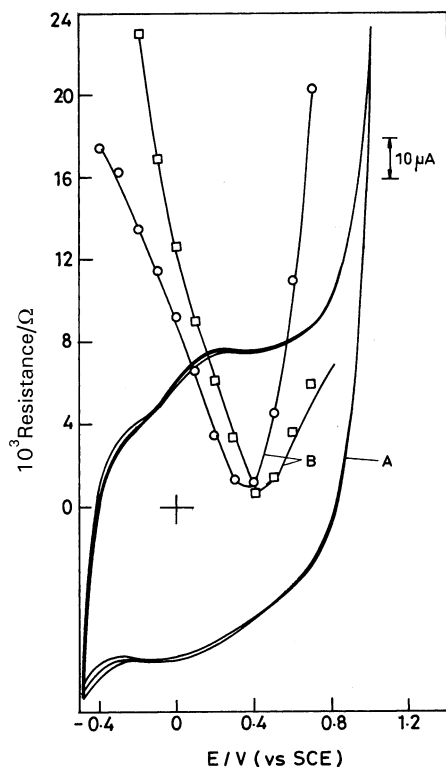


Fig. 10. (A) Cyclic voltammogram of PEDOT film in aqueous solution containing 0.1 M LiClO<sub>4</sub>; scan rate: 25 mV s<sup>-1</sup>. (B) In situ resistance of a PEDOT film as a function of applied potential in aqueous 0.1 M LiClO<sub>4</sub> solution.

which case encapsulation occurs after polymer formation.

### 3.5. Characterization of PEDOT films

The cyclic voltammetric behaviour of PEDOT films deposited on conducting ITO glass substrates from solutions containing 0.026 M EDOT + 0.1 M LiClO<sub>4</sub> + 0.05 M HP-β-CD was studied in a monomer-free aqueous solution containing only 0.1 M LiClO<sub>4</sub> (Fig. 10A) at  $\nu = 25$  mV s<sup>-1</sup>. One broad oxidation peak at ~0.3 V and a reduction peak around -0.05 V versus SCE were observed. The charge consumed in forming the film on ITO was estimated by integration of the anodic part of the voltammogram (Fig. 10A) and was ~50 mC cm<sup>-2</sup>. The electroactivity of the polymer films deposited from solutions containing HP-β-CD is retained even after extensive cycling in a 0.1 M LiClO<sub>4</sub> solution. The change of film resistance with applied potential in the range of -0.4–1.2 V was measured by an in situ method (as described in Section 2) in an aqueous solution of 0.1 M LiClO<sub>4</sub> (Fig. 9b). Minimum resistance was observed in the potential range of 0.3–0.4 V. One can see from Fig. 10B, that even the reduced films possess residual electrical conductivity. The film resistance was found to be very high at -0.4 V in

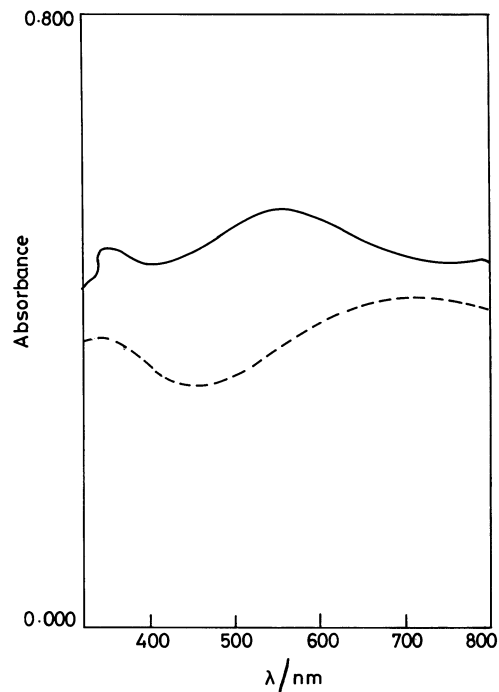


Fig. 11. UV-vis absorption spectra of PEDOT film electrodeposited on an ITO electrode from aqueous 0.1 M LiClO<sub>4</sub> + 0.05 M HP-β-CD solution: oxidized (---) at 0.7 V; reduced (—) at -0.3 V versus SCE.

accord with the behaviour of the reduced films. It is also observed that at potentials positive of 0.8 V, the film resistance increases and this is likely to be due to the instability of the films or over-oxidation of the electro-active polymer film, as is the case with other conducting polymers. The resistance ( $R$ ) of the PEDOT film may be a result of a combination of two factors: (a) the intrinsic nature of the PEDOT polymer; and (b) due to the occlusion of HP-β-CD in the PEDOT film. Further work using a variety of surfactants is needed to assess the effect of occlusion on the resistance of the polymer film.

The film was oxidized at 0.7 V and reduced at -0.3 V for a duration of 1 h in 0.1 M LiClO<sub>4</sub> aqueous solution. The oxidized and reduced PEDOT films were characterized by UV-vis spectroscopy (Fig. 11). The oxidized film shows a weak adsorption in the visible region and strong adsorption maximum in the near-IR region. The reduced film shows a wide band at ~570 nm because of the π-π\* transition. Inhomogeneous doping, a feature common to almost all conjugated polymers after doping is likely to affect the absorption spectrum [24].

## 4. Conclusions

The CV response of EDOT in 0.1 M aqueous LiClO<sub>4</sub> solutions is found to consist of an ill defined diffusion-controlled wave (P<sub>1</sub>) and a clear adsorption peak (P<sub>2</sub>).



Addition of increasing amounts of HP- $\beta$ -CD shifts  $P_1$  positively and  $P_2$  negatively. The peak at [HP- $\beta$ -CD] = 0.05 M is the result of these two opposing effects on the peak potential and appears at a more positive potential relative to the position of  $P_1$  observed in the absence of HP- $\beta$ -CD. The positive shift of the peak and peak current reduction indicate that EDOT (or an oxidized EDOT species) interacts with the outer nucleophilic part of HP- $\beta$ -CD. The plot (Fig. 5) of oxidation peak potential versus [HP- $\beta$ -CD] is a curve and can be seen to consist of two segments. This may suggest that more than one species undergoes electro-oxidation in the presence of HP- $\beta$ -CD. Both dissolved and surface-pre-adsorbed HP- $\beta$ -CD promote solubilization of EDOT and cause the peak potentials to shift. The potential shifts and the reduction in the peak current suggest complex formation between EDOT (or its oxidized species) and HP- $\beta$ -CD. The presence of HP- $\beta$ -CD in solution or as a pre-adsorbed film appears to promote solvation of the radical cations (monomeric or oligomeric), thus reducing the adsorption contribution (Fig. 3). A study on the species that adsorbs in the second step ( $P_2$  in Fig. 3; curve) and its possible participation in the oligomerization/polymerization deserves to be investigated. Our future work will focus on: (a) identifying the possible intermediates during the above processes and their effect on the polymer characteristics (e.g. thiophenes and pyrroles); and (b) classifying the addition agents as catalytic or non-catalytic for electro-oxidation of monomers.

Potentiostatic cycling of the electrode in EDOT solutions results in the formation of adherent homogeneous poly (EDOT) films on the electrode surface. The resistance of the PEDOT film is found to be lowest at its oxidation potential and the film retains a residual conductivity even in the negative potential region.

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## References

- [1] Report of the Committee on Polymer Science and Engineering, Polymer Science and Engineering: Shifting Research Frontiers, National Academy Press, Washington, DC, 1994, pp. 137–178.
- [2] K.L.N. Phani, S. Pitchumani, S. Ravichandran, S. Tamil Selvan, S. Bharathay, *J. Chem. Soc., Chem. Commun.* (1993) 179.
- [3] A. Mani, K.L.N. Phani, *J. Electroanal. Chem.* 513 (2001) 126.
- [4] A. Mani, S. Tamil Selvan, K.L.N. Phani, *J. Solid State Electrochem.* 2 (1998) 242.
- [5] A. Mani, S. Tamil Selvan, K.L.N. Phani, S. Pitchumani, *J. Mater. Sci. Lett.* 17 (1998) 385.
- [6] A. Mani, K. Athinarayanasamy, P. Kamaraj, S. Tamil Selvan, S. Ravichandran, K.L.N. Phani, S. Pitchumani, *J. Mater. Sci. Lett.* 14 (1995) 1594.
- [7] N. Sakmeche, S. Aeiyaeh, J.J. Aaron, M. Jouini, J.C. Lacroix, P.-C. Lacaze, *Langmuir* 15 (1999) 2566.
- [8] K. Naoi, Y. Oura, M. Maeda, S. Nakamura, *J. Electrochem. Soc.* 142 (1995) 417.
- [9] N. Sakmeche, J.J. Aaron, M. Fall, S. Aeiyaeh, M. Jouini, J.C. Lacroix, P.-C. Lacaze, *J. Chem. Soc., Chem. Commun.* (1996) 2723.
- [10] S. Aeiyaeh, E.A. Bazzacui, P.-C. Lacaze, *J. Electroanal. Chem.* 434 (1997) 153.
- [11] D. Gningue-Sall, M. Fall, M.M. Dieng, J.J. Aaron, P.-C. Lacaze, *Phys. Chem. Chem. Phys.* 1 (1999) 1731.
- [12] C. Lagrost, J.C. Lacroix, K.I. Chane-Ching, M. Jouini, S. Aeiyaeh, P.-C. Lacaze, *Adv. Mater.* 11 (1999) 664.
- [13] C. Lagrost, J.C. Lacroix, S. Aeiyaeh, M. Jouini, K.I. Chane-Ching, P.-C. Lacaze, *Chem. Commun.* (1998) 489.
- [14] M.I. Manzanara, V. Solis, R.H. de Rossi, *J. Electroanal. Chem.* 430 (1997) 163 and references therein.
- [15] P.M. Bersier, J. Bersier, B. Klingent, *Electroanalysis* 3 (1991) 443.
- [16] G. Jarzabek, *J. Electroanal. Chem.* 294 (1990) 253.
- [17] M. Goledzinowski, *J. Electroanal. Chem.* 267 (1989) 171.
- [18] Z. Borkowska, *J. Electroanal. Chem.* 246 (1988) 423.
- [19] L.B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, *Adv. Mater.* 12 (2000) 481.
- [20] M. Dietrich, J. Heinze, G. Heywang, G. Jonas, *J. Electroanal. Chem.* 369 (1994) 87.
- [21] G. Li, P.G. Pickup, *Phys. Chem. Chem. Phys.* 2 (2000) 1255.
- [22] V. Tsakova, S. Winkels, J.W. Schultze, *Electrochim. Acta* 46 (2000) 759.
- [23] H. Yamato, K.I. Kai, M. Ohwa, T. Asakura, T. Koshiba, W. Wernet, *Syn. Met.* 83 (1996) 125.
- [24] Q. Pei, G. Zuccarello, M. Ashlskog, O. Inganas, *Polymer* 35 (1994) 1347.
- [25] M. Granstrom, M. Berggren, O. Inganas, *Science* 267 (1995) 1479.
- [26] Baytronics Technical Information (AI-M ASP) Bayer AG 01/97 and 05/97.
- [27] J.C. Lefebvre, Z. Qi, P.G. Pickup, *J. Electrochem. Soc.* 146 (1999) 2054.
- [28] J.C. Carlberg, O. Inganas, *J. Electrochem. Soc.* 144 (1997) 61.
- [29] J. Bobaka, A. Lewenstam, A. Ivaska, *J. Electroanal. Chem.* 489 (2000) 17.
- [30] M. Gholamian, T.N. Suresh Kumar, A.Q. Contractor, *Proc. Ind. Acad. Sci. (Chem. Sci.)* 97 (1986) 457.
- [31] L.G. McIntyre, H.N. Blount, in: K.L. Mittal, E.J. Fendler (Eds.), *Solution Behaviour of Surfactants: Theoretical and Applied Aspects*, vol. 2, Plenum Press, New York, 1982, p. 1101.
- [32] E.R. Brown, R.F. Large, in: A. Weissberger, B.W. Rossiter (Eds.), *Physical Methods of Chemistry, Part IIA*. In: *Electrochemical Methods*, vol. I, Interscience, New York, 1971, pp. 423–530 Chapter VI.
- [33] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., John Wiley, New York, 2001 Chapter 14.
- [34] F. Beck, M. Oberst, R. Jansen, *Electrochim. Acta* 35 (1990) 1841.
- [35] A. Smie, A. Synowczyk, J. Heinze, R. Alle, P. Tschuncky, G. Götz, P. Bäuerle, *J. Electroanal. Chem.* 452 (1998) 87.
- [36] L. Guyard, P. Hapiot, P. Neta, *J. Phys. Chem., Sect. B* 101 (1997) 5698.

- [37] J. Heinze, in: H. Lund, O. Hammerich (Eds.), *Organic Electrochemistry*, 4th ed., Marcel Dekker, Inc, New York, 2000, pp. 1309–1339.
- [38] P. Audebert, J.-M. Catel, G. Le Coustumer, V. Duchenet, P. Hapiot, *J. Phys. Chem., Sect. B* 102 (1998) 8661.
- [39] T. Matsue, D.H. Evans, T. Osa, N. Kobayashi, *J. Am. Chem. Soc.* 107 (1985) 3411.
- [40] C. Lagrost, K.I. Chane Ching, J.C. Lacroix, S. Aeiach, M. Jouini, P.-C. Lacaze, *J. Mater. Chem.* 9 (1999) 2351.
- [41] J.F. Rusling, *Acc. Chem. Res.* 24 (1991) 75.
- [42] C. Lagrost, J. Tanguy, S. Aeiach, J.C. Lacroix, M. Jouini, K.I. Chane-Ching, P.-C. Lacaze, *J. Electroanal. Chem.* 476 (1999) 1.