

Electrocatalysis of Oxidation of 2-Mercaptoethanol, L-Cysteine and Reduced Glutathione by Adsorbed and Electrodeposited Cobalt Tetra Phenoxyppyrole and Tetra Ethoxythiophene Substituted Phthalocyanines

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Abstract

Catalytic activity of cobalt tetra ethoxythiophene and cobalt tetra phenoxyppyrole phthalocyanine complexes towards oxidation of 2-mercaptoethanol, L-cysteine and reduced glutathione is reported. It was found that the activity of the complexes depends on the substitution of the phthalocyanine ring, pH, film thickness and method of electrode modification. The high electrocatalytic activity obtained with adsorbed complexes in alkaline medium clearly demonstrates the necessity of modifying bare carbon electrodes to endow them with the desired behaviour.

1. Introduction

Metallophthalocyanines (MPcs) have been used extensively in wide applications ranging from photodynamic therapy [1] to different types of catalysis, namely biomimetic [2], [3] and [4], photo- [5] and [6] and electrocatalysis [7], [8], [9] and [10]. In the latter case, electrodes are modified with MPcs to afford activation of analytes that require a high overpotential, rendering the desired electrochemical reaction infeasible. Analytes such as thiols and oxygen have been reported to coordinate with the metal centre of the complex [11] resulting in lowering of reaction overpotential. This effect is more pronounced when the metal centre and the analytes have close orbital energies, according to perturbation theory [12].

In general, electrode surface modification by MPcs is needed to enhance the electron transfer reactions. This can be achieved in different ways such as: (i) adsorption by direct deposition of the MPc solution on the electrode [7], (ii) mixing of the MPc with carbon paste making a conductive carbon cement [13], (iii) electrodeposition [14] and (iv) electropolymerisation [15]. During the last decade, there have been several reports on the use of MPc modified electrodes for the oxidation of thiols to disulphides with reduced overpotentials, faster electrochemical reaction rates and increased current densities [16], [17], [18], [19], [20] and [21]. Indeed, such an approach is crucial since thiol oxidation process is of industrial importance as it is involved in oil-sweetening process and food deterioration marking, as well as in biological systems [22], [23] and [24].

It has been reported that the method of electrode modification greatly affects the degree of electrocatalytic activity towards thiol oxidation. Electrodes modified by adsorption of MPcs are unstable and have short lifetimes as MPc films are easily lost from the electrode surface, diminishing activity instantly [16]. They also get passivated rendering further use impossible [17] and [25]. Although MPc adsorption mechanism is based on "simple" π - π interactions between the N_4 macrocycle and the graphite based material, it is not fully understood hence cannot be controlled. This leads to formation of non-flat, irregular and irreproducible films on electrode surfaces hence modified electrodes vary from one to another thus exhibiting different catalytic behaviour. This is also greatly influenced by the general geometrical orientation of the molecule as a whole; flat, planar MPcs are expected to lie flat on the electrode surface forming regular films.

Electrodes modified by electropolymerization have been reported to be more stable than their adsorbed counterparts, probably because the films are more compact. However, it is often difficult to initiate electropolymerisation as it strongly depends on electrode material, polishing and MPc monomer solution [25]. Electrocatalytic activity of electrodes modified by electropolymerized MPcs towards thiol oxidation has been reported to be lower than that of their adsorbed counterparts [16]. Moreover, only outermost layer on the film-solution is reported to be electrochemically active, not the bulk of the film hence film thickness does not dramatically improve electrocatalytic activity [25] and [26].

The search for stable MPc complex based electrode material that affords thiol oxidation at the lowest overpotentials is far from over. It is for this reason that in this work, newly prepared cobalt tetra ethoxythiophene (CoTETHcPc) and cobalt tetra pyrrolephenoxy (CoTPhPyrPc) phthalocyanines (Fig. 1) are used to modify electrodes either by adsorption or electrodeposition of the monomer and the modified electrodes employed in electrocatalytic oxidation of thiols, namely 2-mercaptoethanol (2-ME), reduced glutathione (GSH) and L-cysteine (CYS). These complexes are so chosen based on the fact that the central metal cobalt is known to show better electrocatalytic activity towards thiol oxidation than all transition metals. This is because its orbital energy closely matches that of sulphur, enabling transfer of electron density from the sulphur orbital to the d_{z^2} and d_{xz} orbitals of the metal [27]. Electron donating substituents on the Pc ring are known to enhance oxidation of thiols [9]. Furthermore, the phenoxy-pyrrole substituent is known to polymerize easily while the sulphur-containing ethoxythiophene ligand has potential of forming thin films such as in a self-assembled monolayer configuration. The proposed study is aimed at showing that the above cited cobalt complexes have different catalytic behaviour towards thiol oxidation confirming the fact that substitution of the phthalocyanine ring has an effect which can be easily tuned for further applications.

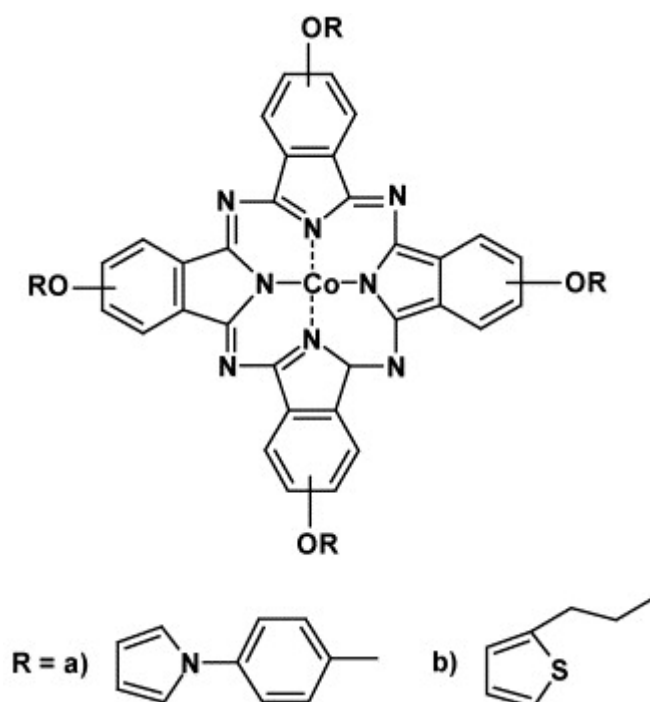


Fig. 1. Structure of (a) cobalt tetra phenoxy-pyrrole phthalocyanine (CoTPhPyrPc) and (b) cobalt tetra ethoxythiophene phthalocyanine (CoTETHcPc).

2. Experimental

Cobalt tetra ethoxythiophene-substituted phthalocyanine (CoTETHcPc) and cobalt tetra phenoxy-pyrrole-substituted phthalocyanine (CoTPhPyrPc) were synthesized and purified according to methods described in the literature [28], [29] and [30]. Tetrahydrofuran (THF), dichloromethane (DCM), ethanol were of HPLC grade; L-cysteine (CYS), 2-mercaptoethanol (2-ME), reduced glutathione (GSH), NaOH, Na_2HPO_4 , NaH_2PO_4 , tetrabutylammonium tetrafluoroborate (TBABF_4) were obtained from Aldrich and used as received.

A vitreous carbon (VC) disk electrode from Radiometer-Tacussel (France) was used as a working electrode for all the electrocatalytic studies of the examined thiols. It was mounted on Teflon and had a geometrical area of 0.071 cm^2 . It was cleaned before each experiment by polishing on 1 and $0.25 \text{ }\mu\text{m}$ diamond pastes, followed by extensive rinsing with ultra-pure Milli-Q water. For the cyclic voltammetry experiments devoted to the

characterization of the solely redox behaviour of the adsorbed catalysts, the working electrode was an ordinary pyrolytic graphite disk (OPG) of 0.44 cm^2 , obtained from Pine Instruments (USA). It was cleaned by polishing on 800 and 1200 grit emery paper and $1 \mu\text{m}$ alumina, followed by rinsing with ultra-pure Milli-Q water. Electrochemical experiments were carried out using the conventional three-electrode cell system and a Princeton Applied Research Inc. potentiostat/galvanostat model 263A (USA). Platinum wire was used as a counter electrode and home-made Ag–AgCl electrode as a reference electrode. The latter was constantly checked against the saturated calomel electrode (SCE), and thus the measured potential values are given versus the SCE. Electrolytic solutions were routinely deoxygenated by bubbling with argon.

Working electrodes were modified with monomers of CoTEThPc and CoTPhPyrPc complexes by placing $10 \mu\text{L}$ of 1 mM solution of the complexes in THF and DCM, respectively, on the electrode surface for 30 min. Excess of unabsorbed complexes were removed with their respective solvents followed by rinsing using ethanol. Electropolymerization of CoTPhPyrPc was achieved by repetitive cycling of the electrode between -0.6 and 1.6 V at 0.2 V s^{-1} in a 1 mM DCM solution of the complex and 0.1 M TBABF₄ as reported before [30]. The growth of the film was observed by monitoring the increase in the charge attributed to the reversible redox couple of the metal centre $\text{Co}^{\text{III/II}}$ located at $\sim 0.85 \text{ V}$ [30]. Electrodeposition of CoTEThPc was achieved in the range 0.2 to 1.6 V at 0.2 V s^{-1} in a 1 mM THF solution of the complex and 0.1 M of TBABF₄ electrolyte and followed through the increase of the signal attributed to the $\text{Co}^{\text{III/II}}$ couple at $\sim 0.90 \text{ V}$ and that at $\sim 1.6 \text{ V}$ due to the oxidation of the thiophene group.

3. Results and discussion

3.1. Electrocatalysis by adsorbed complexes

Adsorption of MPcs was confirmed by recording cyclic voltammograms of modified electrodes in alkaline aqueous solution (0.5 M NaOH). Fig. 2 shows the voltammograms of CoTEThPc and CoTPhPyrPc complexes adsorbed on OPG. In both cases a pair of quasi-reversible peaks which can be related to $\text{Co}^{\text{III/II}}$ redox process was observed at approximately -0.68 and -0.66 V for the CoTEThPc and CoTPhPyrPc, respectively. It should be noted that bare OPG electrode does not exhibit any Faradaic signal in the investigated potential range in alkaline solution [15]. Fig. 3 shows the cyclic voltammograms of CoTEThPc (Fig. 3A) and CoTPhPyrPc (Fig. 3B) adsorbed on VC electrode in presence of thiols, namely 2-ME, CYS and GSH. In all cases, a large oxidation current is observed starting from -0.4 V for 2-ME, -0.3 V for CYS and -0.25 V for GSH, which is related to the electrocatalytic oxidation of the thiols at the modified electrodes. It should be noted that no thiol oxidation was observed at the bare VC electrode within the examined potential range, between -1.30 and 0.20 V . In the particular case of CoTEThPc adsorbed on VC electrode and 2-ME, the appearance of the oxidation peak at -0.3 V is concomitant with that of a reduction peak at -1.1 V , during the reverse scan. According to the previously reported studies on the electrocatalytic oxidation of 2-ME by adsorbed and polymer-based metallophthalocyanines, the large cathodic peak can be attributed to the reduction of the corresponding disulphide [16], [17], [18] and [19]. This result clearly shows that adsorbed CoTEThPc not only acts as a real catalyst towards the oxidation of 2-ME but also acts as a catalyst towards the reduction of the corresponding disulphide. Previously reported studies provided clear evidence that the oxidation of 2-ME is a monoelectronic process, which leads to the formation of 2-hydroxyethylidysulphide [31]. The assignment of the reduction peak to disulphide was clearly reported by studying the electroreduction of 2-hydroxyethylidysulphide (with no 2-ME in solution) at various adsorbed cobalt phthalocyanine modified electrodes [32]. Quantitative analysis can be achieved from the linear variation of measured catalytic current intensity as a function of 2-ME concentration, as shown in Fig. 4.

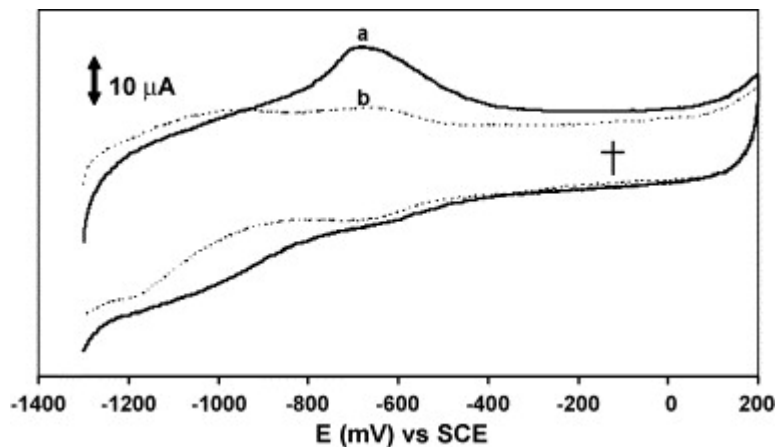


Fig. 2. Cyclic voltammograms of adsorbed CoTPhPyrPc (a) and adsorbed CoTETHc (b) on OPG electrode showing $\text{Co}^{\text{II/I}}$ redox couple in 0.5 M NaOH aqueous solution. Scan rate: 100 mV/s.

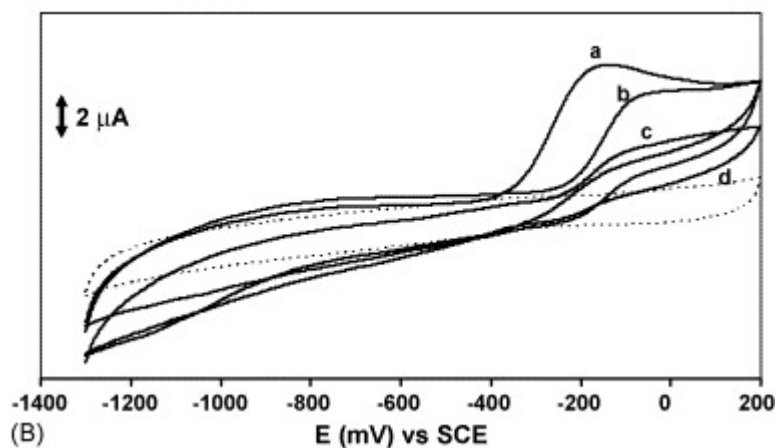
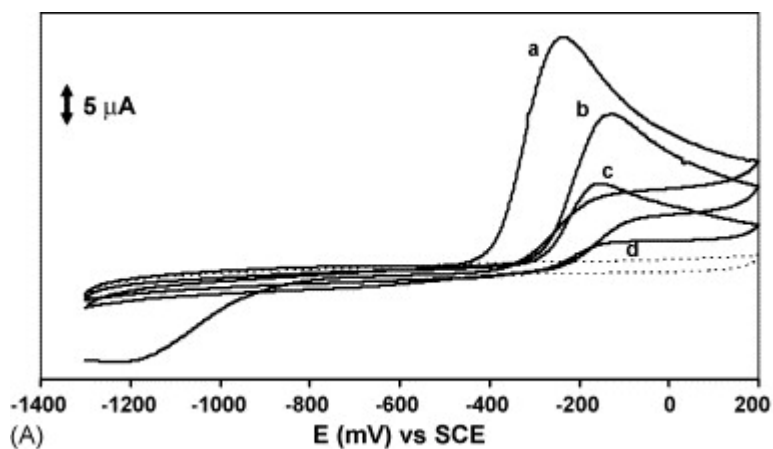


Fig. 3. Cyclic voltammograms of oxidation of 1 mM of (a) 2-ME, (b) CYS and (c) GSH in 0.5 M NaOH aqueous solution catalyzed by adsorbed (A) CoTETHc and (B) CoTPhPyrPc complex on VC electrode. Curves (d) show VC modified electrode in the absence of thiols in 0.5 M NaOH. Scan rate: 100 mV/s.

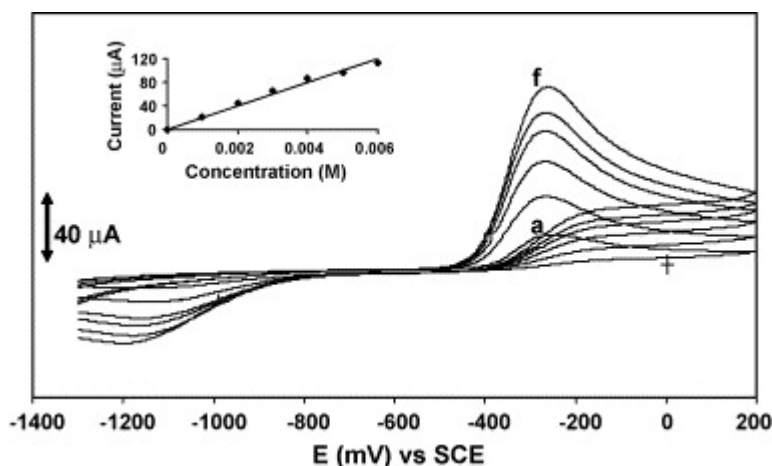


Fig. 4. Cyclic voltammograms of catalytic oxidation of 2-ME by adsorbed CoTETHcPc (on VC electrode) at varying concentrations: a, 1 mM; b, 2 mM; c, 3 mM; d, 4 mM; e, 5 mM; f, 6 mM. Scan rate: 100 mV/s. Inset is a variation of current and concentration.

The electrocatalytic activity of CoTETHcPc and CoTPhPyrPc adsorbed complexes towards thiol oxidation was further examined in terms of both negative shift of the oxidation peak potential E_p and an increase of the oxidation current intensity I_p (Table 1). The measured E_p potentials are -0.22 , -0.11 and -0.14 V, for 2-ME, CYS and GSH at CoTETHcPc-adsorbed electrode, respectively. In the case of adsorbed CoTPhPyrPc, the measured oxidation peak potentials E_p are -0.12 , -0.04 and -0.08 V for 2-ME, CYS and GSH, respectively. For both complexes, the same trend was observed in the case of the oxidation peak current intensity I_p , as it is also shown in Table 1. It is clear that 2-ME is the easily oxidized thiol among the three thiols. It is also noticeable that VC electrodes modified with adsorbed CoTETHcPc complex had better catalytic efficiency than those modified with CoTPhPyrPc, in terms of both current and potential oxidation characteristics. This can be explained by the difference of structures of these two complexes. Indeed, one can imagine that the CoTETHcPc complex lies flat on the electrode, making the metal centre easily accessible to the thiol, while CoTPhPyrPc does not adopt a regular orientation because of ‘twisting’ of the phenoxy substituents bearing the pyrrole groups. It is for the same reason that reproducibility of catalytic activity was unachievable for CoTPhPyrPc modified electrode as the orientation of the complex within the mono layered film is extremely sensitive to modification conditions (electrode polishing, monomer solution, etc.). Finally, the fact that the two above examined complexes show different behaviour clearly indicates that the substitution of the macrocycle plays an important role in favour of tuning the activity of the catalyst.

Table 1.

Catalytic efficiency of adsorbed CoTETHcPc and CoTPhPyrPc in terms of oxidation potential peak E_p and oxidation current peak I_p

Thiol	Catalyst			
	CoTETHcPc		CoTPhPyrPc	
	E_p (mV)	I_p (μ A)	E_p (mV)	I_p (μ A)
2-ME	-220	31	-120	7
CYS	-110	21	-40	5
GSH	-140	12	-80	3

Values obtained from cyclic voltammograms of 2.5 mM thiol in 0.5 M NaOH aqueous solutions. Scan rate: 100 mV/s.

Rotating disk electrodes (RDE) experiments were performed to get further insights into the kinetics of the electron transfer processes occurring at the electrode/solution interface. Typical stationary current–potential curves obtained at different rotation rates are shown in Fig. 5. Typical diffusion plateau-like wave is observed for the catalytic oxidation current. Linear correlations (inserts Fig. 5) indicating

diffusion-controlled mass transport were obtained from plots of I_L versus $\omega^{1/2}$ and I_L versus C where I_L , ω and C represent measured limiting current intensity, electrode rotation rate and thiol concentration, respectively. However, deviations were observed at high thiol concentrations. The order of the reaction is known to be equal to one for the oxidation of 2-ME [12] and of L-cysteine [33] and this was confirmed from slope of one for the plot of $\log I$ versus $\log C$ at constant potential (data not shown). Parallel straight lines were obtained from plots of $1/I$ versus $1/\omega^{1/2}$ (Fig. 6), further confirming the reaction order. The current for the plots in Fig. 6 was obtained from indicated potentials at the rising part of the curves in Fig. 5 for each electrode rotation rate.

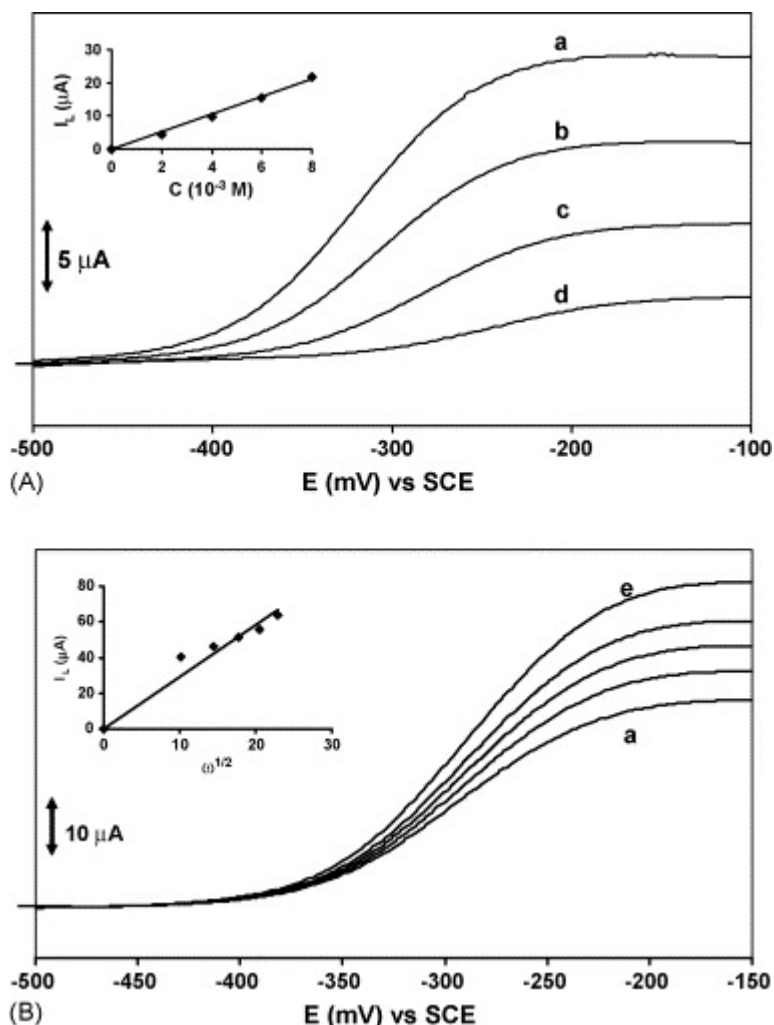


Fig. 5. Rotating disk electrode voltammograms of the catalytic oxidation of 2-ME in 0.5 M NaOH solution catalyzed by adsorbed CoTETHpC at (A) different concentrations of: a, 2 mM; b, 4 mM; c, 6 mM; d, 8 mM at 5000 rpm (inset: variation of limiting current vs. concentration) and (B) different electrode rotation rates of a, 1000 rpm; b, 2000 rpm; c, 3000 rpm; d, 4000 rpm; e, 5000 rpm (2-ME concentration = 2.5 mM). Scan rate: 10 mV/s. Inset: variation of limiting current I_L vs. square root of electrode rotation speed $\omega^{1/2}$.

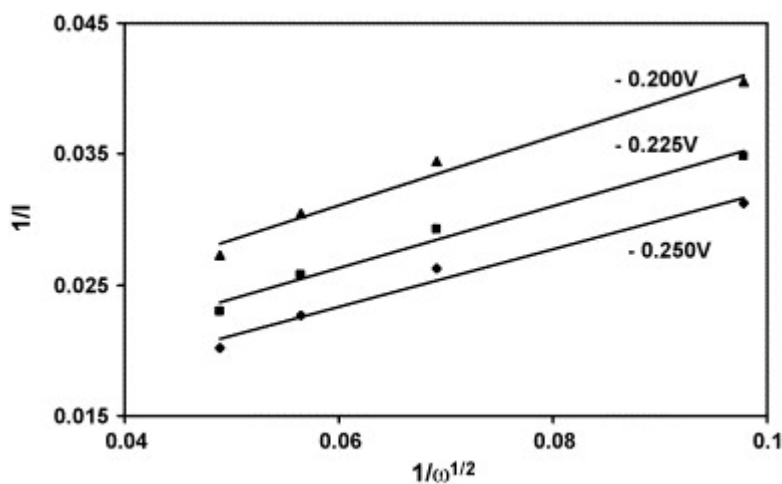


Fig. 6. Plot of $1/I$ vs. $1/\omega^{1/2}$ from RDE data of 2-ME catalytic oxidation at 1000 rpm rotation rate at indicated potential values -0.200 , -0.225 and -0.250 V.

Tafel plots (Fig. 7) were constructed from RDE data with kinetic currents I_k corrected for mass transport versus overpotential ($I_k = (I_L)/(I_L - I)$ where I_L and I are the limiting current and the current at the foot of the wave, respectively). Slopes obtained from these plots were found to be the same for both complexes and for each thiol. They were in the range of 60–79 mV per decade (the slope is equal to $2.3RT/\alpha F$ where α is a transfer coefficient). Slopes from Tafel plots reported in previous work [16], [17], [18], [19], [20] and [21] were close to 120 mV indicating that the transfer of one electron is rate determining (assuming that $\alpha = 0.5$). Thus, Tafel slopes in the range 60–79 mV could indicate that α has high values or that the rate determining step is a chemical step preceded by a fast one electron transfer (in this latter case, the slope would be 59 mV). However, it is more likely that the slow step involves the transfer of one electron according to the following scheme, as found in previous work [18]:



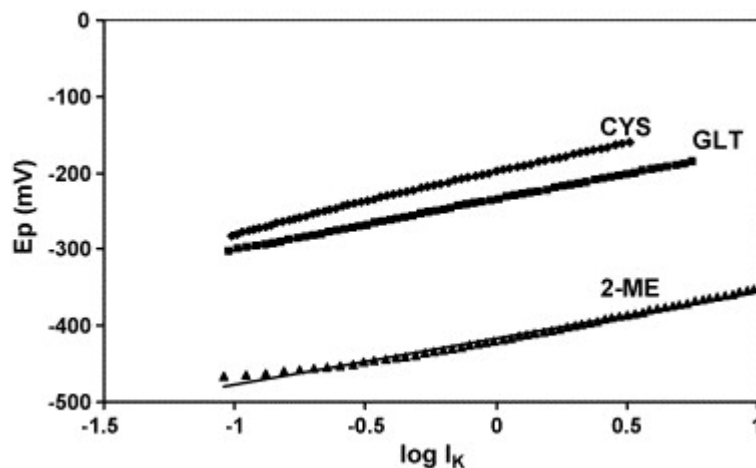


Fig. 7. Tafel plots of thiol oxidation catalyzed by adsorbed CoTETHc.

It is important to note that the differences observed in currents and potentials do not reflect a different mechanism for each complex and/or thiol, but only different catalytic activity (in terms of efficiency).

Electrocatalytic reactions were also performed in phosphate buffer solution at pH 7.2 so as to get information about how well the modified electrodes could behave in physiological conditions since this is one area of application. In the case of the more easily oxidized thiol, 2-ME, it was observed that catalytic activity is decreased at pH 7.2, as shown in Fig. 8 both in terms of potential and current. This is not surprising since the active species that interacts with the adsorbed catalyst is RS^- anion which predominates at pH values higher than the pK_a (which is in the range 9–10 [12] and [33]).

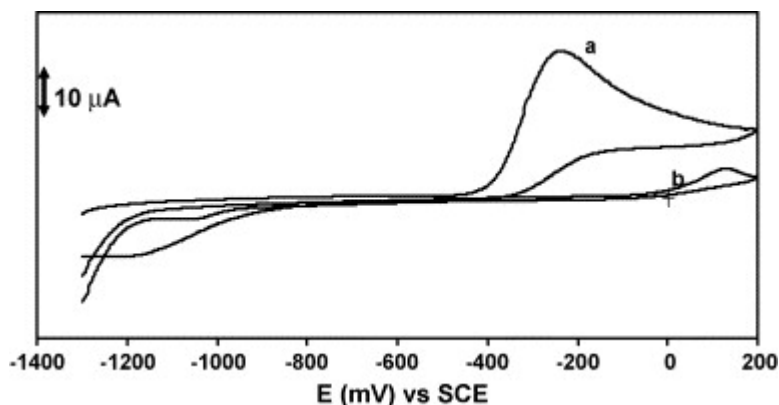


Fig. 8. Cyclic voltammograms of oxidation of 2.5 mM 2-ME in (a) 0.5 M NaOH aqueous solution and (b) phosphate buffer solution (0.1 M; pH 7.2) catalyzed by adsorbed CoTETHc complex. Scan rate: 100 mV/s.

3.2. Electrocatalysis by electrodeposited complexes

Electropolymerization of CoTPhPyrPc and electrodeposition of CoTETHc complexes was achieved as specified in the experimental section. Amount of complex deposited on the electrode was controlled by varying the number of potential scans. Electrodeposition and electropolymerization were confirmed from cyclic voltammograms of modified electrodes which had been rinsed with the appropriate solvents. CoTPhPyrPc complex polymerized very well as it has been previously reported [30]. $Co^{II/I}$ and $Co^{III/II}$ redox couples are located at ca. -0.25 and 0.70 V, respectively while the pyrrole oxidation peak is at ca. 1.1 V. CoTETHc complex was electrodeposited; it did not electropolymerise since electropolymerization of thiophene-based complexes is known to be possible with thiophene groups with no substituents on the 2 and 5 positions of the ring. In addition, the introduction of the Pc ring close to the coupling position may also produce a blocking of the polymerization process and the radicals formed during electrooxidation may be too unstable to participate in further coupling so that no polymers are formed.

Catalytic oxidation of thiols, characterized by cyclic voltammetry, was observed in all cases but the activity was not as high as that of the adsorbed complexes. This is shown in Table 2. Activity was found to be dependent on MPc film thickness deposited on the electrode, assuming that it is directly proportional to number of “electropolymerizing” scans. For both complexes, higher activity was observed with scan number 10, than 20 and 30. This shows that the active site is the outermost film layer not the bulk of the film on the electrode. This is in agreement with previous reports [16] and [25], indicating that catalytic activity does not increase with amount of modifier on the electrode.

Table 2.

Catalytic current intensities of electrodeposited CoTETHpC and electropolymerized CoTPhPyrPc (obtained by 10, 20 and 30 electropolymerizing scans) on VC electrode towards the electrooxidation of 2-ME

Procedure of electrode modification	Catalyst	
	CoTETHpC (μA)	CoTPhPyrPc (μA)
Electrodeposition (10 cyclic scans)	42	10
Electrodeposition (20 cyclic scans)	38	4
Electrodeposition (30 cyclic scans)	37	3

Values obtained from cyclic voltammograms of 2-ME (2.5 mM) in 0.5 M NaOH aqueous solution. Scan rate: 100 mV/s.

In the case of CoTETHpC complex, RDE experiments allow observing linearity from Koutechy–Levich plots (data not shown), indicating diffusion controlled mass transport. For a given number of electrodeposition scans, electrocatalytic activity based on current intensity was found to depend on the anodic limit potential. It was found to be optimum at 1.6 V; it decreased by ca. 40% and 50% at 1.4 and 1.8 V, respectively.

4. Conclusion

Adsorbed CoTETHpC and CoTPhPyrPc complexes showed higher catalytic activity towards oxidation of 2-mercaptoethanol, L-cysteine and reduced glutathione than the electrodeposited/electropolymerized counterparts. Concentration of MPc complex on the electrodes does not increase the catalytic activity which indicates that only the external layers are active and the analyte does not have access to the bulk of the film. The order of thiol activation (in terms of current) was found to be 2-ME > CYS > GSH, for both MPc complexes. Moreover, catalytic activity was found to be pH dependent and it involved interaction of analyte with the metal centre in the complex.

As a final conclusion it can be stated that the present study offers a new range of cobalt substituted phthalocyanine aimed at acting as possible electrocatalysts for the highly demanded oxidation of thiols in aqueous solutions.

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