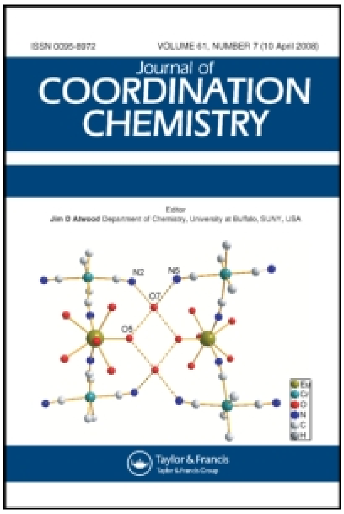

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EVIDENCE OF A STABLE CHARGE-TRANSFER ADDUCT BETWEEN 2-MERCAPTOETHANOL AND COBALT-POLYTETRAAMINOPHTHALOCYANINE

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EVIDENCE OF A STABLE CHARGE-TRANSFER ADDUCT BETWEEN 2-MERCAPTOETHANOL AND COBALT-POLYTETRAAMINOPHTHALOCYANINE

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The electro-oxidation of 2-mercaptoethanol by poly-Co-tetraaminophthalocyanine (p-CoTAPc) and poly-metal-free-tetraaminophthalocyanine (p-H_2TAPc), absorbed on electrode surfaces has been investigated by UV-visible spectroelectrochemistry and electrochemical techniques. In the case of p-CoTAPc, an irreversible oxidation wave is obtained by cyclic voltammetry, whereas p-H_2PcTA practically does not show activity. The foot of the oxidation, as the open circuit potential measurements indicate that the responsible redox couple is Co(II)/Co(I). The p-CoTAPc modified-electrode loses its activity after a first potential cycle. UV-visible spectroelectrochemical measurements show a charge transfer band (metal to ligand) for the p-CoTAPc between Q and Soret bands when negative potentials are applied and Co(I) is obtained. The presence of 2-mercaptoethanol promotes the appearance of the charge transfer band at open circuit potential and retain this band even at potentials as positive as $+0.2$ V where normally the Co center is in $+2$ oxidation state. The permanence of a stable charge transfer band indicates the formation of a stable charge-transfer adduct between Co(I) and the thiol. This adduct would be responsible for the loss of catalytic activity for p-CoTAPc after the first oxidation cycle.

Keywords: 2-Mercaptoethanol; Cobalt phthalocyanine; Charge transfer adduct

Cobalt-phthalocyanine-modified electrodes have been used as electrocatalysts in many redox reactions and the electro-oxidation of thiols has been extensively studied [1–3]. Previous electropolymerization of a complex on

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*Corresponding author. Tel.: 56 2 681 2575, Fax: 56 2 681 2108, e-mail: maguirre@lauca.usach.cl the surface electrode could modify its catalytic characteristics and stability, and even the reaction mechanism by which the catalysis takes place [4, 5]. In this work, the electro-oxidation of 2-mercaptoethanol by poly-Co-tetraaminophthalocyanine (p-CoTAPc) and poly-metal-free-tetraaminophthalocyanine (p-H_2TAPc), adsorbed on electrode surfaces has been investigated by UV-visible spectroelectrochemical and electrochemical techniques.

The electropolymerization of both polymers on glassy carbon or glass/SnO_2:F electrodes was performed by continuously cycling the potential between -0.4 and $+0.9$ V (*vs.* Ag/AgCl) at 100 mV s^{-1}, for 100 cycles. The electrolyte consisted of a 0.1 M tetrabutylammonium perchlorate (TBAP)/DMF deaerated-solution containing 1 mM of the monomer. The resulting polymers are stable in basic solution (pH ≥ 8) and show the profile of Figure 1. Figure 2 shows the square wave voltammograms of p-CoTAPc and p-H_2TAPc/glassy carbon electrodes, at pH 10. Comparisons of voltammograms of Figure 2 with respect to signals observed in Figure 1

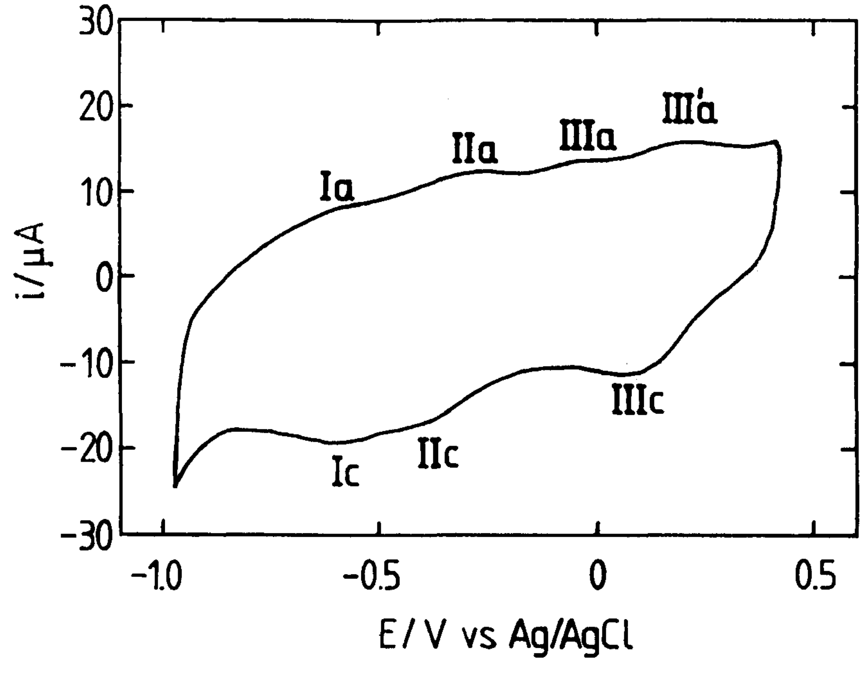

FIGURE 1a Voltammetric response of a 100 cycles p-CoTAPc/glassy carbon electrode in N_2-deareated aqueous solution at pH 10. Electrolyte: $NaHCO_3/Na_2CO_3$ mixed 0.1 M solutions. Scan rate: 0.1 V s^{-1}.

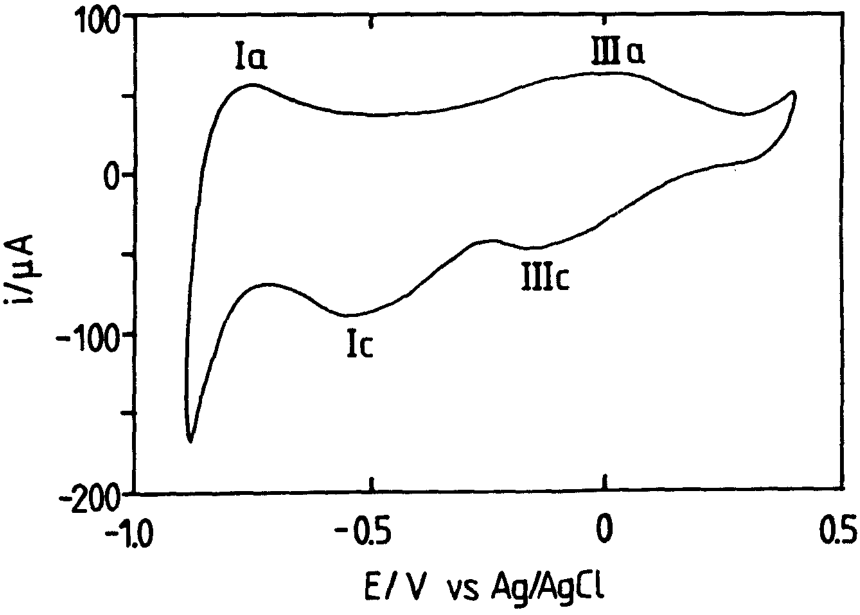

FIGURE 1b Voltammetric response of a 100 cycles p-H_2TAPc/glassy carbon electrode in N_2-deareated aqueous solution at pH 10. Electrolyte: $NaHCO_3/Na_2CO_3$ mixed 0.1 M solutions. Scan rate: 0.1 $V s^{-1}$.

allow us to assign the obtained redox couples. Thus, redox couple IIa/IIc can be assigned to the redox process of the metal Co(II)/Co(I) and Ia/Ic and IIIa/IIIc as processes of the ring [5].

In Table I the potentials of the redox couples and their assignment as metal or ring processes are listed.

Figure 2 shows that the IIa/IIc process would have a component of the ring with predominance of the contribution of the metal in the case of p-CoTAPc. It is based on signals appearing between −0.2 and −0.5 V, where the response of the metal is very noticeable (see Fig. 2a), but also a series of signals of small intensity appear, corresponding to the ligand (see Fig. 2b). On the other hand, the voltammetric response of both polymers grown on SnO_2 : F or glassy carbon electrodes is similar.

Figure 3 shows the voltammograms of both polymers in the presence of 3 mM 2-mercaptoethanol, at pH 10. An irreversible oxidation wave is observed for p-CoTAPc, but practically no catalysis is obtained for p-H_2TAPc. p-CoTAPc catalyses the oxidation of this thiol, although it loses its activity after the first potential cycle. The foot of the oxidation wave is near −0.5 V which could indicate that the redox couple responsible in the

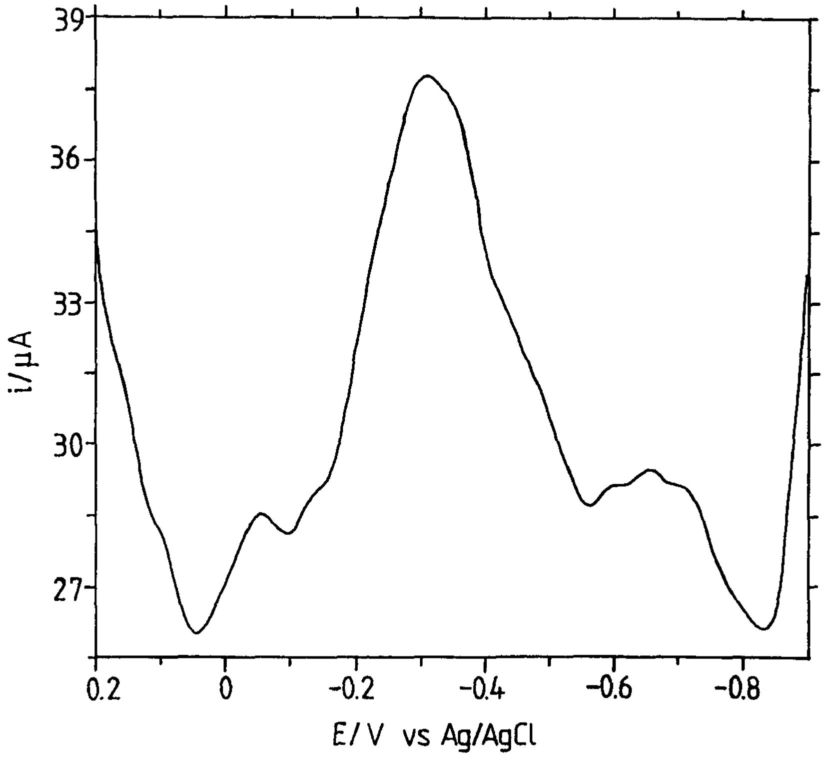

FIGURE 2a Square wave voltammogram of a 100 cycles p-CoTAPc/glassy carbon electrode in N_2-deareated aqueous solution at pH 10. Potential scan: −0.9 up to + 0.2 V *vs.* Ag/AgCl. Potential step: 4 mV. Square wave amplitude: 25 mV. Frequency: 20 Hz. Scan rate: 0.1 V s^{-1}. Electrolyte: $NaHCO_3/Na_2CO_3$ mixed 0.1 M solutions.

catalysis is Co(II)/Co(I). This result agrees with data obtained from open circuit potentials (OCP) listed in Table II. OCP was measured for both polymers/SnO_2 : F electrodes, in deaerated pH 10 solution, with and without 2-mercaptoethanol. OCP drastically changes when 2-mercaptoethanol is present in the solution. The difference in OPC indicates that an electronic transference from the thiol toward the polymers occurs.

However, the transferred electronic density is higher for p-CoTAPc than for p-H_2TAPc. In the case of p-CoTAPc, the charge would be received by the Co (II) which becomes Co (I) because the redox couple Co(II)/Co(I) is near the potential of the OCP measurement in the presence of the thiol. In the case of p-H_2TAPc, the electronic receptor would be a redox couple or couples near −0.4 V (redox signals appearing between −0.2 and −0.5 V). OCP values do not change with the thickness of the films because both

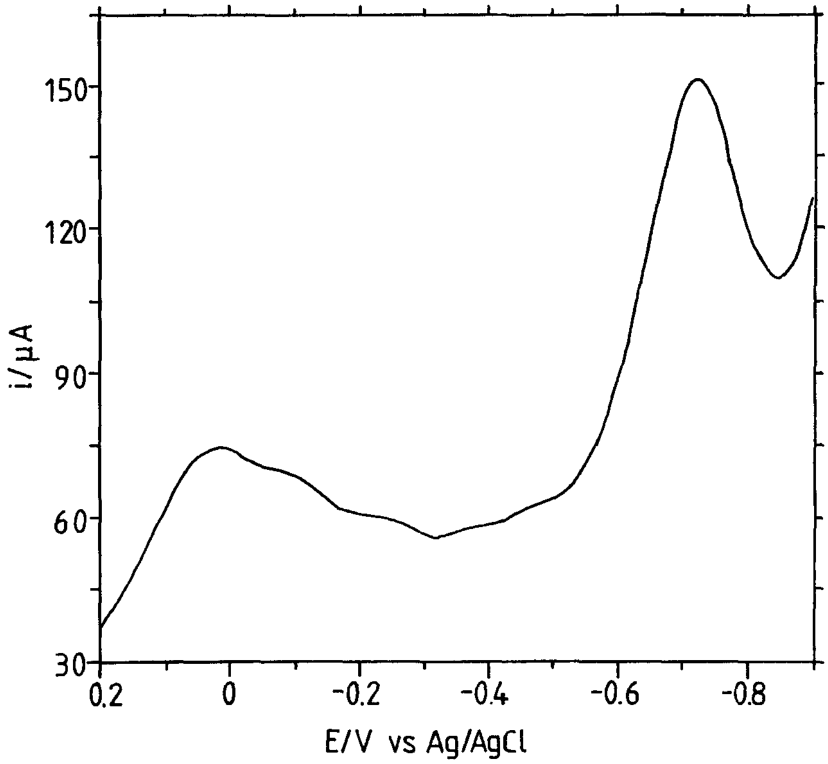

FIGURE 2b Square wave voltammogram of a 100 cycles p-H_2TAPc/glassy carbon electrode in N_2-deareated aqueous solution at pH 10. Potential scan: −0.9 up to +0.2 V *vs.* Ag/AgCl. Potential step: 4 mV. Square wave amplitude: 25 mV. Frequency: 20 Hz. Scan rate: 0.1 V s^{-1}. Electrolyte: $NaHCO_3/Na_2CO_3$ mixed 0.1 M solutions.

TABLE I Assignment of redox couples of p-CoTAPc and p-H_2TAPc at pH 10

	Epa/Epc/V vs. Ag/AgCl	*Assignment*
p-CoTAPc	− 0.7/ − 0.6	Ia/Ic = Ligand
	− 0.3/ − 0.4	IIa/IIc = Co(II)/Co(I)
	− 0.1, + 0.2/+0.1	IIIa/IIIc = Ligand
p-H_2TAPc	− 0.7/ − 0.6	Ia/Ic = Ligand
	0.0/ − 0.1 V	IIIa/IIIc = Ligand

polymers present the same values independent of the number of cycles during the polymerization (from 20 up to 100 cycles).

UV-visible spectra of SnO_2 : F/polymers were recorded under potentiostatic conditions and are shown in Figures 4 and 5. Figure 4 shows the spectrum of p-CoTAPc at OCP and the spectra corresponding to negative

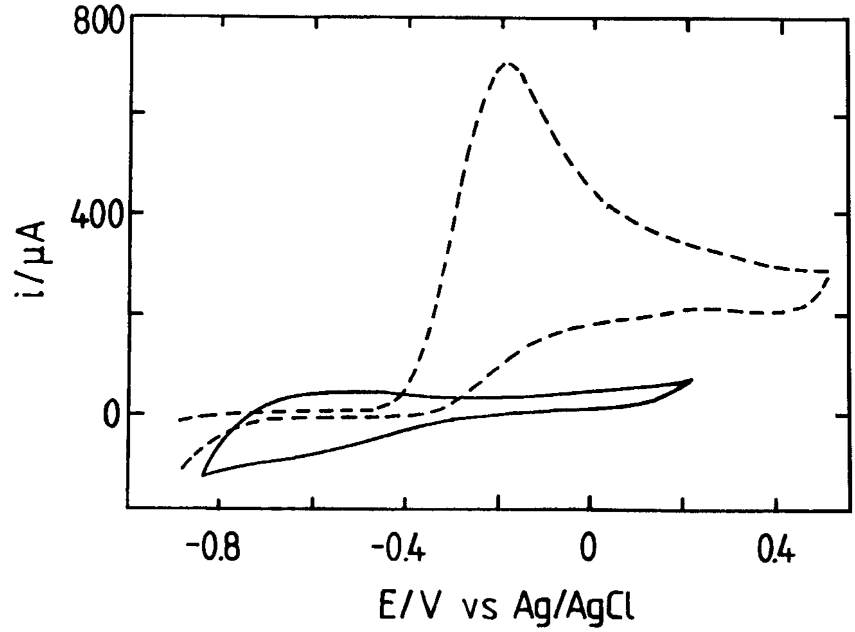

FIGURE 3 Voltammetric first cycle response of both polymers/glassy carbon electrodes in the presence of 3 mM of 2-mercaptoethanol, at pH 10. Scan rate: $0.1\,V s^{-1}$. Dashed line: p-CoTAPc/modified electrode. Continuous line: p-H_2TAPc/modified electrode.

TABLE II Open circuit potentials (V *vs.* Ag/AgCl) for p-CoTAPc and p-H_2TAPc/SnO_2F-electrodes, both with and without 2-mercaptoethanol in the electrolyte (pH 10)

OCP/V, Ag/AgCl	*Without mercaptoethanol*	*With mercaptoethanol*	ΔEC_A, *V*
p-H_2TAPc	−0.130	−0.380	0.250
p-CoTAPc	−0.012	−0.487	0.475

potentials, with respect to OCP. They show the Soret and Q band characteristics [6] for this kind of complex. Both bands are due to $\pi-\pi^*$ ($a_{1u}-e_g$ and $a_{2u}-e_g$) allowed transitions. Figure 4 also shows a charge transfer band, (CTB) with a maximum at 463 nm [7] and two isosbestic points (397 and 454 nm) corresponding to the equilibrium [7, 8]. Co(I)-L $\leftrightarrow$ Co(II)-L^{-1}. This equilibrium is due to negative potentials applied because Co(II) is reduced to Co(I) and Co(I) promotes the metal-ligand CTB. When positive potentials with respect to OCP are applied, the spectrum of p-CoTAPc does not change. Figure 5 shows the p-H_2TAPc spectrum at OCP. The application of positive or negative potentials with respect to OCP does not modify this spectrum. Figure 6 shows, for

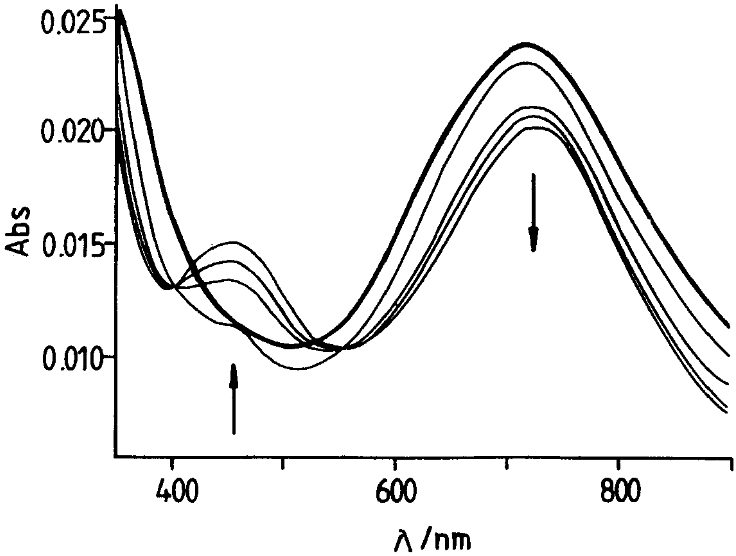

FIGURE 4 UV-visible spectra for the p-CoTAPc/SnO_2 : F electrode in aqueous solution (pH 10) under potentiostatic conditions. The response at OCP is showed with a bold line. Arrows indicate the sense of the change in the spectra when −0.4 V, −0.52 V, −0.56 V and −0.6 V *versus* Ag/AgCl are applied.

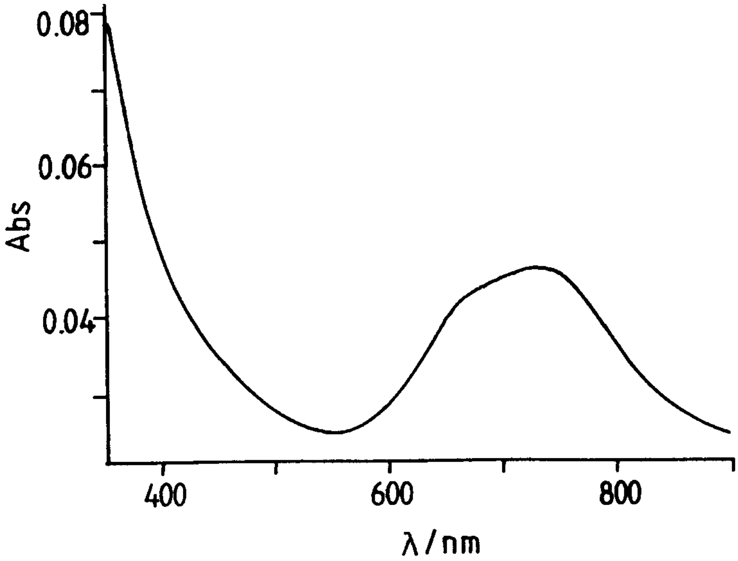

FIGURE 5 UV-visible spectra for the p-H_2TAPc/SnO_2 : F electrode in aqueous solution (pH 10) under potentiostatic conditions. The response at OCP coincides with the response under the application of negative or positive potentials respect to OCP.

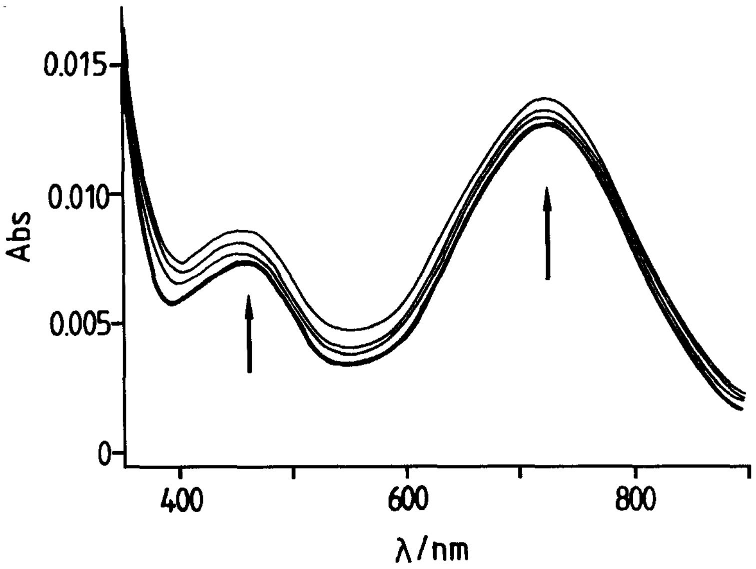

FIGURE 6 UV-visible spectra for the p-CoTAPc/SnO_2 : F electrode in aqueous solution (pH 10) at the presence of 3 mM of 2-mercaptoethanol, under potentiostatic conditions. The response at OCP is showed with a bold line. Arrows indicate the sense of the change in the spectra when −0.52 V, −0.56 V and −0.6 V *versus* Ag/AgCl are applied.

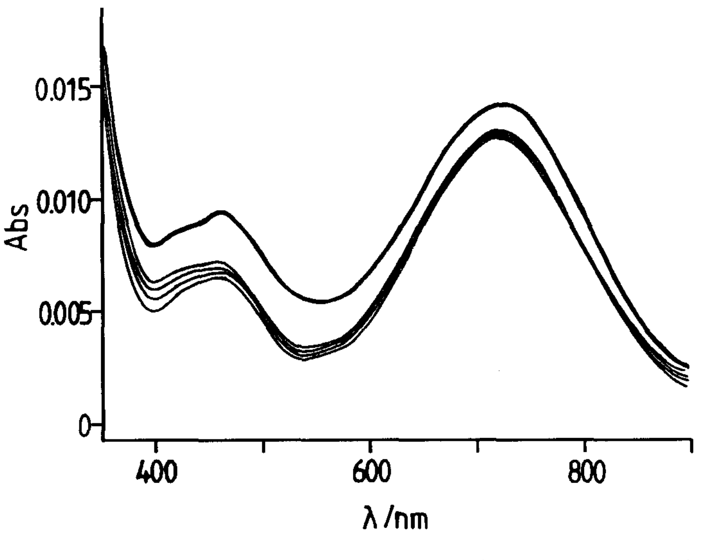

FIGURE 7 UV-visible spectra for the p-CoTAPc/SnO_2 : F electrode in aqueous solution (pH 10) at the presence of 3 mM of 2-mercaptoethanol, under potentiostatic conditions. The response at OCP is showed with a bold line. An almost unique signal is obtained when positive potentials with respect to OCP are applied (−0.36 V, −0.2 V, 0.0 V and +0.2 V *versus* Ag/AgCl) that keeps the charge transfer band.

p-CoTAPc, that the presence of 2-mercaptoethanol promotes the appearance of the CTB at OCP. This fact proves that the electronic receptor is Co(II) which becomes Co(I). In the case of p-H_2TAPc, the thiol does not promote change at OCP, or when positive or negative potentials are applied. The spectrum of p-CoTAPc, when 2-mercaptoethanol is present and negative potentials are applied shows a slightly increase in the intensity of the CTB and a small decrease in the intensity of the Q band (see Fig. 6). When 2-mercaptoethanol is present and positive potentials are applied, the spectra of p-CoTAPc retain the CTB even at potentials as positive as $+0.2$ V where normally the Co center is in the $+2$ oxidation state (see Fig. 7). The permanence of the CTB at positive potentials would indicate the formation of a stable charge-transfer adduct between Co(I) and the thiol. This adduct would be responsible for the loss of catalytic activity of p-CoTAPc after the first oxidation cycle.

Acknowledgements

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