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Volcano correlations for the reactivity of surface-confined cobalt N₄-macrocyclics for the electrocatalytic oxidation of 2-mercaptoacetate

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Abstract We have investigated the electrocatalytic activity of several substituted and unsubstituted cobalt–phthalocyanines of substituted tetraphenyl porphyrins and of vitamin B₁₂, for the electro-oxidation of 2-mercaptoacetate, with the complexes pre-adsorbed on a pyrolytic graphite electrode. Several N₄-macrocyclic were used to have a wide variety of Co(II)/(I) formal potentials. The electrocatalytic activity, measured as current at constant potential, increases with the Co

(II)/(I) redox potential for porphyrins as Co–pentafluorotetraphenylporphyrin < Co–tetrasulfonatotetraphenylporphyrin < Co–2,2',2'',2'''tetra-aminotetraphenylporphyrin and decreases for cobalt phthalocyanines as Co–3,4-octaethylhexyloxyphthalocyanine > Co–octamethoxyphthalocyanine > Co–tetranitrophthalocyanine > Co–tetraaminophthalocyanine > Co–unsubstituted phthalocyanine > Co–tetrasulfonatophthalocyanine > Co–perfluorinated phthalocyanine. Vitamin B₁₂ exhibits the maximum activity. A correlation of log *I* (at constant potential) versus the Co(II)/(I) formal potential of the catalysts gives a volcano curve. This clearly shows that the search for better catalysts for this reaction point to those N₄-macrocyclic complexes with Co(II)/(I) formal potentials close to –0.84 V versus SCE, which correspond to an optimum situation for the interaction of the thiol with the active site.

Dedicated to Prof. Dr. Teresa Iwasita on the occasion of her 65th birthday in recognition of her numerous contributions to interfacial electrochemistry.

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Introduction

Metal complexes of N₄-ligands, such as metallophthalocyanines, are extremely versatile compounds with a great variety of applications [1–5]. When confined or incorporated onto electrode surfaces, they exhibit electrocatalytic activity for a great variety of reactions including the reduction of molecular oxygen, nitrite, nitrate, thionyl chloride, disulfides, and for oxidation reactions such as the electro-oxidation of hydrazine, hydroxylamine, nitrite, nitrogen monoxide, glucose, just to mention a few [2–5]. These complexes are active for the electrochemical oxidation of a great variety of thiols such as 2-mercaptoethanol, 2-aminoethane thiol, L-cysteine, and reduced-glutathione [2–29]. Thus, these metal complexes act

as catalysts by lowering, particularly, the overpotential of oxidation or reduction of the target molecules [2–29]. It is interesting to establish the parameters that determine their electrocatalytic activity to develop more efficient catalysts. Over the years, we have found that the electrocatalytic activity of metallophthalocyanines for the oxidation of some thiols such as 2-mercaptoethanol (2-ME) and 2-aminoethanethiol [18, 19, 22, 25] follows linear correlations with the redox potential (driving force) of the complex, when immobilized on graphite electrodes. It has been found that the activity increases as the $M(II)/(I)$ formal potential of the catalyst becomes more negative. For the reduction of 2-mercaptodisulfide, the activity also increases as the $Co(II)/(I)$ becomes more negative [30]. Similar linear correlations are also observed for the electrochemical reduction of O_2 where the activity increases as the $M(III)/(II)$ formal potential of the catalyst becomes more positive [16, 19]. However, we believe that if a wide-enough potential window using different catalysts is chosen, the complete correlation follows a volcano shape or parabolic curve, as observed for the oxidation of hydrazine [31, 32]. Indeed, for the oxidation of 2-ME, when only five cobalt complexes are used, including porphyrins and phthalocyanines bearing $Co(II)/(I)$ redox potentials in the range of -1.2 to -0.6 V, volcano plots are obtained [24], with Co-tetraaminophenylporphyrin having a $Co(II)/(I)$ formal potential at about -0.9 V versus SCE showing the highest activity.

In this study, we have investigated these correlations employing adsorbed substituted metallotetraphenylporphyrins and metallophthalocyanines with Co as the central metal and substituents on the periphery of the phthalocyanine ligand, using both electron-donor and electron-acceptor groups to achieve a great variety of $Co(II)/(I)$ redox potentials. The complexes were adsorbed on an ordinary pyrolytic graphite (OPG) electrode, and the reaction investigated was the electro-oxidation of 2-mercaptoacetate in alkaline media. Cobalt-tetraphenylporphyrin and substituted derivatives provided $Co(II)/(I)$ redox potentials in the very negative range, where we observed that the activity (as $\log I$ at constant potential) increases as the redox potential become more positive. For a series of substituted cobalt phthalocyanines, with more positive redox potentials, the activity of the catalyst decreases with E° . This illustrates the concept that the redox potential of the catalysts needs to be “tuned” in a potential range for achieving maximum activity. These findings have an impact on the design of metal complex catalysts for applications in electrocatalysis and the development of electrochemical sensors.

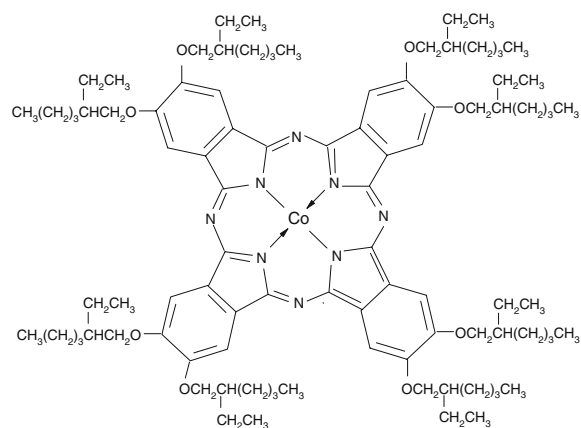
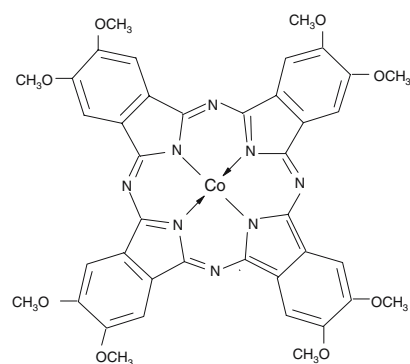
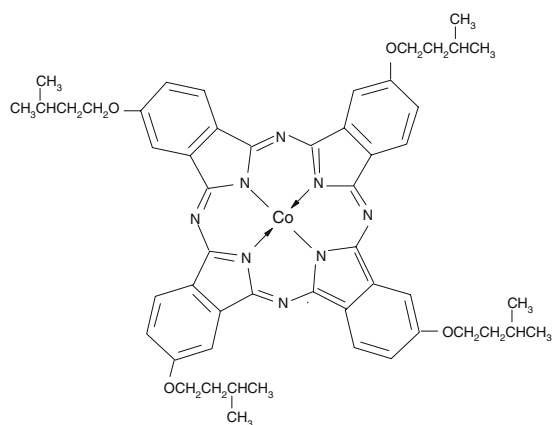
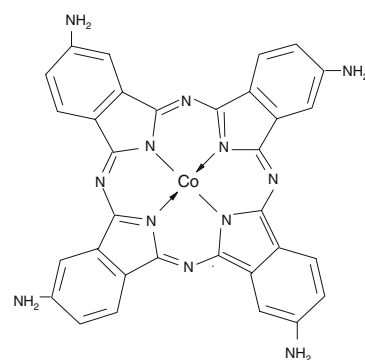
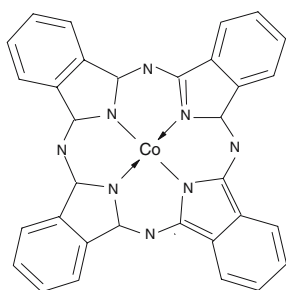
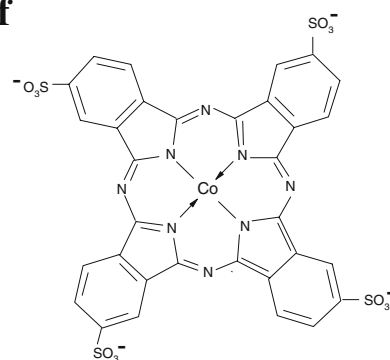
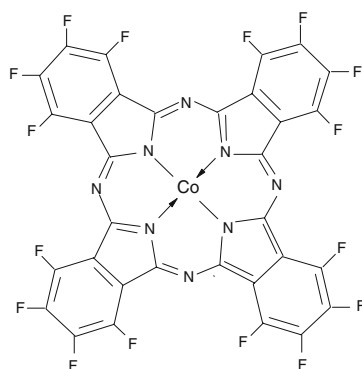
Experimental

Cobalt-2,2',2'',2'''-tetra-aminotetraphenylporphyrin (Co2TAPP), cobalt-tetrasulfonatotetraphenyl-porphyrin (CoTsPP), cobalt-

pentafluorotetraphenylporphyrin (CoF₂₀PP), cobalt-tetraaminophthalocyanine (CoTAPc), and cobalt-tetraneopentoxypthalocyanine (CoTNPPc) were obtained from Mid-Century Chemicals (Posen, IL, USA). Cobalt-phthalocyanine (CoPc) and Cobalt-hexadecafluorophthalocyanine (CoF₁₆Pc) were obtained from Aldrich. Cobalt-octaethylhexyloxyphthalocyanine (CoOEHPc) was synthesized according to the literature [14]. Cobalt-octamethoxyphthalocyanine (CoOMePc) was obtained from Prof. A. A. Tanaka (University of Sao Luis de Maranhao, Brazil). Cobalt-tetrasulfonato phthalocyanine (CoTsPc) was synthesized and purified according to the literature [33]. Vitamin B₁₂, as cyanocobalamine, was obtained from Sigma. Mercaptoacetic acid was obtained from Aldrich and used as provided. The working electrode was OPG disk electrode of 0.44 cm^2 from Pine Instruments, USA, which was modified with different cobalt porphyrins, cobalt phthalocyanines, and with vitamin B₁₂. Modification of the graphite was achieved by the dip-in method using solutions of the complexes in different solvents. Before each experiment, the electrode was polished with 2400 silicon carbide paper and cleaned by ultrasonic treatment in purified water for 2 min. The modification conditions were the following, using 10^{-4} M solutions of the complex: The electrode was dipped in a CoOEHPc solution in dichloromethane for 1 min, CoOMePc in dimethylformamide (DMF) for 150 min, CoTAPc in DMF for 5 min, CoTNPPc in DMF for 1 min, CoTsPc in 0.1 M NaOH in water for 2 min, CoPc in DMF for 1 min, CoF₁₆Pc in ethanol for 1 min, vitamin B₁₂ in water for 20 min, CoTsPP in 0.1 M aqueous NaOH for 1400 min, CoF₂₀PP in DMF for 1400 min, and CoT2APP in acetonitrile for 45 min. Different immersion times were used for the different catalysts to achieve similar coverages because we have found that, for example, porphyrins require much longer immersion times than phthalocyanines.

All measurements were carried out at 25°C in a conventional three-compartment glass cell. A saturated calomel electrode was used as reference and a platinum wire of 5-cm^2 geometrical area as auxiliary electrode. The electrolyte was a 0.1-M NaOH solution saturated with N_2 , and the concentration of 2-mercaptoacetate was 9.2×10^{-4} M. Electrochemical measurements were conducted on a BAS CV 50-W voltammetric analyzer.

Fig. 1 Structures of the cobalt phthalocyanines bearing different substituents: **a** cobalt-octaethylhexyloxyphthalocyanine (CoOEHPc), **b** cobalt-octamethoxyphthalocyanine (CoOMePc), **c** cobalt-tetraneopentoxypthalocyanine (CoTNPPc), **d** cobalt-tetraaminophthalocyanine (CoTAPc), **e** cobalt-phthalocyanine (CoPc), **f** cobalt-tetrasulfonatophthalocyanine (CoTsPc), and **g** cobalt-hexadecafluorophthalocyanine (CoF₁₆Pc)

a**b****c****d****e****f****g**

Results and discussion

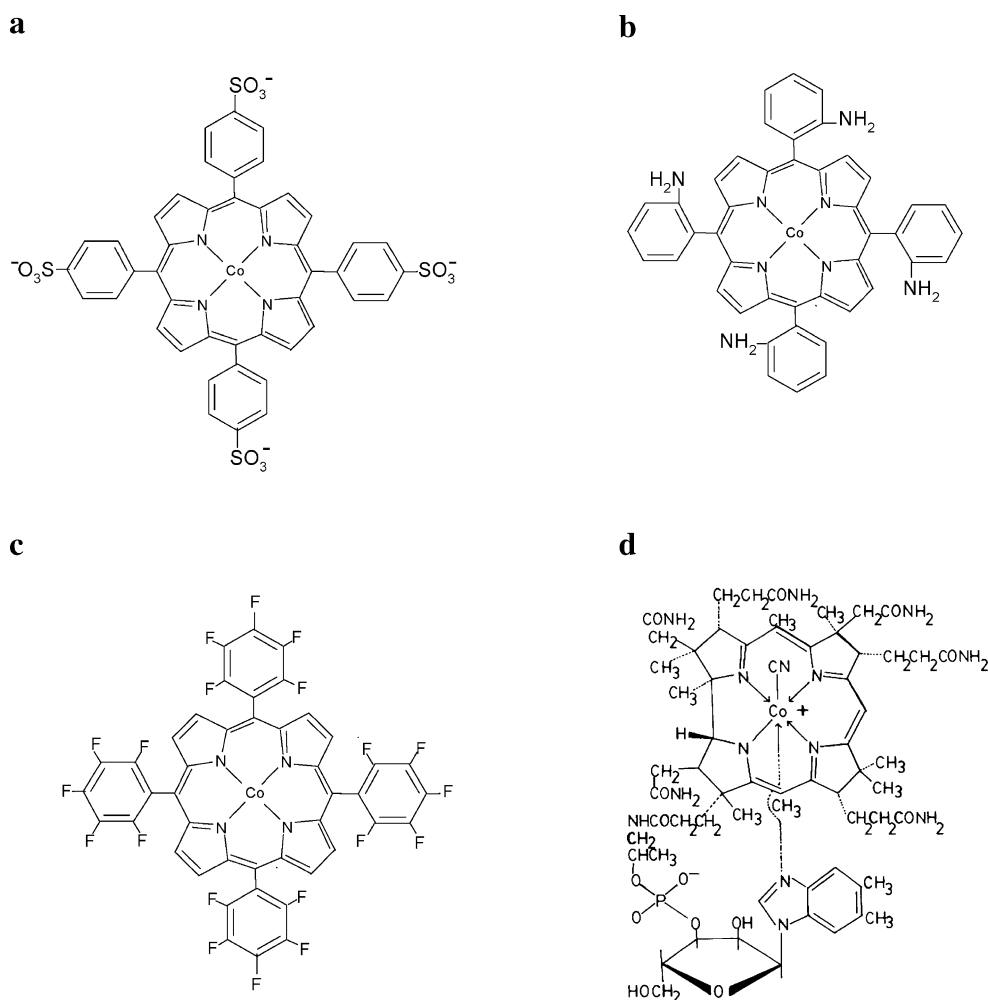
Figure 1 shows the structures of the different cobalt phthalocyanines bearing different substituents on the ligand. Tetra-substituted phthalocyanines can have one group in position 2 or 3 of each of the benzene rings and are almost, invariably, mixtures of isomers randomly distributed [34–36]. Therefore, it can be assumed that the effect of the substituents is correlated to the para-substitution of Hammett parameters, irrespective of its position 2 or 3 in the benzene ring [19, 30, 34–36]. Figure 2 shows the structure of different cobalt tetraphenylporphyrins used in this study. The structure of vitamin B₁₂ is also included.

Figure 3 illustrates the cyclic voltammograms recorded on OPG modified with pre-adsorbed layers of different cobalt phthalocyanines. All complexes exhibit a reversible pair of peaks between −0.8 and 0.0 V that is assigned to the Co(II)/(I) reversible process [16–20]. CoTAPc shows an additional pair of peaks at around −0.3 V that is assigned to the substituted phthalocyanine ring [37, 38]. The formal potential of the Co (II)/(I) redox process shifts to more negative values by the effect of electron donating groups (CoOEHPc, CoMeOPc,

CoTNPPc, and CoTAPc), as these groups increase the electron density on the metal center, making its oxidation more favorable compared to unsubstituted CoPc. The opposite effect is observed for electron withdrawing groups, as the formal potential is clearly shifted to more positive values in comparison to CoPc. In previous work, it has been shown that the effect of substituents can be explained in terms of the Hammett parameters of these groups [17, 19, 30, 34–37]. Plots of Co(II)/(I) redox potential versus the sum of the Hammett parameters give straight lines indicating that any synergistic effects of the groups are minimal. Theoretical calculations conducted on unsubstituted and substituted CoPcs have shown that electron-withdrawing groups stabilize the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the complexes compared to unsubstituted CoPc, and this is reflected in a positive shift of the redox potentials of these chelates compared to CoPc [17, 30]. The opposite is true for electron-donating groups [17, 30].

Vitamin B₁₂ exhibits reversible peaks at ca. −0.8 and at −0.1 V, which have been assigned to the Co(II)/(I) and Co (III)/(II) reversible transitions [3]. All peak currents

Fig. 2 Structures of the studied cobalt porphyrines bearing different substituents: **a** Co-tetrasulfonatotetraphenylporphyrin (CoTsPP), **b** Co-2,2',2'',2'''tetra-aminotetraphenylporphyrin (Co2TAPP), **c** Co-pentafluorotetraphenylporphyrin (CoF₂₀PP), and **d** vitamin B₁₂



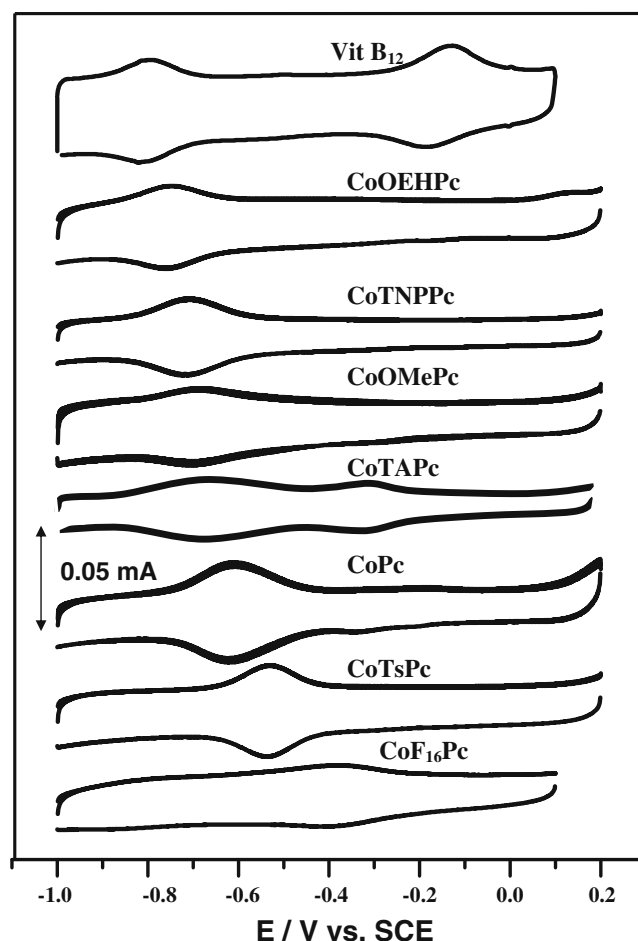


Fig. 3 Cyclic voltammograms of an OPG electrode modified with adsorbed different cobalt phthalocyanines in deaerated 0.1 M NaOH aqueous solution (scan rate, 0.1 V/s)

exhibited by the different complexes vary linearly with the potential scan rate, which is typical of adsorbed species. Peak potentials do not vary with scan rates up to 1 V s^{-1} , indicating that the processes are reversible.

Figure 4 illustrates the cyclic voltammograms recorded on OPG modified with pre-adsorbed layers of different substituted cobalt tetraphenylporphyrins. All complexes exhibit a reversible pair of peaks between -1.2 and -1.1 V that is assigned to the Co(II)/(I) reversible process [21, 39–41]. CoT2APP exhibits a signal at ca. -0.7 V that probably corresponds to a redox process attributed to the amino groups located on the ligand. CoTsPP also exhibits a redox process at ca. 0.05 V that can be assigned to the Co(III)/(II) reversible transition.

It has been shown in previous work for the electro-oxidation of thiols that the thiolate anion is the active species [3, 4, 14–16, 19], and the reaction is first order in OH^- ions. The $\text{p}K_a$ of the $-\text{SH}$ group of mercaptoacetate is 10.07 [42]. To ensure that the thiolate anion was the predominant species, kinetic measurements were conducted in 0.1 M NaOH alkaline solution.

Figure 5 compares polarization curves for the oxidation of 2-mercaptoacetate in 0.1 M NaOH aqueous solution obtained on a rotating graphite disk electrode modified with differently substituted cobalt phthalocyanines. It is clear from this figure that the reactivity of the complexes is sensitive to the type of substituents located on the ligand. The more active complex is CoOEHPc, which has the more electron-donating substituents and exhibits the most negative formal potential for the Co(II)/(I) redox process. On the opposite side, the phthalocyanine with the more electron-withdrawing groups (CoF_{16}Pc) exhibits the lowest activity, as it corresponds to the oxidation wave that appears at the most positive potentials. In all cases, a maximum current is observed, and it varies linearly with the square root of the rotation rate as a diffusional limiting current does. However, some passivation of the electrode is observed at more positive overpotentials as suggested by the decrease of the currents at higher overpotentials. The formation of some intermediate or product of the reaction seems to block the active sites, but they are regenerated during the scan in the reverse direction (not shown). The passivation is more pronounced for CoOEHPc, which exhibits the highest activity. The decrease in activity after the maximum current observed is not the same for all catalysts. It is not clear for the moment why this passivation depends on the nature of the substituents on the phthalocyanine ring. It is possible that each type of phthalocyanine adopts different orientation on the graphite surface, and this

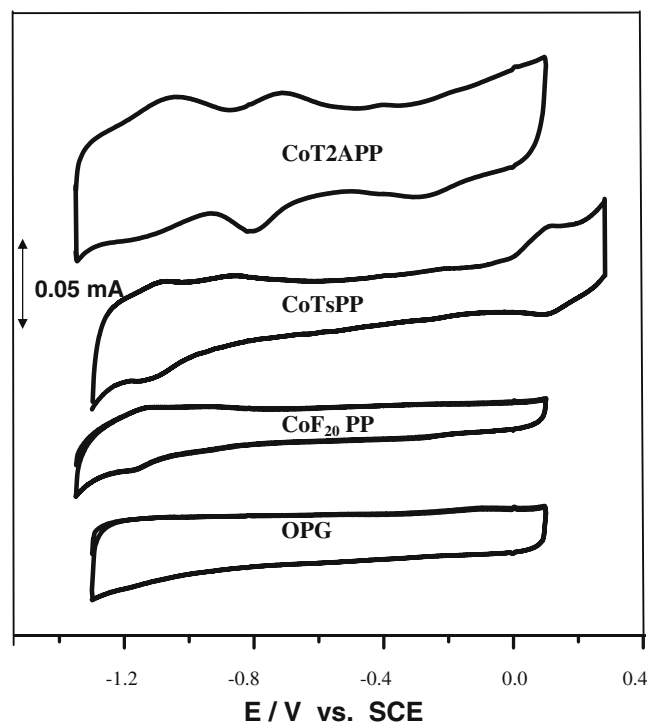


Fig. 4 Cyclic voltammograms of an OPG electrode modified with adsorbed different cobalt porphyrins and vitamin B_{12} in deaerated 0.1 M NaOH aqueous solution (scan rate, 0.1 V/s). Response of bare OPG also shown

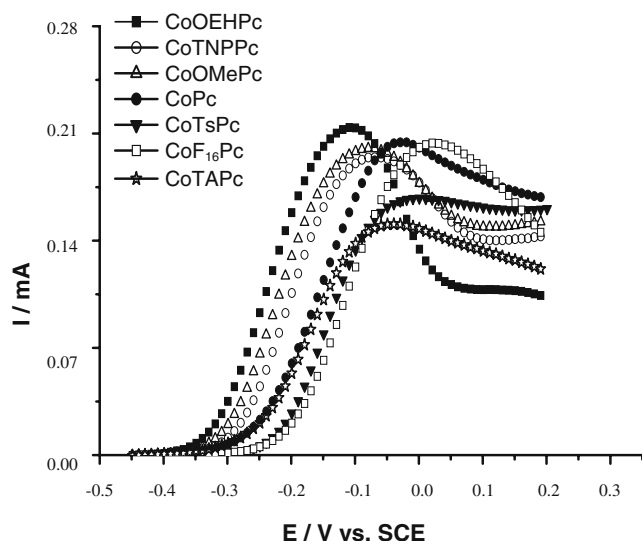


Fig. 5 Rotating disk electrode polarization curves obtained for the electro-oxidation of 2-mercaptoacetate (0.92 mM) in deaerated 0.1 M NaOH aqueous solution on OPG electrode modified with different cobalt phthalocyanines. Rotation rate, 1,600 rpm; scan rate, 0.005 V/s

could affect the passivation phenomena, as we have previously observed in the case of the oxidation of 2-mercaptoethanol on adsorbed tetra-hydroxy and tetra-aminophenyl porphyrin catalysts [24] and for the oxidation of 2-aminoethane thiol [25]. In contrast, electropolymerized layers of Co tetra-aminophthalocyanine do not exhibit this phenomenon [23, 24] and are more suitable for sensor applications.

Figure 6 compares polarization curves for the oxidation of 2-mercaptoacetate in alkaline solution (0.1 M NaOH) obtained on a rotating graphite disk electrode modified with different substituted Co-tetraphenylporphyrins. The activity of the OPG/vitamin B₁₂ electrode is also shown. The most

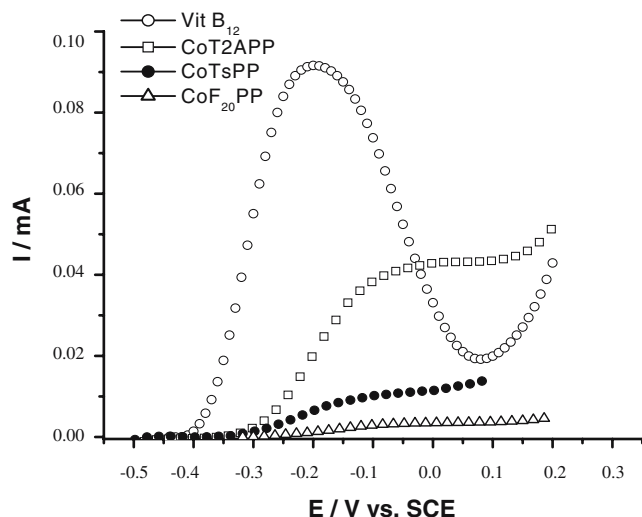


Fig. 6 Rotating disk electrode polarization curves obtained for the electro-oxidation of 2-mercaptoacetate (0.92 mM) in deaerated 0.1 M NaOH aqueous solution on OPG electrode modified with different cobalt porphyrins and with vitamin B₁₂. Rotation rate 1,600 rpm; scan rate 0.005 V/s

active catalyst of this series is vitamin B₁₂, as the foot of the wave starts at the most negative potential (ca. -0.4 V). The typical plateau observed for diffusion-limiting currents generally observed with a rotating disk electrode is not obtained with the OPG/vitamin B₁₂ electrode. The currents exhibit a maximum and a sharp decrease at higher overpotentials, much more pronounced than that observed with phthalocyanines. The maximum current observed is lower than that observed with phthalocyanines, suggesting that the limiting current is not controlled by mass transport. This loss in activity at higher overpotentials could be associated to the oxidation of the Co(II) centers to Co(III) that occurs at potentials more positive than 0.1 V (see Fig. 4). The Co(III) centers are probably inactive for the oxidation of 2-mercaptoacetate. The oxidation waves for the other complexes exhibit current plateaus of different intensities. If these limiting currents were controlled by transport, they should have similar magnitudes, as they should only depend on the concentration of 2-mercaptoacetate, its diffusion coefficient, and the rotating speed of the electrode. Therefore, it is possible that some kinetic limitation is occurring or that the presence of an adsorbed intermediate or product of the reaction blocks the active sites. These limitations are also observed when cobalt phthalocyanines are examined but they are not as pronounced as in the case of cobalt porphyrins.

Figure 7 shows a series of Tafel plots constructed from the data in Fig. 5 for the oxidation of 2-mercaptoacetate catalyzed by cobalt phthalocyanines. The kinetic currents I_k can be calculated using the Koutecky–Levich equation [43] with $I_k = I \times I_L / (I_L - I)$, where I_k is the kinetic current, corrected for mass transport, I is any experimentally measured current below the diffusional plateau and I_L is the diffusion-limiting current for a given rotation rate. This

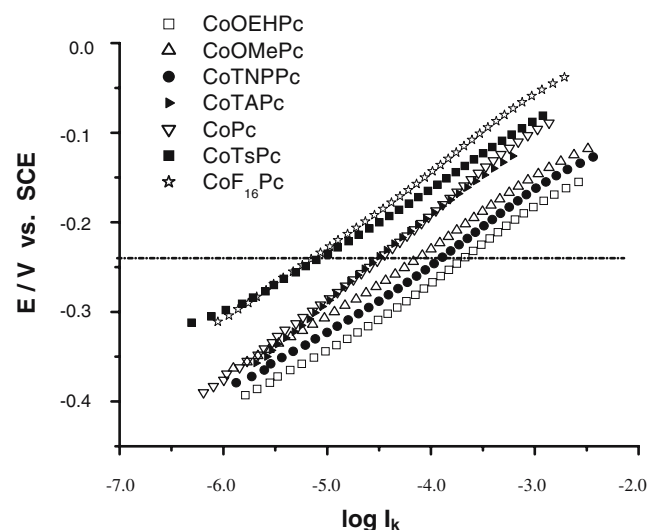


Fig. 7 Tafel plots for the oxidation of 2-mercaptoacetate (data from Fig. 5) on OPG modified with different cobalt phthalocyanines

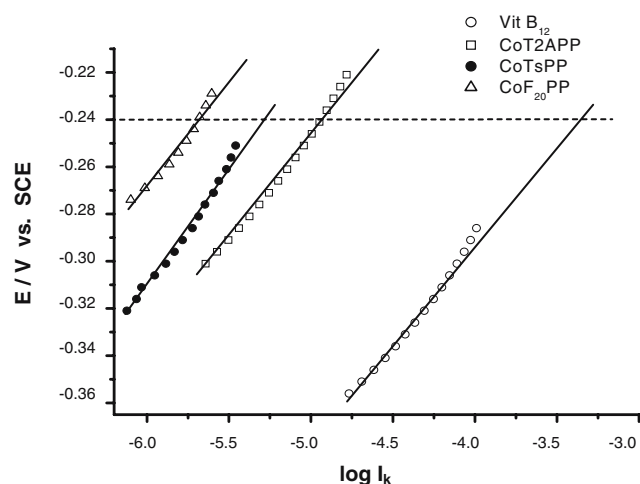
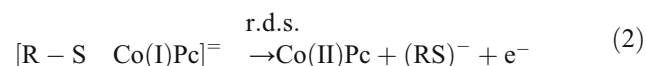
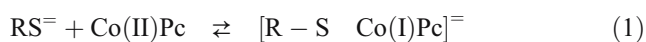


Fig. 8 Tafel plots for the oxidation of 2-mercaptoacetate (data from Fig. 6) on OPG modified with different cobalt porphyrines and modified with vitamin B₁₂

correction can be made on the basis that the reaction is first order in thiol [14]. The Tafel slopes are 0.080 for CoOEHPc, 0.076 for CoTNPC, 0.078 for Co(MeO)₈Pc, 0.095 for CoPc, 0.075 for CoTsPc, and 0.085 V/decade for CoF₁₆Pc. These values are lower than the classical slope of 0.120 V/decade observed before for the electro-oxidation of other thiols like 2-mercaptoethanol and L-cysteine [11–21] catalyzed by metallophthalocyanines.

Figure 8 shows a series of Tafel plots constructed from the data in Fig. 6 for the oxidation of 2-mercaptoacetate catalyzed by Co porphyrines and by vitamin B₁₂. These currents were corrected for mass transport using an average diffusion-limiting current of 0.18 mA observed with most complexes. The correlations are linear, and the slopes are 0.092 V/decade for vitamin B₁₂, 0.094 V/decade for CoT2APP, 0.103 V/decade for CoTsPP, and 0.093 V/decade CoF₂₀PP. Again, as observed for phthalocyanines, the deviation of the slopes from 0.119 V/decade could be attributed to a symmetry factor β higher than 0.5. Therefore, it seems from our results that the nature of the thiol affects the symmetry of the energy barrier, as departure of β from 0.5 is observed for all catalysts (Tafel slopes lower than 0.118 V/decade). Because the rate-determining step for this reaction is the same for all complexes investigated, this can be explained according to the following reaction scheme:



RS[−] is doubly charged, as both the thiol and carboxylic groups are dissociated at pH~13. There is e.p.r. evidence in the literature that an adduct like that formed in step 1 is produced when the thiol L-cysteine interacts with CoTsPc in solution at low temperatures [44]. Therefore, it is likely that a adduct between mercaptoacetate and the adsorbed Co phthalocyanine is formed, as a precursor of the catalytic process.

Figure 9 illustrates the general trend in reactivities for all cobalt complexes examined as a function E° , the Co(II)/(I) formal potential of the catalyst. A volcano curve is obtained with a maximum activity located at $E^\circ = -0.84$ V. In spite of the rather few data points on one side of the volcano, they fit well in the linear correlation on the left side. The volcano curve is of fundamental importance in catalysis and electrocatalysis. It has been established empirically that a volcano-shape curve is obtained when the activity of the catalyst for a given reaction is plotted versus a parameter related to the ability of the catalyst to form chemical bonds with reactants, reaction intermediates, or products [45]. These relations are important from the fundamental point of view, as they provide important information about the reaction, and about the parameters to consider to design better catalysts. In the particular case of electrode materials modified with metal complexes, it is important to first ascertain that two necessary conditions are met:

- (1) Reaction rates must be compared over a series of catalysts under identical conditions.
- (2) The rate-determining step of the reaction must be the same for all catalysts.

Conditions 1 and 2 are met in this work. For all cases, the oxidation of 2-mercaptoacetate leads to the formation of the corresponding disulfide, which is common for the

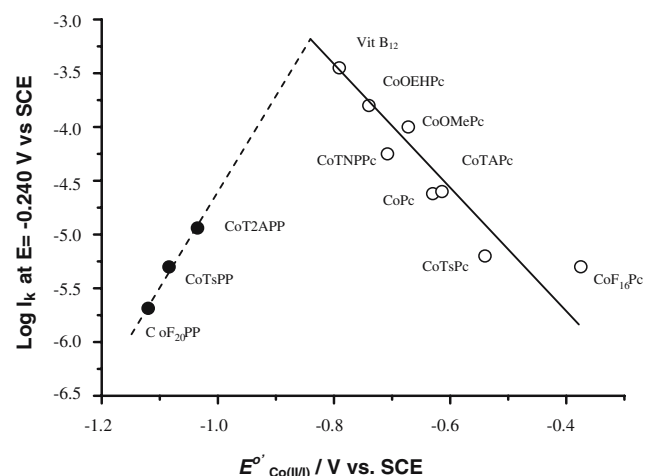


Fig. 9 Volcano plot for the oxidation of 2-mercaptoacetate in 0.1 M NaOH on OPG modified with different cobalt N-4 macrocycles. Data obtained from Tafel plots at $E = -0.250$ V versus SCE

oxidation of many thiols [11–21]. Tafel slopes that are in the range 0.074 to 0.103 V/decade seems to indicate a common rate-determining step as discussed in the reaction scheme of steps 1–3. As discussed above, departure from the classical value of 0.118 V/decade for reactions where the first electron transfer is rate controlling are probably attributed to a symmetry factor greater than 0.5. Tafel slopes close to 0.118 V/decade have been observed for the oxidation of other thiols promoted by several cobalt phthalocyanines [3, 4, 14–16, 18–21, 24, 25], so there is no particular reason for the oxidation of 2-mercaptoacetate not following a similar electron transfer mechanism. In the case of the data in Fig. 9, the redox potential is used because heats of adsorption of thiols on the different cobalt N_4 -macrocycles are not available in the literature. Heats of adsorptions of the molecules on different catalysts or bond strengths between active site and the adsorbed molecule are generally used in volcano plots [45]. However, the Co(II)/(I) formal potential is related to the reactivity of the Co center toward the thiol, as adduct formation $[R-S-Co(I)Pc]^-$ is linked to the Co(II)/(I) redox process and to the thermodynamics of step 1, i.e., ΔG_1^0 . According to the mechanisms proposed, the equilibrium constant of step 1 affects the rate of the reaction in the following way: Step 1 is favored by redox potentials that are gradually more positive, and this will explain the ascending portion of the volcano. This will correspond to a situation where values of ΔG_1^0 are positive, and they become gradually smaller as the coverage of the surface by the adduct θ formed in step 1 increases [45, 46]. Therefore, increasing the Co(II)/(I) redox potential increases the reactivity of the Co centers towards the thiol. However, increasing the Co(II)/(I) redox potential beyond a certain value becomes detrimental, as this will stabilize the adduct ($\theta \rightarrow 1$) as the equilibrium of step 1 becomes shifted to the right. Because step 2 is slow, the adduct would accumulate on the surface when ΔG_1^0 becomes negative. This can explain the declining portion of the volcano plots, that includes most of the catalysts studied because, as $\theta \rightarrow 1$, the surface coverage of Co-free sites (uncovered by the thiol) become gradually zero. The maximum in the volcano plot probably corresponds to a surface coverage of the adduct $\theta=0.5$ and $\Delta G_1^0 = 0$ [44, 45]. Therefore, the data in Fig. 9 clearly shows that the search for better catalysts for this reaction point to those N_4 macrocyclic complexes with Co(II)/(I) formal potentials close to -0.84 V versus SCE, which correspond to an optimum situation for the interaction of the thiol with the active site.

Conclusions

It can be concluded that the $E^{\circ'}$ formal potential of the catalyst is an indication of the reactivity of the central metal toward the thiol molecule. The volcano curve clearly

indicates that intermediate values of $E^{\circ'}$ are optimum for achieving maximum activity, probably corresponding to surface coverages of a Co-thiol adduct equal to 0.5 and to free energies of adsorption of thiol on the Co centers equal to zero. All these results indicate that the catalytic activity of metallo-macrocyclics for the oxidation of mercaptoacetate can be “tuned” by simply manipulating the $E^{\circ'}$ formal potential of the catalyst using the proper groups on the ligand or changing the ligand. This can be applied to many other reactions catalyzed by complexes of this type [24, 31–33, 46].

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