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Статья

Electrochemical Deposition of Aggregated Cobalt Sulfophthalocyanines at Gold Surfaces in Alkaline Solutions

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*In this paper, the method of cyclic voltammetry was used for the first time to study the electrochemical behavior of series of peripheral substituted cobalt phthalocyanines with consistently changing sulfonated fragments (cobalt phthalocyanine tetrasulfonic acid (**CoPcI**), cobalt tetra-4-[(6-sulfo-2-naphthyl)oxy]phthalocyanine (**CoPcII**), cobalt tetra-4-[(6,8-disulfo-2-naphthyl)oxy]phthalocyanine (**CoPcIII**), cobalt tetra-4-[(4-sulfo-1-naphthyl)oxy]-tetra-5-(1-benzotriazolyl)phthalocyanine (**CoPcIV**), cobalt tetra-4-[(1,6-disulfo-2-naphthyl)oxy]-tetra-5-(1-benzotriazolyl)phthalocyanine (**CoPcV**), cobalt tetra-4-[(1,6-disulfo-2-naphthyl)oxy]-tetra-5-(nitro)phthalocyanine (**CoPcVI**), cobalt tetra-4-{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}-tetra-5-(nitro)phthalocyanine (**CoPcVII**), and cobalt octa-4,5-{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}phthalocyanine (**CoPcVIII**)) in an aqueous alkaline solution. Comparative analysis of the electrochemical behavior depending on the functional substitution in the macrocycle molecule was carried out. For all the compounds, central metal ion oxidation ($Co^{2+} \rightarrow Co^{3+}$) and reduction ($Co^{2+} \rightarrow Co^{1+}$) processes, as well as phthalocyanine ring activity were registered. Based on the occurrence of some peaks in the first scan numbers and the appearance/disappearance of other peaks, a hypothesis regarding the mechanism of electrodeposition of cobalt phthalocyanine derivatives at gold electrodes was formulated. It was shown that the electrodeposition process is generally independent on the nature of the substituent in the phthalocyanine macroring. It was also confirmed that reacting species are adsorbed on the electrode surface without specific diffusion.*

Keywords: Cobalt phthalocyanines, redox behavior, electrodeposition, cyclic voltammetry, aggregation.

Электрохимическое осаждение агрегированных сульфофталоцианинов кобальта на поверхности золота в щелочных растворах

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*В настоящей работе методом циклической вольтамперометрии впервые изучено электрохимическое поведение ряда периферически замещенных фталоцианинов кобальта с последовательно изменяющимися сульфированными фрагментами (тетрасульфофталоцианинат кобальта (**CoPcI**), тетра-4-[(6-сульфо-2-нафтил)окси]фталоцианинат кобальта (**CoPcII**), тетра-4-[(6,8-дисульфо-2-нафтил)окси]фталоцианинат кобальта (**CoPcIII**), тетра-4-[(4-сульфо-1-нафтил)окси]-тетра-5-(1-бензотриазолил)фталоцианинат кобальта (**CoPcIV**), тетра-4-[(1,6-дисульфо-2-нафтил)окси]-тетра-5-(1-бензотриазолил)фталоцианинат кобальта (**CoPcV**), тетра-4-[(1,6-дисульфо-2-нафтил)окси]-тетра-5-(нитро)фталоцианинат кобальта (**CoPcVI**), тетра-4-{4-[1-метил-1-(4-сульфофенил)этил]фенокси}-тетра-5-(нитро)фталоцианинат кобальта (**CoPcVII**) и окта-4,5-{4-[1-метил-1-(4-сульфофенил)этил]фенокси}фталоцианинат кобальта (**CoPcVIII**)) в водно-щелочном растворе. Проведен сравнительный анализ электрохимического поведения данных комплексов в зависимости от функционального замещения в молекуле макроцикла. Для всех соединений были зарегистрированы процессы окисления ($Co^{2+} \rightarrow Co^{3+}$) и восстановления ($Co^{2+} \rightarrow Co^{1+}$) центрального иона металла, а также выявлена актив-*

ность фталоцианинового кольца. На основании появления/исчезновения пиков на циклических вольтамперо-граммах была сформулирована гипотеза о механизме электроосаждения изучаемых объектов на золотых электродах. Было установлено, что процесс электроосаждения в целом не зависит от природы заместите-ля во фталоцианиновом макрокольце. Также было подтверждено, что реагирующие частицы адсорбируют-ся на поверхности электрода без специфической диффузии.

Introduction

Supramolecular systems with electrochemically active fragments are considered the basis of the construction of artificial molecular devices and machines, increasing the attention of researchers.[1–3] At present, the chemistry of tetrapyrrole macroheterocyclic compounds is rapidly developing, since functional materials created on the basis of these compounds can successfully implement a set of applied functions.[4,5]

Phthalocyanines (**Pc**) and their metal complexes (**MPc**) occupy a special place among the wide class of macroheterocyclic compounds. Due to the easily adjustable physicochemical properties of molecules, phthalocyanine complexes are used today as dyes and pigments,[6] catalysts for a number of chemical redox reactions,[7-9], active and passive media in quantum electronics,[10,11] photochemical converters of solar energy into electrical energy,[12,13] biologically active substances and medicines,[14] *etc.*

The catalytic activity of **MPc** is primarily due to their ability to additionally coordinate molecular ligands into the fifth and sixth coordination positions of the complexing metal.[15,16] Its electrochemical characteristics are directly related to the extensive delocalization of π-electrons of the **Pc**-rings, the redox activity of the central metals, and the functionality of the environment of the substituents of the molecule.[17–19] Addition of a metal ion into the macrocycle shifts the potentials of both oxidation and reduction towards negative values. The same direction of change in potentials upon metallation is also characteristic of most of the known porphyrin and phthalocyanine systems studied electrochemically,[20,21] in cases where the transfer of an electron to (from) a complex molecule leads to radical ions delocalized in the ligand without significant participation of metal orbitals.

There are a number of scientific papers in the literature on electrochemistry and electrocatalysis involving *d*-metal phthalocyanines.[22-35] However, they are often contradictory and limited in the number of objects of study. The lack of systematic data on the effect of the structural and functional modification of metal phthalocyanine compounds on their electrochemical and electrocatalytic properties creates great difficulties in understanding the kinetics and mechanism of electrochemical processes occurring on the electrodes of chemical current sources, as well as in carrying out a targeted synthesis of complexes with predetermined properties.

The most promising medium for performing liquid-phase processes in view of green chemistry is undoubtedly aqueous solutions. The study of the behaviour of macroheterocyclic complexes in aqueous alkaline solutions is required to solve a number of practical problems to improve existing and create new generation current sources. In our previous works,[36,37] we have briefly summarized the catalytic properties for a number of sulfonated derivatives of cobalt phthalocyanines, which have peripheral substituents regularly varying in structure. Sulfonic acid fragments being part of phthalocyanine macrocycle impart solubility in aqueous and aqueous-alkali media within a broad range of concentrations, that is positive in terms of catalytic application.

In this regard, this work represents a logical continuation of previously begun studies and is devoted to elucidating regularities in the effect of peripheral substituents in sulfonated derivatives of cobalt phthalocyanines (**CoPc**, Scheme 1) on their redox behaviour at a gold electrode in aqueous alkaline solutions. Our choice for these catalysts was based on their well described behaviour in literature, the knowledge in electrodeposition of these compounds on different surfaces and their good water solubility, making it possible to perform electrodeposition in environmentally friendly solutions. These phthalocyanines have been investigated by cyclic voltammetry (CV) to estimate their electron transfer properties and corresponding mechanism.

Experimental

Cobalt phthalocyanine tetrasulfonic acid (**CoPcI**) was synthesized by the known Weber-Busch method.[38,39] In the electron absorption (UV-vis) spectra of an aqueous **CoPcI** solution (pH 7.2), two absorption maxima (λ_{max}) were observed at 625 (dimer) and 665 nm (monomer). Cobalt tetra-4-[(6-sulfo-2-naphthyl)oxy]phthalocyanine (**CoPcII**) was synthesized as described in [40] from the corresponding nitrile. Cobalt tetra-4-[(6,8-disulfo-2-naphthyl)oxy]phthalocyanine (**CoPcIII**) synthesis procedure is described.[41] Cobalt tetra-4-(4-sulfo-1-naphthyl)oxy]-tetra-5-(1-benzotriazolyl)phthalocyanine (**CoPcIV**) was synthesized according to the method [42,43] by sulfonation of the initial phthalocyanine. Cobalt tetra-4-[(1,6-disulfo-2-naphthyl)oxy]-tetra-5-(1-benzotriazolyl) phthalocyanine (**CoPcV**), cobalt tetra-4-[(1,6-disulfo-2-naphthyl)oxy]-tetra-5-(nitro)phthalocyanine (**CoPcVI**), cobalt tetra-4-{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}-tetra-5-(nitro) phthalocyanine (**CoPcVII**), and cobalt octa-4,5-{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}phthalocyanine (**CoPcVIII**) were synthesized by the same method as for **CoPcIV**.[42,43] The full characterization was performed for all the synthetized compounds and described.[40]

Tetrabutylammonium perchlorate (TBAP, Aldrich) with a concentration of 0.1 M was used as a supporting electrolyte. The buffer solution of pH 12 (Na$_2$HPO$_4$/NaOH) was prepared from disodium hydrogen phosphate dihydrate and sodium hydroxide purchased from Merck. All the purchased chemicals were of analytical grade and were used without further purification. A double distilled water was used for making solutions.

Cyclic voltammograms were recorded using an Ecotest-VA potentiostat (EKONIKS-EXPERT, Russia) at 25.00 ±0.01 °C. Data were recorded using a personal computer with preliminary signal processing on an interface device. A thermostatically controlled three-electrode cell was used in the work. A silver-silver chloride electrode (3.5 M KCl) was used as the reference electrode. In the text and graphs, the potentials are given relative to this electrode. A platinum wire served as an auxiliary electrode. A gold electrode was used as a working electrode. The geometrical surface of gold electrode was 0.258 cm^2.

In order to activate the working electrode surface in a reproducible and repeatable way, it was pretreated by mechanical and electrochemical polishing as it was recommended.[44] Firstly, the electrode surface was scoured briefly on 1200-grit SiC-emery paper to obtain a fresh surface. To smooth this relatively rough surface, it was further subjected to sequential polishing on a polishing cloth covered with alumina (Buehler) powder of 1, 0.3 and 0.05 μm particle size for 5, 10 and 20 min respectively. To remove any adherent Al$_2$O$_3$ particles, the electrode surface was rinsed thoroughly with water and cleaned in an ultrasonic bath for 2 min. Finally, the electrode was pretreated electrochemically by scanning it in a Na$_2$HPO$_4$/NaOH buffer solution (pH 12) between -1.2 and 0.6 V (vs. Ag/AgCl) until five subsequent scans were identical. This pretreatment was done to smooth the gold surface and the remove any oxides.

During the modification procedure ("potential cycling method"), a gold electrode was modified with **CoPc** by recording successive cyclic voltammetric scans (100 scans) in a potential window from -1.2 to 0.6 V (vs. Ag/AgCl) in a pH 12 buffer solution containing ~ 10^{-3} mol/L of **MPc**. The scan rate for all CV experiments was 100 mV/s. Before each experiment, pure argon (99.99%) was bubbled through the cell solution for 10 min. Potentials of the cathodic (E_c) and anodic (E_a) peaks of the electrode processes with the participation of the studied compounds were determined up to an accuracy of ±0.01 V.
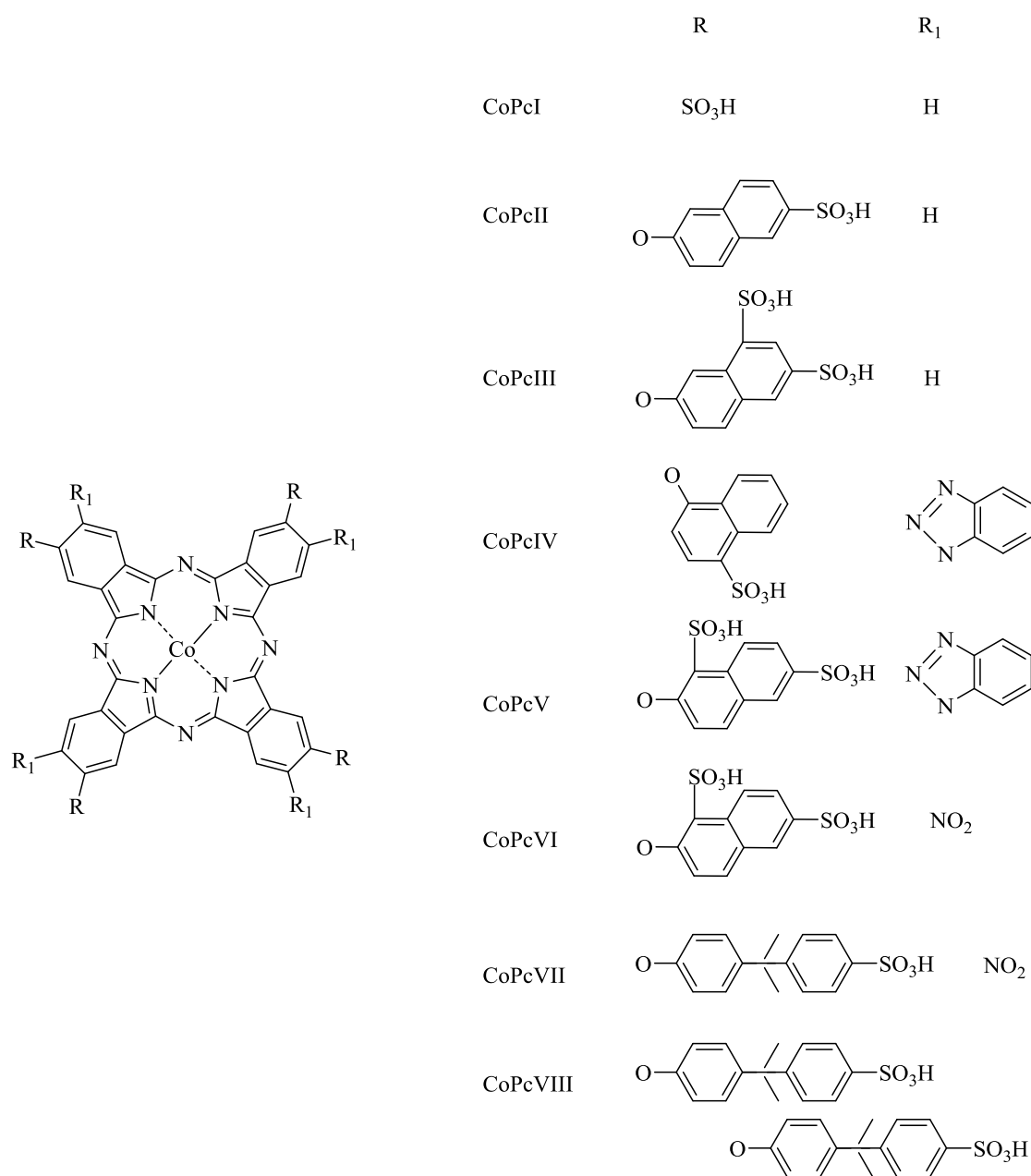

**Scheme 1.** Molecular model of CoPc complexes.

Results and Discussion

The data in Figure 1 show 100 cyclic voltammetric scans recorded at a gold electrode in a p*H* 12 buffer solution (curve 1) and a solution containing 10^{-3} mol/L of **CoPcI** (curves 2-7). In the first scan (curve 1) a well-defined oxidation wave I_a at 0.39 V (*vs.* Ag/AgCl) and a reduction peak I_c at 0.087 V (*vs.* Ag/AgCl) can be observed, attributed to the oxidation of the gold surface and reduction of the gold oxide formed during surface oxidation.[45] The curves 2-7 in Figure 1 show the growth of the Co^{2+}/Co^{1+} and Co^{2+}/Co^{3+} redox couples during the voltammetric scans, which implies that some of the **CoPcI** is adsorbed onto the gold surface. The intensity of these peaks increased gradually with scanning of the electrode in the buffer containing complex until a stable curve was obtained (curve 7 in Figure 1). The peaks at -0.36 V (II_c) and 0.29 V (II_a) (vs. Ag/AgCl) reflect the reduction/oxidation behavior of adsorbed **CoPcI**. Another peak attributed to a ring reaction of adsorbed CoPcI appears at -0.79 V (vs. Ag/AgCl) and is indicated by III in Figure 1.
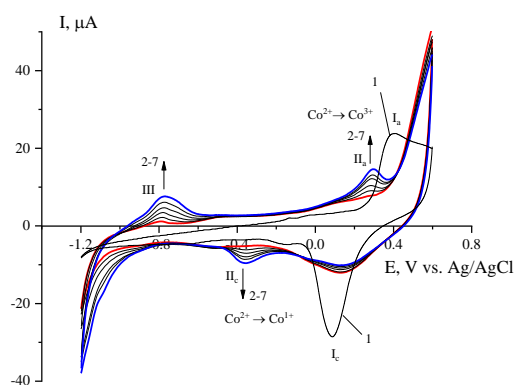
Figure 1. Current–potential curves recorded at a gold disc electrode in a p*H* 12 buffer solution in the absence (curve 1) and presence (curve 2–7) of 10^{-3} mol/L CoPcI at a scan rate of 100 mV/s (25 °C) as a function of scan number. Scan numbers are (2) 10, (3) 20; (4) 40; (5) 60; (6) 80 and (7) 100.
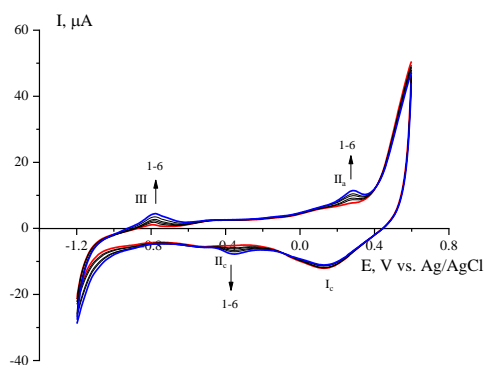
Figure 2. Current–potential curves recorded at a gold disc electrode in a p*H* 12 buffer solution in the presence (curve 1–6) of 10^{-3} mol/L CoPcII at a scan rate of 100 mV/s (25°C) as a function of scan number. Scan numbers are (1) 10, (2) 20; (3) 40; (4) 60; (5) 80 and (6) 100.
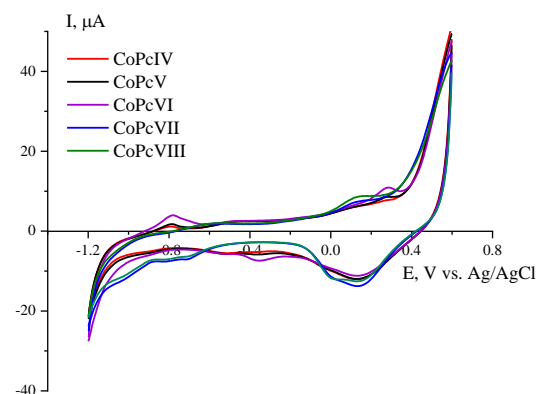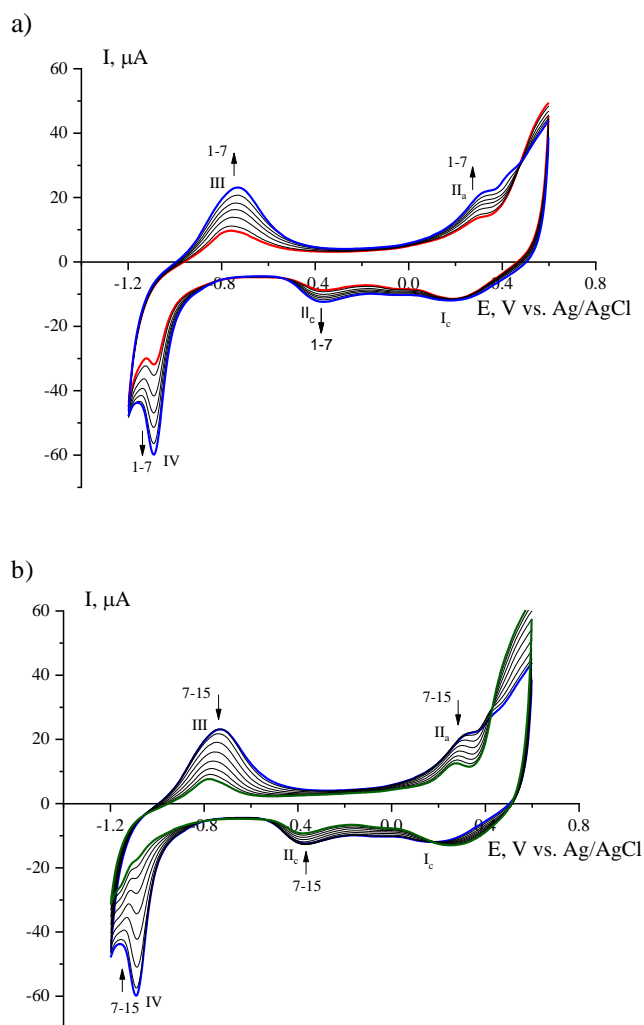
Figure 3. Current–potential curves recorded at a gold disc electrode in a p*H* 12 buffer solution containing 10^{-3} mol/L CoPcIV-CoPcVIII at a scan rate of 100 mV/s (25°C).

Further investigations show that the gold electrode demonstrates approximately the same behavior for **CoPcII**, **CoPcIV**, **CoPcV**, **CoPcVI**, **CoPcVII**, and **CoPcVIII** complexes. Figure 2 shows 100 cyclic voltammetric scans recorded at a gold electrode in a solution containing 10^{-3} mol/L of **CoPcII**. In Figure 3 the final scans of the deposition of macroheterocycles **CoPcIV-CoPcVIII** are shown. It can be concluded that the redox processes occurring at the periphery of the phthalocyanine macroring do not participate (or participate weakly) in the electrochemical processes. It is known that metal complexes of **Pc** derivatives exhibit a high tendency to aggregation in solutions with the formation of higher-order dimeric, trimeric and other associates due to $\pi-\pi$ interaction of their extended π-system.[46,47] Dimerization significantly reduces their catalytic activity, because during the formation of several dimeric structures, for example, $\pi-\pi$-dimers, the reaction center is closed, and prevents the formation of bonds with the substrate. However, we can assume that in the case of metal complexes that are structural analogs, even the presence of strong aggregation will not significantly change the overall picture of the electrochemical behavior of these objects.

Figure 4a shows the first 20 cyclic voltammetric scans recorded at a gold electrode in a p*H* 12 buffer solution containing 10^{-3} mol/L **CoPcIII** (curves 1–7). In curves 1–7 the new reduction peak is observed at -1.09 V (IV) (*vs.* Ag/AgCl), it grows with increasing of scan number. The location of the I_c, II_a, II_c and III peaks is similar to the location of the corresponding redox peaks of the metal phthalocyanines discussed above. The increase of the oxidation peaks II_a and III and the reduction peaks II_c and IV continue until scan 20. Continuation of the scanning beyond scan 20 results in different behavior. The increase of the previously mentioned peaks with scan number is due to the deposition of **CoPcIII** at the gold surface. With each scan the fraction of deposited **CoPcIII** increases, which results in higher peaks because more adsorbed **CoPcIII** is present at the surface in the next scan. This feature also explains the gradual decay of peak I_c (Figure 1). Covering the gold surface with metal complex prevents its oxidation and reduction, therefore the gold oxide formation and reduction peaks (I_a and I_c) decrease (Figure 1). Figure 4b shows curves obtained during the following 80 scans, from

scan 20 (curve 7) to scan 100 (curve 15). It can be seen that both oxidation peaks (II_a and III) and reduction peak II_c, and the associated charges, decrease with increasing scan number while the peak IV disappears completely. This indicates that **CoPcIII** initially adsorbed at the electrode surface is again released. These observations correlate with the fact that compared to other complexes, **CoPcIII** has the lowest stability of dimeric associates in water.[37]

Useful information involving electrochemical mechanism generally can be acquired from the relationship between peak current and scan rate. Scan rate studies were carried out to assess whether the process on gold electrode was under diffusion or adsorption controlled. A plot of logarithm of peak current versus logarithm of the scan rate within the range 25-200 mV/s, gave a straight-line relation with a slope from 0.97 to 1.10 for all **CoPc** complexes. The slope values correspond to theoretically expected value 1 for processes in which the electroactive species of metal complexes adsorbed at the electrode surface without being specifically diffused (except for peak IV in Figure 4).

For all data obtained in this work it should be noted that the same potential region was used. The reason for this is that, by using smaller potential regions, no electrodeposition of **CoPcI-CoPcVIII** at gold was observed. By scanning only in the positive or negative region, no marked immobilisation of metal complex species was observed, nor when potential regions smaller than those shown in Figures 1-4 were used. This indicates that both the negative and positive regions are important in the electrodeposition reaction.

Conclusions

A hypothesis for the electrodeposition of a series of cobalt sulfopthtalocyanines at gold electrode surfaces has been formulated based on electrochemical observations by correlating the evolution in time of the different peaks observed as a function of scan number and macroheterocycle concentration in solution. It was found that the electrodeposition process is generally independent of the nature of the substituent in the phthalocyanine macroring.

a)

b)

Figure 4. Current–potential curves recorded at a gold disc electrode in a pH 12 buffer solution in the presence (curve 1–15) of 10^{-3} mol/L CoPcIII at a scan rate of 100 mV/s (25°C) as a function of scan number. Scan numbers are: a) (1) 1, (2) 2; (3) 4; (4) 6; (5) 8, (6) 10 and (7) 20; b) (7) 20, (8) 30, (9) 40, (10) 50, (11) 60, (12) 70, (13) 80, (14) 90, (15) 100.

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