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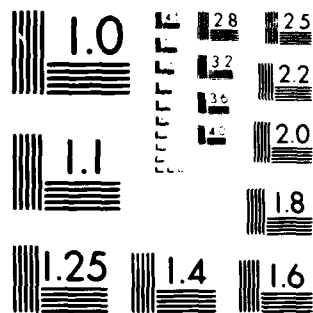
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ELECTRON TRANSFER AND AXIAL COORDINATION REACTIONS OF COBALT
TETRA(AMINOPHENYL)PORPHYRINS COVALENTLY BONDED TO CARBON ELECTRODES

by

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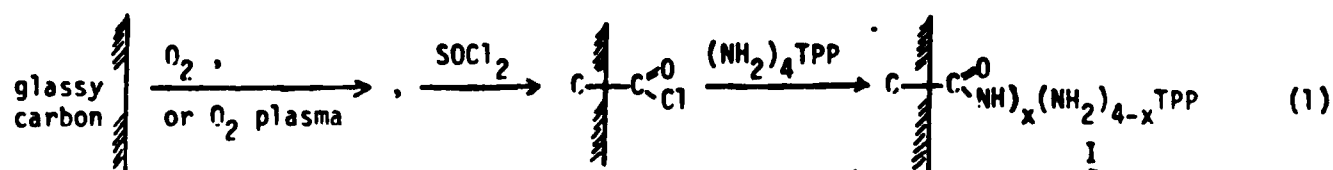
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ABSTRACT

Electrochemistry of tetra(aminophenyl)porphyrin covalently attached to glassy carbon and then cobalt-metalled, was investigated in DMSO and CH_3CN solvents in the presence of pyridine. Shifts in formal potential were used to measure complex stability constants and coordination number for the pyridine complexes of the immobilized metalloporphyrin. Unusually slow electrochemistry of the Co(III/II) reaction was also studied by cyclic voltammetry and by reflectance spectroelectrochemistry. It is proposed that coordination of cobalt by surface carboxylate groups causes extraordinarily slow electron transfer for the Co(III/II) step.

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This laboratory has in previous reports [1-3] described the covalent immobilization of tetrakis(*p*-aminophenyl)porphyrin, $(p\text{-NH}_2)_4\text{TPP}$, on glassy carbon electrodes by the reaction sequence



The number of amine bonds formed to the surface was determined by X-ray photoelectron spectroscopy, XPS, to be two, on the average [2]. The surface porphyrin I can be metallated in situ with first row transition elements such as Fe and Co [1-3]. All these immobilized species exhibit electron transfer reactions with the carbon electrode with formal potentials $E_{\text{surf}}^{\circ'}$ near those of their unattached molecular analogs [4].

It is well-known [5] that metalloporphyrins immobilized within the framework of biological macromolecules can exhibit special chemistry associated with proximity of axially coordinating ligands attached to the framework or with steric restrictions imposed by the framework on the axial coordination of otherwise potent ligands. Inasmuch as some analogies between the circumstances of biological macromolecular and electrode immobilization can be envisioned, a better understanding of the axial coordination chemistry of metalloporphyrins prepared from Structure I was of interest. With this in mind, a further study of the cobalt-metallated form of Structure I, $\text{C}-\text{Co}(\text{NH}_2)_4\text{TPP}$, in contact with solutions containing the ligand pyridine, has been carried out and is described here. Results are also given for the monoamine tetraphenylporphyrin, $\text{C}-\text{Co}(\text{NH}_2)\text{TPP}$. Of interest was how the

coordination number of axially bound pyridine depends on the oxidation state of the immobilized cobalt porphyrin and its complex stability constants. A base of comparative electrochemical data for the interaction of pyridine with dissolved cobalt tetraphenylporphyrin is available[6-8]. Also of interest was a better understanding of the previously noted[2] abnormally small electrochemical surface wave for reduction of immobilized $C\text{--}Co(III)(NH_2)_4TPP$ as compared to $C\text{--}Co(II)(NH_2)_4TPP$.

EXPERIMENTAL

Immobilization. Glassy carbon electrodes (Atomergic Chemetals Corp., Plainview, N Y., Grade V10-50, 3-4 mm diameter) with freshly polished ends were oxidized in vacuo at ca. 400° C for one hour or in an RF plasma[9] chamber at ca. 200 mtorr O_2 and 5 watts for 30 minutes. Lower background currents were observed with plasma oxidized electrodes. The oxidized electrodes were refluxed in ca. 2 ml freshly distilled $SOCl_2$ in 15 ml of sodium dried toluene for one hour, briefly rinsed with dry toluene, and refluxed for 3 hours in a hot solution of ca. 1 mg. of $(NH_2)_4TPP$ or $(NH_2)TPP$ porphyrin in 15 ml of dry toluene. Thorough rinses with dry toluene and reagent grade methanol were used to remove adsorbed porphyrin. The immobilized porphyrins were metallated by refluxing the air-dried electrodes in a solution of ca. 0.5 gram of $CoCl_2$ in 20-30 ml CH_3CN followed by washing with CH_3CN . The electrodes were mounted for electrochemical experiments in a cylinder of heat-shrinkable Teflon, leaving the cylinder end exposed. Cobalt metallation was ordinarily complete as indicated by the absence of electrochemical waves for residual free base.

Electrochemistry. Electrochemical experiments were carried out in dimethylsulfoxide (DMSO) and acetonitrile solvents predried over molecular sieves and containing 0.1 M Et_4NClO_4 supporting electrolyte and various concentrations of pyridine ligand. The solutions were degassed with N_2 pre-saturated with vapor of a pyridine/solvent mixture identical to that in the electrochemical cell. The pyridine had been distilled and stored over molecular sieves.

The electrochemical cell was conventional, with a Luggin capillary to the NaCl-saturated calomel reference electrode (SSCE). To ascertain that junction potential effects at the Luggin tip were unimportant as the pyridine concentration was varied over a wide range, the formal potential of the ferrocene/ferricenium couple was measured as a function of [Py]. Its potential was constant, $+0.496 \pm 0.006$ volts vs. SSCE.

Electrochemical equipment was a Princeton Applied Research Model 174 as potentiostat for cyclic voltammetry and differential pulse voltammetry with a locally designed triangular wave generator[10] as signal source for the former. A freshly prepared electrode was first inspected by cyclic voltammetry, then voltammograms were determined at a series of [Py] with differential pulse voltammetry, whose application to immobilized electrode reactants has been described by Brown and Anson[11]. $E_{\text{surf}}^{\circ'}$ is the average of the potentials for current peaks observed on cathodic and anodic-going scans. The differential pulse experiment allowed accurate determination of peak potentials even at the very slow potential scan rates desirable for $E_{\text{surf}}^{\circ'}$ measurements.

Chemicals. Tetrakis(p-aminophenyl)porphyrin, $(\text{NH}_2)_4\text{TPP}$, and mono(p-amino)-tetraphenylporphyrin, $(\text{NH}_2)\text{TPP}$, were prepared as previously [2,3] and generously

supplied by S.M.Elliott (Stanford University), respectively. Cobalt tetraphenylporphyrin (Man-Win Chemicals, Washington, D.C.) was used as received.

Determination of x in Reaction 1. The dangling amine groups remaining on the immobilized porphyrin in Reaction 1 were coupled to 3,5-dinitrobenzoyl chloride and the relative XPS N 1s band intensities for nitro and porphyrin nitrogens determined as described previously[2]. This measurement was carried out on electrodes prior to metallation and also on electrodes after cobalt insertion. XPS spectra were obtained with a DuPont Model 650B Electron Spectrometer with the assistance of Dr. M Umaña.

RESULTS AND DISCUSSION

Some general characteristics of the cyclic voltammetry of tetra(p-amino-phenyl)porphyrin attached to carbon as in eq. 1 and then cobalt metallated, $C\text{--}Co(NH_2)_4TPP$, and of its monoamine analog, $C\text{--}Co(NH_2)TPP$, are illustrated by Figures 1-3. In both DMSO and CH_3CN solvents, the $Co(III/II)$ and $Co(II/I)$ porphyrin reactions occur at potentials similar to the E° values for unattached CoTPP (+0.12 and -0.82 volts vs. SSCE in DMSO), typical of modified electrodes [3, 4]. The voltammograms in DMSO and CH_3CN are unusual however in that in the absence of added pyridine ligand (Figures 1A, 2A), the $Co(III/II)$ wave is typically only 1-5% as large as the $Co(II/I)$ wave. When pyridine is added (compare Figures 1A, 1B), and for $C\text{--}Co(NH_2)_4TPP$ as compared to $C\text{--}Co(NH_2)_4TPP$ (compare Figures 1A, 2B), the $Co(III/II)$ wave is enhanced, but remains < 1:1 in relation to the $Co(II/I)$ step. Voltammetry of $C\text{--}Co(NH_2)_4TPP$ in pyridine as solvent is similar to that in $> 1\text{ M}$ solutions of pyridine in DMSO.

The cathodic Co(II/I) wave in both DMSO ($E^\circ' = -0.87$ v. vs. SSCE) and CH_3CN ($E^\circ' = -0.87$ v. vs. SSCE) exhibits an irreversible prewave whose definition varies from electrode to electrode (Figures 1A, 3A), and which has no anodic counterpart. If the potential scanning region is restricted (Figure 3B) or if the electrode is pre-potentiostatted at -0.4 volt for a few minutes, the cathodic prewave is largely eliminated.

From these general observations it seems that only a fraction of the immobilized metalloporphyrin population undergoes the Co(III/II) reaction at its reversible potential, but that most if not all of the Co(II/I) reaction proceeds normally especially if the electrode is pre-potentiostatted as described above. We will return to this point after considering the axial ligation properties as deduced from the reversible (Co(III/II) sites and the Co(II/I) reaction.

Coordination With Pyridine. Theory for the shift in reversible redox potential of an electrode immobilized metal complex caused by a change in coordination has not been discussed previously. It is formally similar to the conventional solution relations, replacing solution concentrations by surface excess Γ (moles/cm.²). We will assume that $r_0 = r_R$ for the surface interaction terms[11]. Thus for the reactions of $\text{C} \sim \text{Co}(\text{NH}_2)_4\text{TPP}$

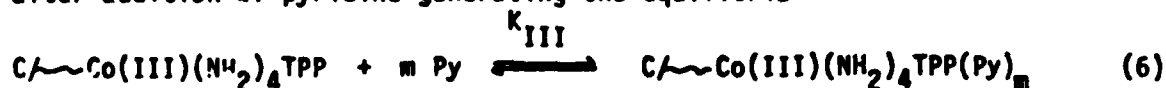


the reversible potentials in the absence of pyridine are

$$F = F_{\text{surf(III/II)}}^\circ - 0.059 \log [\Gamma_{\text{Co(II)}} / \Gamma_{\text{Co(III)}}] \quad (4)$$

$$E = F_{\text{surf(II/I)}}^\circ - 0.059 \log [\Gamma_{\text{Co(I)}} / \Gamma_{\text{Co(II)}}] \quad (5)$$

and after addition of pyridine generating the equilibria



we obtain

$$E_{\text{surf/complex(III/II)}}^{\circ'} = E_{\text{surf(III/II)}}^{\circ'} - 0.059 \log [K_{\text{III}}/K_{\text{II}}] - 0.059(m-p) \log [\text{Py}] \quad (8)$$

$$E_{\text{surf/complex(II/I)}}^{\circ'} = E_{\text{surf(II/I)}}^{\circ'} - 0.059 \log [K_{\text{II}}] - 0.059(p) \log [\text{Py}] \quad (9)$$

Measurement of $E_{\text{surf/complex}}^{\circ'}$ as a function of $[\text{Py}]$ yields p (the number of pyridine axially coordinated to Co(II)) and K_{II} from eq. 9 and thence m (the number of axially coordinated pyridines for Co(III)) and K_{III} from eq. 8. These values may depend on solvent since solvent coordinates competitively with pyridine.

To accurately measure peak potentials for the Co(III/II) and Co(II/I) waves, differential pulse voltammetry produces sharply defined waves at the slow potential scan rates desirable to ensure Nernstian charge transfer equilibrium for the reactions. Also, the small Co(III/II) wave, detected with difficulty by cyclic voltammetry is easily seen (Figure 1) in the DPV experiment. $E^{\circ'}$ was taken as the average of E_{peak} negative and positive-going potential sweeps (see Figure 1C, 1D insets). Table I shows that DPV peak potential separations (ΔE_p) are small, with differences between the Co(III/II) and Co(II/I) steps and between $\text{C} \sim \text{Co(NH}_2)_4\text{TPP}$ and $\text{C} \sim \text{Co(NH}_2)_2\text{TPP}$. In DMSO, a spurious wave at -0.10 volt (Figure 1C)

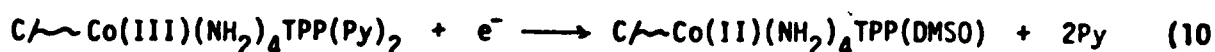
which disappears when a small concentration (2 mM) of pyridine is added, is thought to arise via adventitious ligands such as trace water. The potential of the more positive wave is taken as $E_{\text{surf(III/II)}}^{\circ} = +0.124$ volt vs. SSCE.

Data for E_{surf}° as a function of [Py] are displayed in Figure 4. Results for different experiments are overlaid. The potential becomes more negative as pyridine is added, since the Co(III) state is more stabilized by pyridine coordination than the Co(II) state. In DMSO, clearly defined changes in slope for both $C\text{--}Co(NH_2)_4\text{TPP}$ and $C\text{--}Co(NH_2)\text{TPP}$ occur at $[Py] \sim 0.05$ M and the slopes are approximate multiples of 0.059. At low [Py], $m-p$ for the Co(III/II) reaction is for both porphyrins near two and p for Co(II/I) is zero. At these concentrations, both axial sites on $C\text{--}Co(III)(NH_2)_4\text{TPP}$ and $C\text{--}Co(III)(NH_2)\text{TPP}$ are occupied by pyridine, and these are both displaced upon reduction to $C\text{--}Co(II)\text{TPP}$. At high [Py], we find $m-p = 1$, so only one of the two initially present pyridines becomes displaced in $C\text{--}Co(II)\text{TPP}$, the second being lost upon reduction to $C\text{--}Co(I)\text{TPP}$.

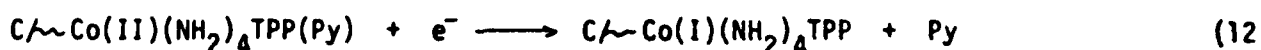
Acetonitrile is a less strongly coordinating solvent and so it is not surprising that Figure 4 shows that only one pyridine is dissociated upon reduction to $C\text{--}Co(II)\text{TPP}$, over the entire range of [Py]. As before, the second pyridine is lost upon further reduction to $C\text{--}Co(I)\text{TPP}$. The data from different determinations in acetonitrile show greater scatter than in DMSO; the weaker ligand CH_3CN probably allows greater coordinative interference from impurity ligands such as water.

These results are summarized in the reactions:

In DMSO, at $[Py] < 0.05 \text{ M}$,



In DMSO at $[Py] > 0.05 \text{ M}$, and in CH_3CN ,



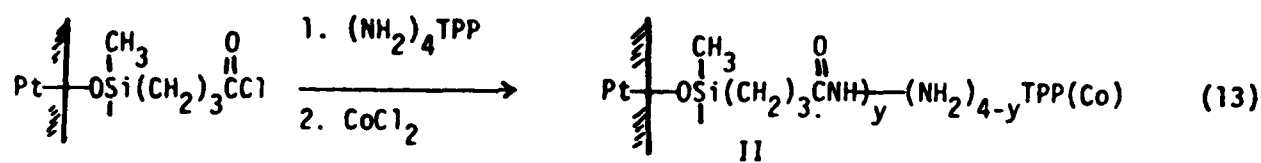
Reactions 10-12 for immobilized cobalt porphyrin are consistent with previous electrochemical information on solutions of cobalt porphyrin[6,7]. In structural studies of cobalt porphyrins[12-16], Co(III) is generally six coordinate (two axial ligands), Co(II) is generally five coordinate, and square pyramidal with the metal displaced 0.1-0.2 Å out of the plane of the porphyrin ring, and Co(I) is four coordinate (no or very weak axial ligation). The data of Figure 4 for all cases, show six coordinate Co(III), i.e., $C\text{---}Co(III)(NH_2)_4TPP(Py)_2$, at most one pyridine coordinated to Co(II), and overall dissociation of two pyridines upon complete reduction of Co(III) to Co(I). Similar results for axial coordination of pyridine in solutions of CoTPP in DMSO and propionitrile solvents were reported by Davis[6]. In DMSO, Kadish and coworkers[7] reported an additional reduction wave at intermediate $[Py]$ which we did not observe for the immobilized cobalt porphyrins.

Stability constants for eqs. 6 and 7 calculated using eqs. 8 and 9 are summarized in Table I. Except for K_{III} for $C\text{---}Co(III)(NH_2)_4TPP$, which is notably larger, K_{III} and K_{II} agree fairly well with the values cited by Kadish[7] for solutions of CoTPP in DMSO. K_{III} and K_{II} are larger in the less coordinating acetonitrile solvent, consistent with coordination number results in Figure 4, and in good agreement with results in propionitrile[6].

Aspects of Surface Binding and The Co(III/II) Reaction. The above results show that the axial coordination numbers and stability constants for the reversibly reacting $C\text{--}Co(NH_2)_4TPP$ and $C\text{--}Co(NH_2)TPP$ are little different from that for solutions of CoTPP. However, we have also observed that only a small fraction of the total immobilized cobalt porphyrin population seems to react at the reversible Co(III/II). Associated with this effect is the appearance of a prewave of the Co(II/I) wave (Figures 1A, 2A, 3A). The combined charge of this prewave and the Co(II/I) wave, Q_{cath} , relative to that of the subsequent Co(I/II) wave, Q_{anod} , as shown for $C\text{--}Co(NH_2)_4TPP$ in DMSO in Table II, depends upon the potential scanning history of the electrode. On a fresh electrode, Q_{cath}/Q_{anod} is nearly 2/1. This value drops upon succeeding potential scans, especially for continuous scanning, and falls to 1.02 if the potential scan is restricted to the vicinity of the Co(II/I) wave. The value of Q_{cath}/Q_{anod} which is observed after brief potentiostating at 0 volts especially increases if pyridine is present since the reversible Co(III/II) potential is then more negative than 0 volts.

The strong implication of this behavior is that immobilized Co(III) porphyrin which does not react in the small, reversible Co(III/II) wave, reacts as the prewave of the Co(II/I) wave. The electron transfer rate for this "slow Co(III) porphyrin" must be very slow. Further, the overlap of the "slow Co(III/II)" wave (the prewave) and the reversible Co(II/I) wave suggests that the onset of the latter catalyzes the former, perhaps through generation of some Co(I) sites from the reversibly reacting Co(III/II) population.

To observe the slow Co(III/II) reaction by a different method, we have conducted reflectance spectroelectrochemistry on the same porphyrin system attached to Pt electrodes using organosilane chemistry

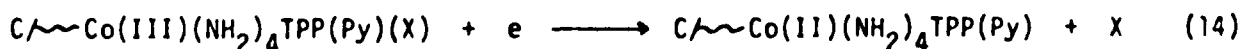


As shown in Figure 5, voltammetry of the silane-bound cobalt porphyrin, II is similar to that seen on glassy carbon, i.e., an abnormally small Co(III/II) wave and a prewave to the Co(II/I) reaction. Reflectance spectra taken (*in situ*, acquisition time ca. 15 seconds) with the surface II potentiostatted at +0.4, -0.4, -1.1, -0.4, and +0.4 volt vs. SSCE in DMSO are shown in the Figure. Details of the reflectance experiment are given elsewhere [17]. The +0.4 volt spectrum (Curve A) should correspond to the Co(III) state, and its 452 nm λ_{max} is in good agreement with the 450 nm value obtained for a solution of Co(III)(NH₂)₄TPP in DMSO in an optically transparent thin layer electrochemical cell [17]. When the potential is changed to -0.4 volt, appropriate for the Co(II) state, a spectral change commences (Curves B, C, D), but this is very slow; even after 10 minutes there is only a 3 nm shift in λ_{max} . In contrast, changing the applied potential to -1.1 volt is accompanied by an immediate change of the reflectance spectrum to that of Co(I) as shown in Figure 5, Curve E. Likewise, return of the potential to -0.4 immediately results in a Co(II) porphyrin spectrum (Curve F) with $\lambda_{\text{max}} = 435$ nm (the corresponding solution value is 433 nm). Finally, return of the potential to +0.4 volt vs. SSCE also restores the

Co(III) spectrum (Curve G); the Co(II/III) spectral change occurs much more rapidly than that for the Co(III/II) reaction. These spectral results confirm the extraordinarily slow Co(III/II) electrochemistry, and also indicate that the reversible potential for the "slow Co(III/II)" species is more positive than -0.4 volt.

To verify the absence of artifacts in our solutions, cyclic voltammetry of unattached Co(III)TPPCl in DMSO solution was re-examined at glassy carbon electrodes. The Co(III/II) wave is indeed fully developed (with $i_p/v^{1/2} = \text{constant}$ for $v = 0.05\text{--}0.2$ v./sec.) as compared to the Co(II/I) wave as shown in Figure 6.

We propose that the slow electron transfer in the "slow Co(III/II)" species involves an axial coordination effect, in which a potent ligand $\underline{X}$ axially binds to one axial side of the immobilized $C\sim\text{Co(III)(NH}_2)_4\text{TPP}$, leaving the other side open to coordination by solvent or pyridine. Thus, in DMSO containing $[\text{Py}] > 0.05$ M, a small population of $C\sim\text{Co(NH}_2)_4\text{TPP}$ is not coordinated by $\underline{X}$ at all and undergoes reaction 11 at the reversible potential as found in Figure 4, whereas most of the immobilized metalloporphyrin undergoes a very slow electron transfer from the electrode or a faster one from neighbor Co(I) sites according to the reaction



In eq. 14, $\underline{X}$ becomes dissociated rather than pyridine as attested by the results of Figure 4 (i.e., $p = 1$). The Co(II) product of both eqs. 11 and 14 thereafter undergo the expected Co(II/I) reaction 12.

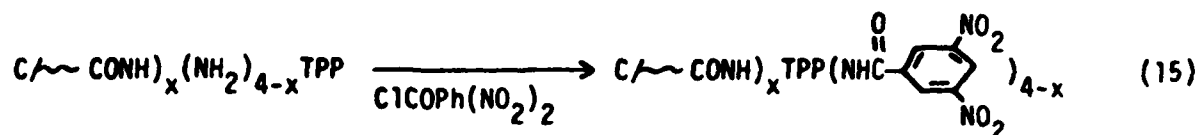
Intervention of ligand $\underline{X}$ in the electrochemistry of $C\sim\text{Co(NH}_2)_4\text{TPP}$ is supported by several experimental results. First, we expect that to some extent $\underline{X}$ should be displaced by added ligands, with an associated increase in the magnitude of the reversible Co(III/II) wave. Figure 1 shows that indeed the reversible Co(III/II) wave is enhanced in the presence

of added pyridine, i.e., a larger proportion of the porphyrin reacts as in equation 11 rather than equation 14. Secondly, a sterically small, hard ligand such as chloride produces a similar effect as shown in Figure 7. A large excess of chloride both attenuates the prewave and enhances the reversible Co(III/II) wave which in the case of $C\text{---}Co(NH_2)_4TPP$ (Curve D) exhibits a charge nearly equal now to that of the Co(II/I) wave, suggesting nearly complete replacement of $\underline{X}$ by chloride.

Whatever $\underline{X}$ is, it has the property of being stably bound (competes well with large excess of pyridine) and of dramatically slowing the electron transfer for the Co(III/II) reaction. We must consider $\underline{X}$ as being either a trace constituent of the solvent-electrolyte system contacting the electrode, or a chemical functionality which is attached to the surface molecular framework. For some time we suspected that traces of dioxygen in the solvent might coordinate to the cobalt porphyrin. In aqueous acid, immobilized $C\text{---}Co(NH_2)_4TPP$ does catalyze dioxygen reduction, at potentials suggesting H_2O_2 as product, and with eventual deactivation of the porphyrin. Also, deliberately added small amounts of dioxygen in DMSO and CH_3CN enhance current at the potential of the prewave. Scrupulous degassing, however, neither eliminates the prewave or restores the Co(III/II) wave to a normal magnitude. We do not have satisfying evidence for the involvement of dioxygen and propose instead that $\underline{X}$ is a ligand constituent of the surface itself.

Immobilized ligands on surfaces I and II include dangling amine functionalities of $(NH_2)_4TPP$ which did not couple to the surface acid chloride groups, and carboxylic acid groups which are eventual hydrolytic products of the

latter. The dangling amine groups can be investigated by the amidization reaction



by measuring the relative intensities of the X-ray photoelectron N 1s spectral bands for the nitro groups and for the overlapping porphyrin plus amide nitrogens as we have earlier described[2]. For unmetallated porphyrin, we redetermined $4-x$ as 1.85 ± 0.28 , in agreement with the earlier result from which we concluded that an average of two amide bonds formed between each $(\text{NH}_2)_4\text{TPP}$ and the carbon surface. In a new experiment, the porphyrin was metallated with cobalt prior to reaction 15; the result was again $4-x = 1.82 \pm 0.54$ (average of three measurements). Thus, cobalt does not change the number of dangling amines with the implication that such amines are not pre-empted from reaction 15 by axial coordination to cobalt. Also cobalt-metallated electrodes still exhibit small Co(III/II) waves after reaction 15. Finally, neighbor amine donors should not be possible on $\text{C} \sim \text{Co}(\text{NH}_2)_4\text{TPP}$ surfaces, which exhibit the "slow Co(III/II)" effect, albeit to a lesser degree (Figures 2B, 7C).

The second surface ligand model, in which $\underline{X}$ is a carboxylate function of the glassy carbon lattice which centrally underlies $\text{C} \sim \text{Co}(\text{NH}_2)_4\text{TPP}$ sites and coordinates axially with the cobalt from the electrode side of the porphyrin ring, is thought to be a stronger possibility. Since carboxylate groupings on glassy carbon occur with sufficient surface density to permit two groups to fall into register with and amide bond to (on the average) two amine sites on each porphyrin, it is therefore plausible that many axial porphyrin sites should also

achieve a register with a third carboxylic acid surface group. On surface II, there is of course a large population of dangling carboxylic acid groups not consumed by the amide bonding reaction but still attached by the silane linkage to the Pt electrode.

Figure 6B shows a cyclic voltammogram of unattached CoTPP in the presence of a 10^2 -fold excess of benzoate ion (a molecular analog of a graphite carboxylate edge site). The Co(III/II) wave is split. A diminished solvent-coordinated Co(III/II)TPP wave remains visible and so the stability constant for benzoate coordination is small. A diffuse, second Co(III/II)TPP wave with large ΔE_p is seen at more negative potentials. This behavior shows that benzoate coordination by itself retards the electron transfer rate for the Co(III/II) reaction.

In six coordinate Co(III)TPP complexes, the low spin Co(III) lies in the plane of the four porphyrin nitrogens[12,18]. In five coordinate Co(II)TPP, on the other hand, the usual cobalt coordination geometry is square pyramidal with the low spin Co(II) protruding from the porphyrin plane toward the axial ligand by 0.1-0.2 Å[12,13,19] or more. Thus reduction of Co(III) in eq. 11 and 14 is accompanied by an adjustment of the metal site geometry as well as loss of one axial ligand. To the extent that the rate of electron transfer depends on either or both of these events, and it is likely that it does, involvement of a ligand X which is affixed indirectly to the porphyrin itself (via the surface) could cause severe constraints on the electron transfer rate. Neither the proposed X, carboxylate groups, or the $\text{Co}(\text{NH}_2)_4\text{TPP}$,

attached as they are to the surface, have unrestricted motion on the surface, especially relative to one another. The mobility of C/ Co(NH₂)TPP should be greater than that of C/ $\sim$ Co(NH₂)₄TPP, being attached by one amide bond rather than two, and correspondingly Co/ Co(NH₂)TPP exhibits prewave and small Co(III/II) wave effects less pronounced than for C/ $\sim$ Co(NH₂)₄TPP.

The above model of th- axial ligand X as carboxylate groups attached to surfaces I and II, while consistent with the available experimental results, is nonetheless admittedly speculative. The evidence for some interfering ligand X is strong, but we have no direct, only circumstantial evidence identifying X as carboxylate. Precedent for our model is found, however, in a prior proposal by Kuwana and coworkers [21] that carbon surface oxides can axially bind to and induce the adsorption of cobalt tetrapyrrolylporphyrin from aqueous acid.

Acknowledgement. This research was supported in part by a grant from the Office of Naval Research. This is Part XXIII of a series on Chemically Modified Electrodes.

TABLE I

Stability Constants^a for Complexation of Pyridine by
Immobilized Cobalt Aminotetraphenylporphyrins

<u>Solvent</u>	<u>Porphyrin</u>	<u>Log K_{III}</u>	<u>Log K_{II}</u>	<u>E⁰_{surf}</u>	<u>ΔE_{peak} C_{mv}</u>
DMSO	C ₆ H ₄ -Co(⁻ NH ₂) ₄ TPP	7.26 ± 0.15	1.44 ± 0.18	$\frac{III, II^b}{+0.124}$	$\frac{III, II}{43 \pm 22}$
CH ₃ CN	C ₆ H ₄ -Co(⁻ NH ₂) ₄ TPP	8.51 ± 0.19	2.25 ± 0.11	+0.060	$\frac{II, I^b}{-0.869}$
DMSO	C ₆ H ₄ -Co(⁻ NH ₂)TPP	6.32 ± 0.13	1.25 ± 0.12	+0.115	$\frac{II, I^b}{-0.821}$
DMSO	CoTPP	5.86 ^d , 6.41 ^e	2.15 ^d , 1.32 ^e		$\frac{II, I^b}{-0.821}$
PrCN	CoTPP	9.10 ^f	2.60 ^f		$\frac{II, I^b}{-0.821}$

- Stability constants were calculated for integral $\bar{m}$ and $\bar{p}$, using eq. 8 and 9 and E⁰_{surf} listed in Table.
- Average of cathodic and anodic peak potential from DPV.
- Difference between cathodic and anodic peak potential in DPV at 2 mv/sec., 25 mv. modulation amplitude.
- Reference 6.
- Reference 7.
- Reference 20.

TABLE II

Ratio of Cathodic Charge for Co(II/I) Wave Plus Prewave
to Anodic Charge for Co(I/II) Wave

<u>DMSO, C/$\sim$Co(NH₂)₄TPP</u>	<u>Q_{cath}/Q_{anod}</u>
Virgin scan	1.89 $\pm$ 0.44
Continuous Scanning +0.3 v. $\rightarrow$ -1.5 v.	1.26 $\pm$ 0.11
Continuous Scanning -0.6 v. $\rightarrow$ -1.5 v.	1.02
After potentiostat ($\sim$ 1 min) at 0.0 volt ^a , [Py]=0	1.38 $\pm$ 0.24
After potentiostat ($\sim$ 1 min) at 0.0 volt ^a , [Py]>0.005	1.71 $\pm$ 0.51
<u>CH₃CN, C/$\sim$Co(NH₂)₄TPP</u>	
After potentiostat ($\sim$ 20 sec.) at 0.0 V., [Py]>0.02	1.89 $\pm$ 0.65
<u>DMSO, C/$\sim$Co(NH₂)TPP</u>	
After potentiostat ($\sim$ 20 sec.) at 0.0V.	1.20 $\pm$ 0.31

a. Following previous potential scan +0.3 v. $\rightarrow$ 1.5 v. $\rightarrow$ +0.3 v. $\rightarrow$ 0.0 v., stop.

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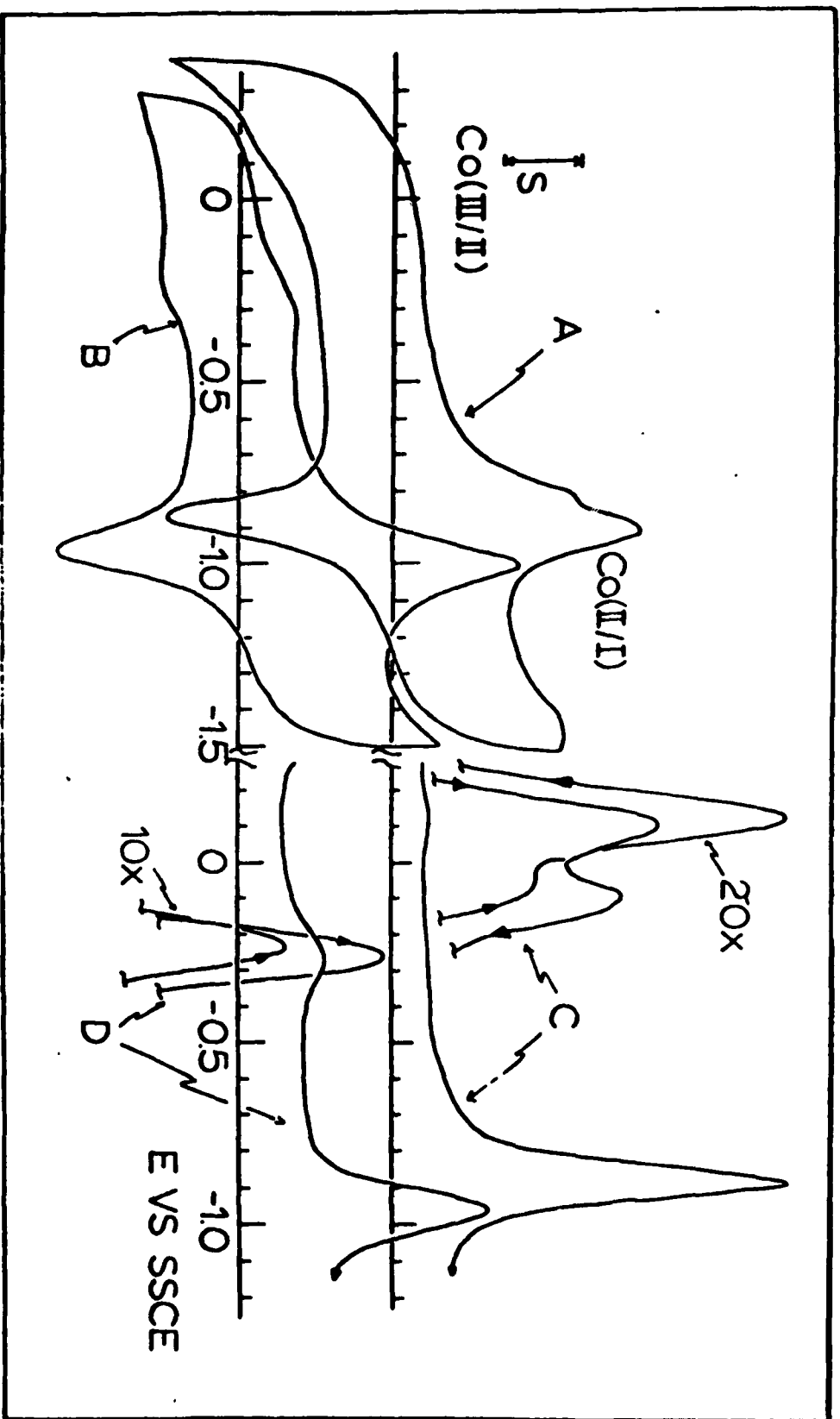
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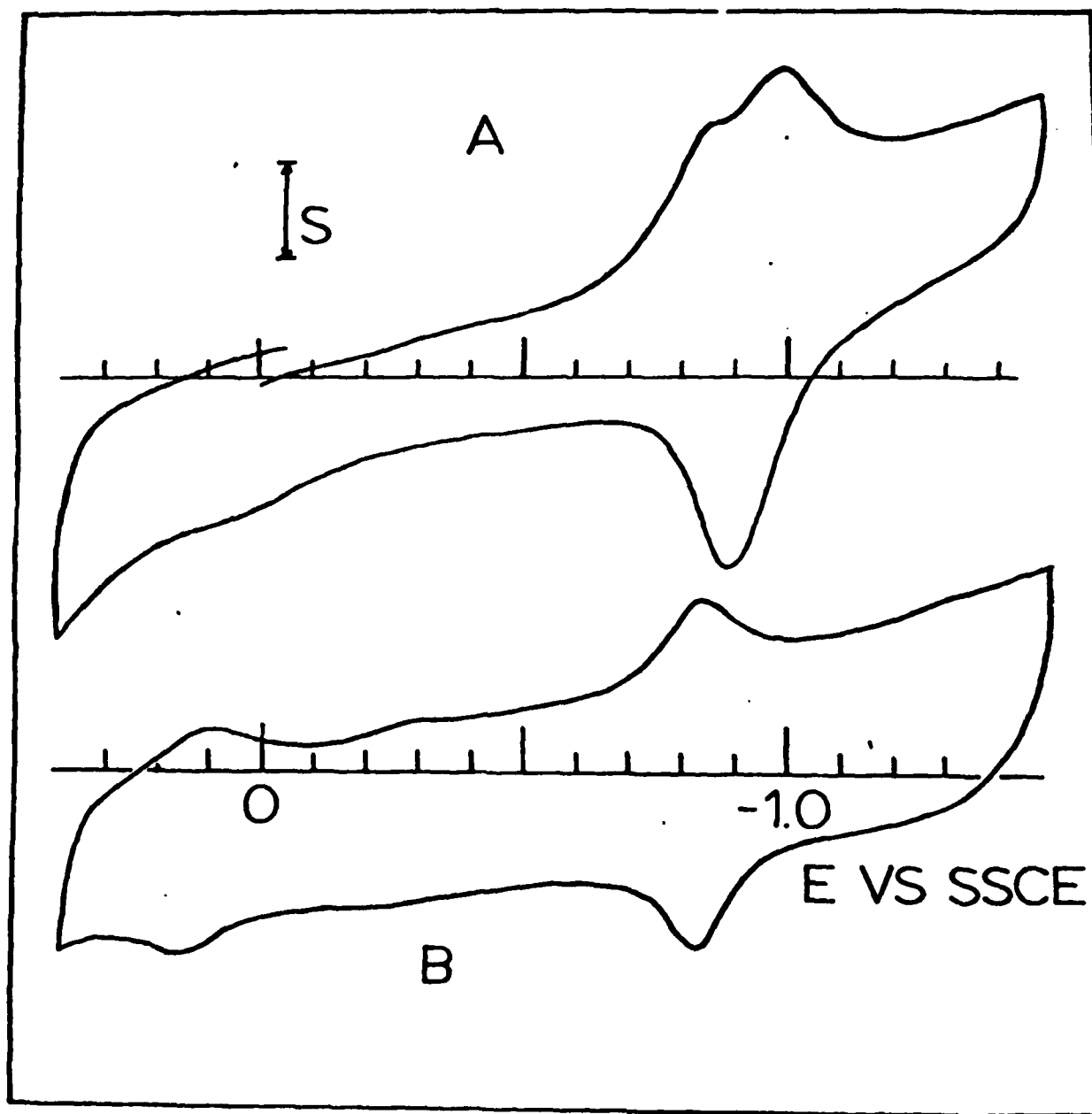
Figure Legends

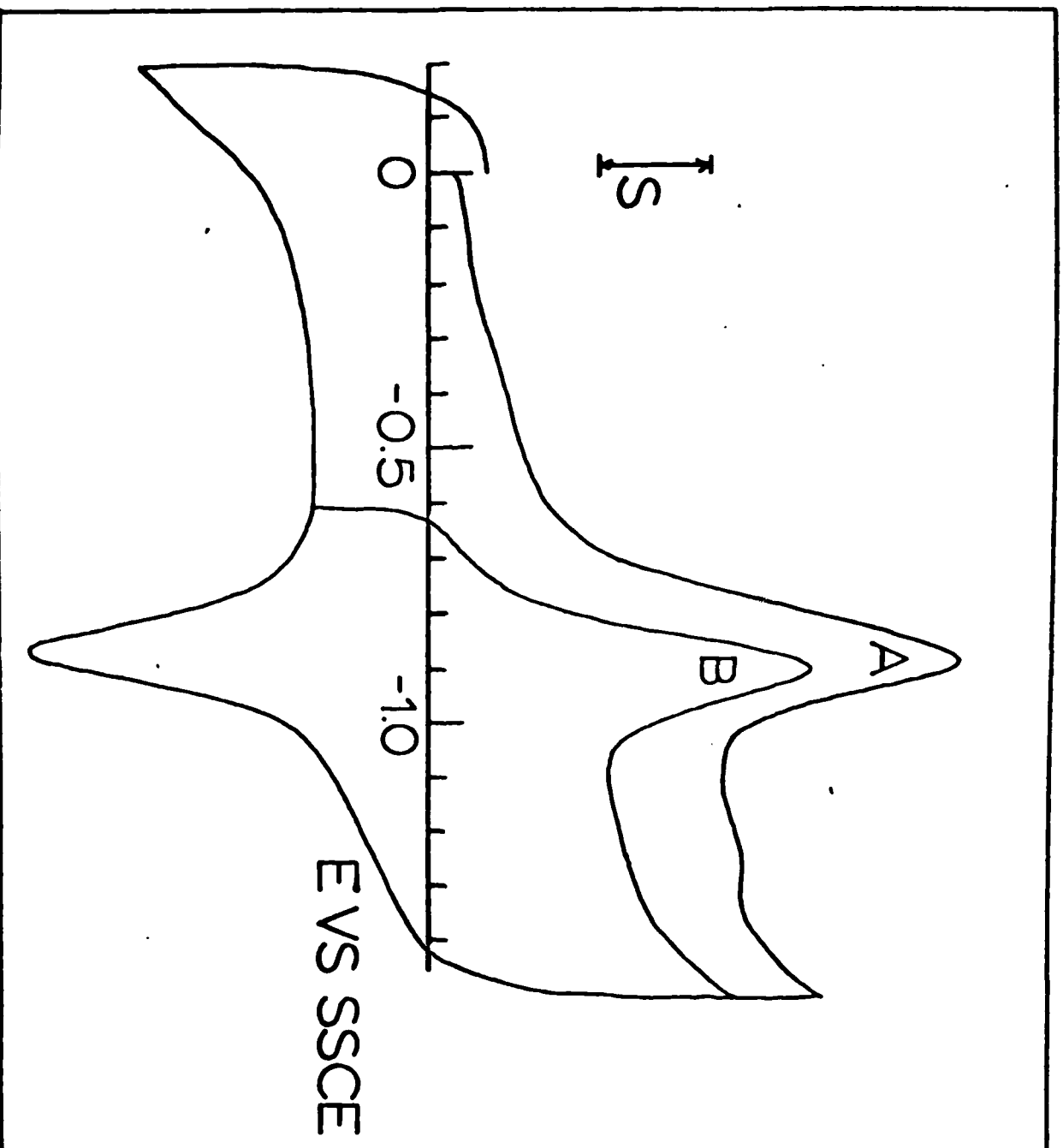
- Figure 1. Cyclic voltammetry at 100 mv/sec of 6×10^{-10} mole/cm² $C\text{---}Co(NH_2)_4TPP$ in DMSO (Curve A) and in 3.47 M pyridine in DMSO (Curve B). Differential pulse voltammetry (2 mv/sec scan rate, 0.5 sec/cycle, 25 mv. modulation) of 5.7×10^{-10} mole/cm² $C\text{---}Co(NH_2)_4TPP$ in DMSO (Curve C) and in 3.47 M pyridine in DMSO (Curve D). $S = 13.8 \mu A/cm^2$ (Curves A, B); $27.6 \mu A/cm^2$ (Curves C, D). Insets are Co(III/II) DPV responses of Curves C and D amplified as indicated for precise measurement of E_{peak} .
- Figure 2. Cyclic voltammetry at 100 mv/sec of 1.1×10^{-9} mole/cm² $C\text{---}Co(NH_2)_4TPP$ in CH₃CN (Curve A) and of 3.2×10^{-10} mole/cm² $C\text{---}Co(NH_2)_4TPP$ in DMSO (Curve B). $S = 27.6 \mu A/cm^2$ (Curve A); $2.8 \mu A/cm^2$ (Curve B).
- Figure 3. Cyclic voltammetry at 100 mv/sec of $C\text{---}Co(NH_2)_4TPP$ in DMSO. Curve A: Potential scan after potentiostatting at 0 volts for ca. one minute, $Q_{cath}/Q_{anod} = 1.38$; Curve B: Steady state scan between -0.6 and -1.5 volts vs. SSCE, $Q_{cath}/Q_{anod} = 1.02$.
- Figure 4. Formal potential $E_{surf}^{\circ'}$ (average of E_{peak} of positive and negative DPV sweeps) as a function of log[Py]. Curves A, B, C are Co(II/I) wave, Curves D, E, F are Co(III/II) wave. Curves A, D: $C\text{---}Co(NH_2)_4TPP$ in DMSO; Curves B, E: $C\text{---}Co(NH_2)_4TPP$ in DMSO; Curves C, F: $C\text{---}Co(NH_2)_4TPP$ in CH₃CN. Numbers by curves are least square slopes.
- Figure 5. Reflectance spectroelectrochemistry of Structure II (3.3×10^{-10} mole/cm²) in DMSO. Spectra are taken successively Curves A to G. Curve A: potential applied to +0.4 volt vs. SSCE; Curve B: after ca. 30 sec. at -0.4 volt; Curve C: after ca. 1 min. at -0.4 volt; Curve D: after ca. 10 min. at -0.4 volt; Curve E: after ca. 30 sec. at -1.1 volt; Curve F: after ca. 30 sec. at -0.4 volt; Curve G: after ca. 1 min. at +0.4 volt.

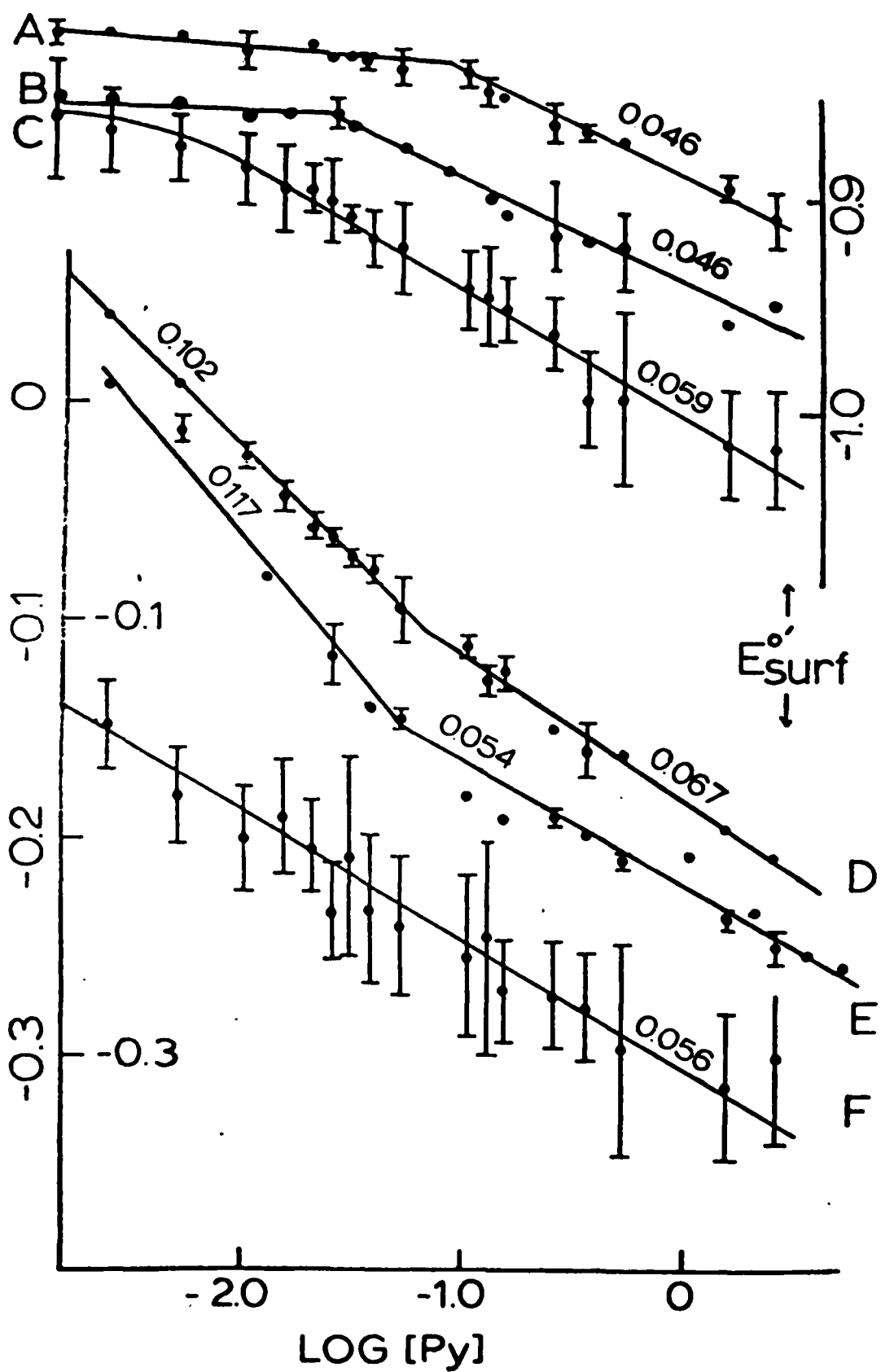
Figure 6. Cyclic voltammograms at 100 mv/sec of a 0.4 mM solution of cobalt tetraphenylporphyrin in DMSO (Curve A) with 0.4 M tetraethylammonium benzoate added (Curve B). $S = 27.6 \mu\text{A}/\text{cm}^2$.

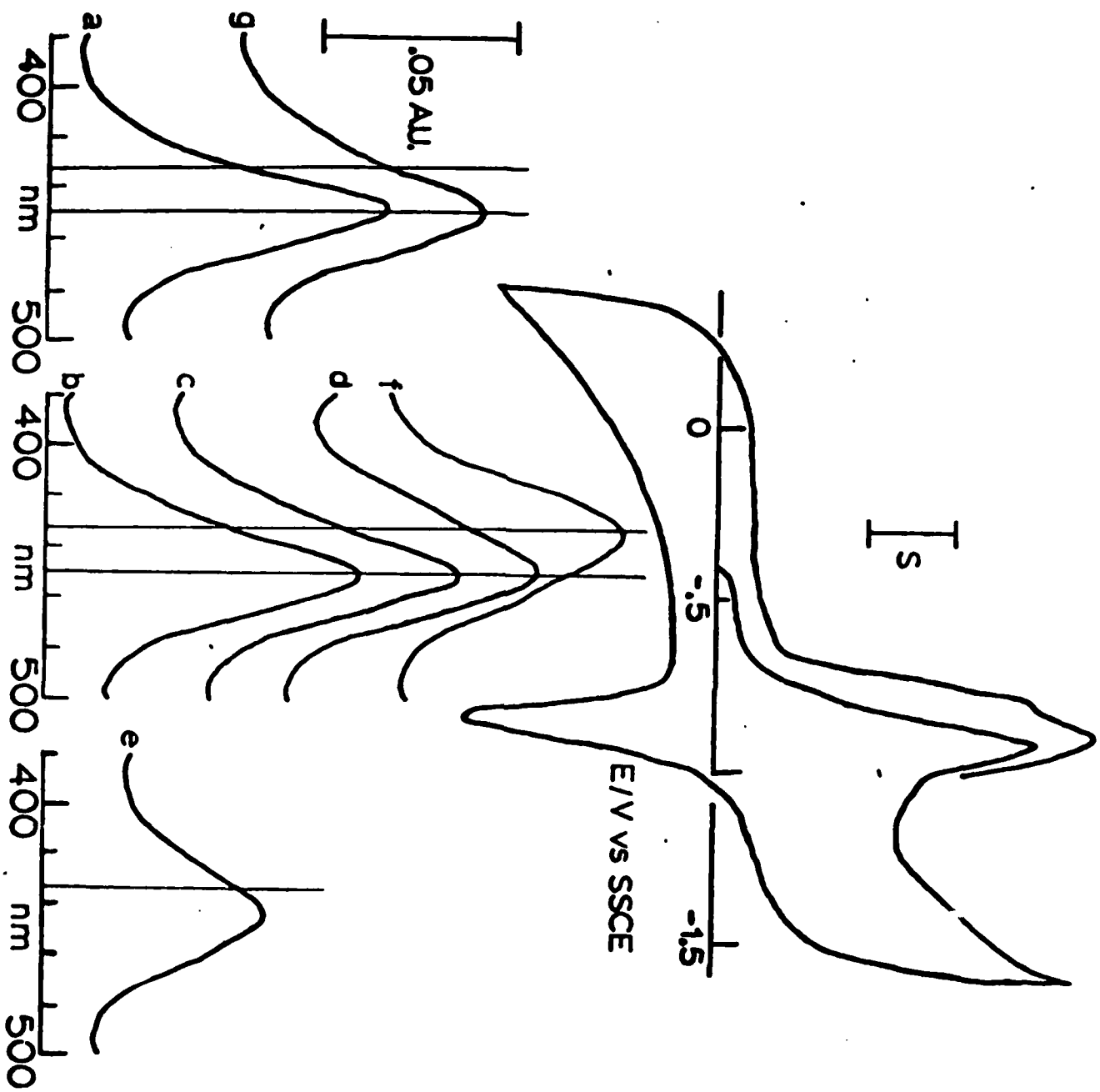
Figure 7. Cyclic voltammograms at 100 mv/sec in DMSO of $2.2 \times 10^{-10} \text{ mole}/\text{cm}^2$ $\text{C}\sim\text{Co}(\text{NH}_2)_4\text{TPP}$ (Curve A) with excess tetraethylammonium chloride added (Curve B), and of $6.2 \times 10^{-10} \text{ mole}/\text{cm}^2$ $\text{C}\sim\text{Co}(\text{NH}_2)_4\text{TPP}$ (Curve C) with excess $\text{Et}_4\text{N}^+\text{Cl}^-$ added (Curve D). $S = 13.8 \mu\text{A}/\text{cm}^2$ (Curves A, B); $55.5 \mu\text{A}/\text{cm}^2$ (Curves C, D).

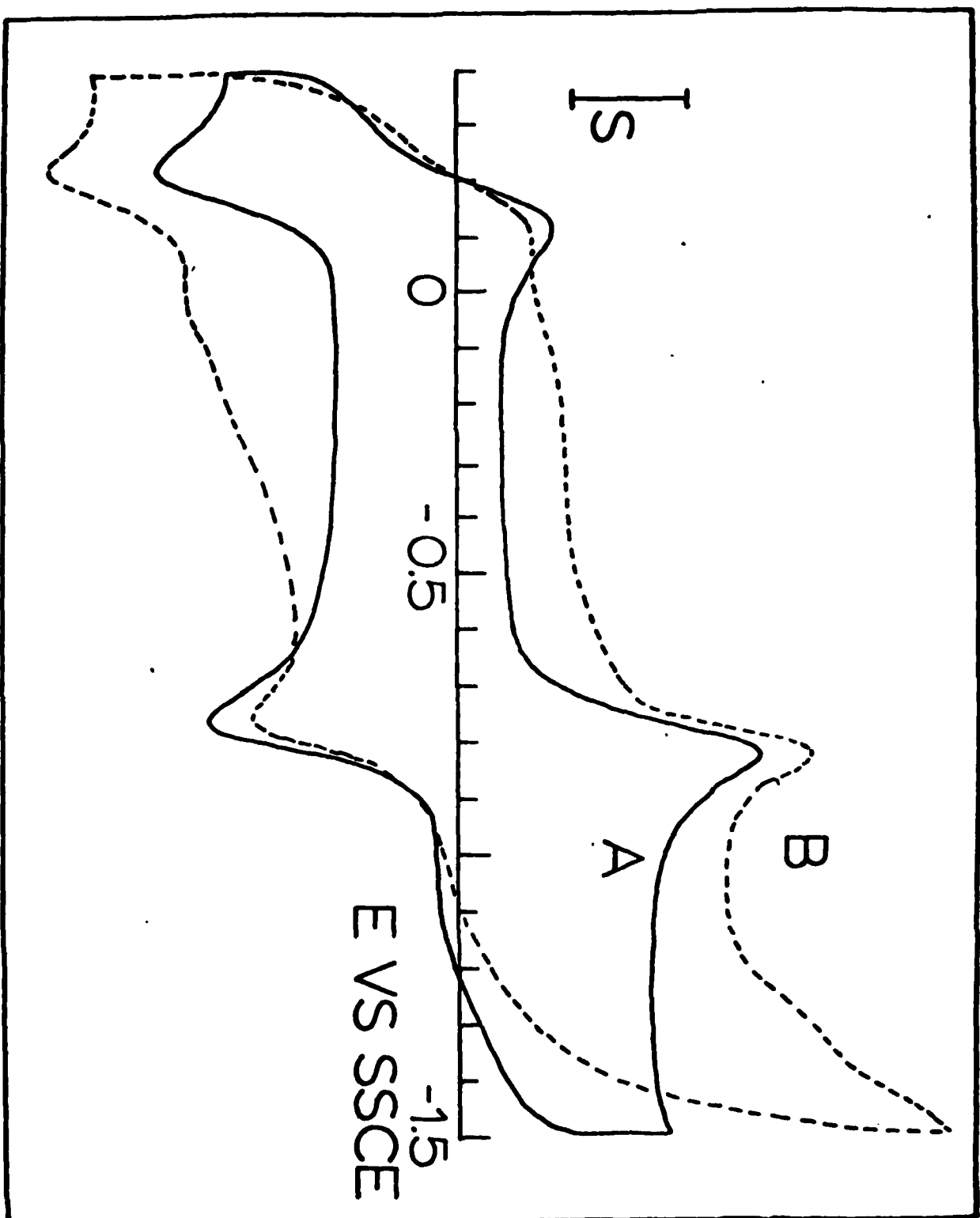


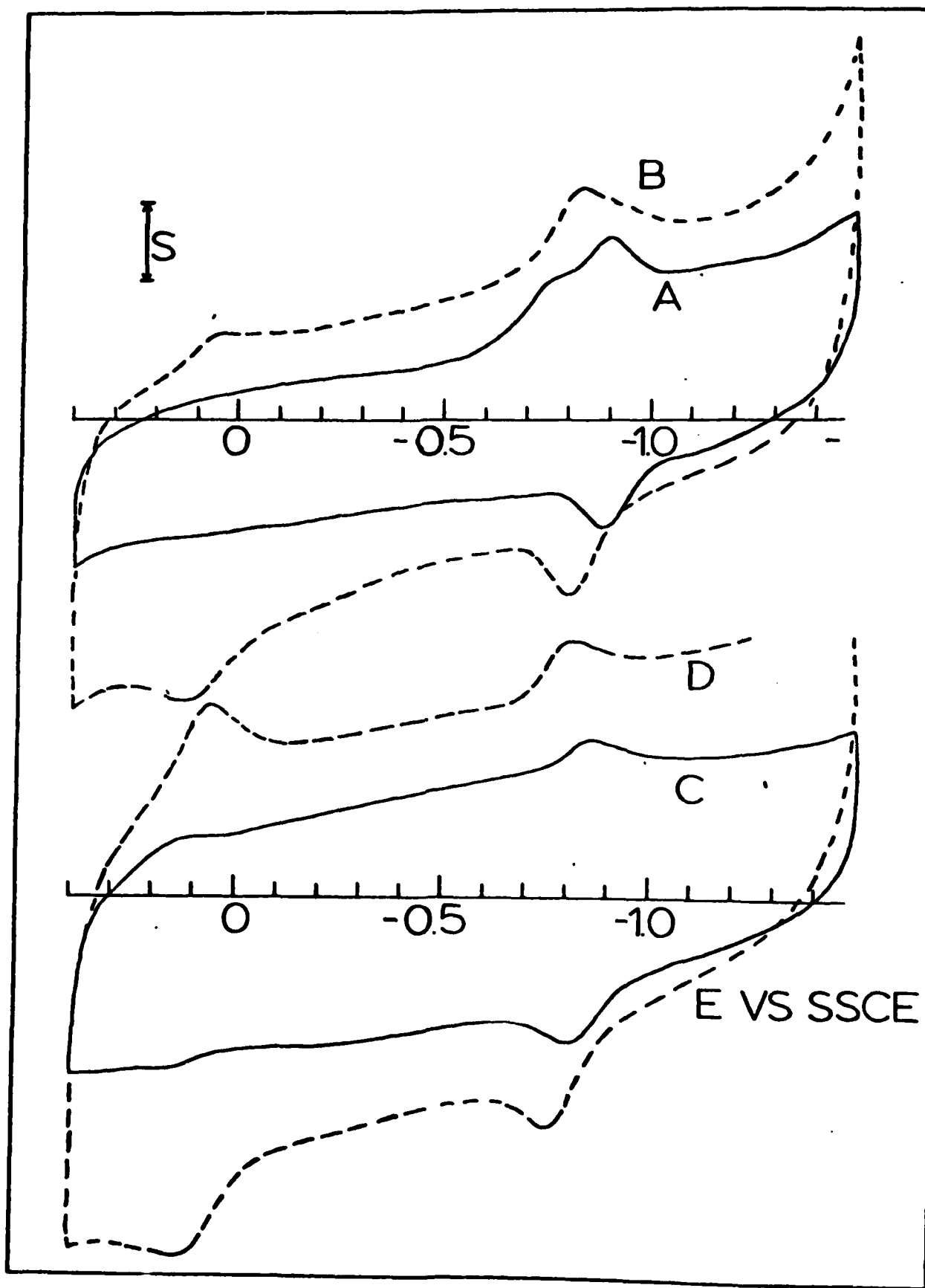












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