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INTERACTION OF METHYLATED ADENINE DERIVATIVES WITH THE MERCURY --ETC(U)
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20. $\hookrightarrow$ suggests that 1-methyl-6-aminopurine, 3-methyl-6-aminopurine, and N-methyl-6-aminopurine can be determined by cathodic stripping voltammetry, and that detection limits for N-methyl-6-aminopurine are comparable to those for adenine (10^{-9} M).

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INTERACTION OF METHYLATED ADENINE
DERIVATIVES WITH THE MERCURY ELECTRODE

by

EMIL PALECEK, JANET OSTERYOUNG
AND R. A. OSTERYOUNG

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BRIEF

The anodic oxidation of mercury in the presence of adenine and its methylated derivatives, 1-methyl-6-aminopurine, 3-methyl-6-aminopurine, N-methyl-6-aminopurine, and N,N-dimethyl-6-aminopurine, has been studied by polarography and voltammetry.

ABSTRACT

Adenine and its methylated derivatives, 1-methyl-6-aminopurine, 3-methyl-6-aminopurine, N-methyl-6-aminopurine, and N,N-dimethyl-6-aminopurine, were studied in alkaline solution by DC, normal pulse and differential pulse polarography and by cyclic voltammetry and cathodic stripping voltammetry at hanging mercury drop electrodes. All save N,N-dimethyl-6-aminopurine gave polarographic currents and cathodic stripping peaks due to the formation of slightly soluble compounds with mercury. It was concluded that the 6-amino group of adenine is the mercury binding site in these cases. Cathodic stripping behavior suggests that 1-methyl-6-aminopurine, 3-methyl-6-aminopurine, and N-methyl-6-aminopurine can be determined by cathodic stripping voltammetry, and that detection limits for N-methyl-6-aminopurine are comparable to those for adenine (10^{-9} M).

INTRODUCTION

The reaction of mercury(II) with nucleic acids and their constituent compounds in solution has been studied extensively due to its importance for better understanding of the structure and interactions of the genetic material (1-4). On the basis of titration and spectrophotometric studies, it had been suggested already in the early sixties that in aqueous solution at pH 9 Hg(II) was bound to the amino group of adenosine, a nucleoside of adenine(I) (5,6). This suggestion was based

on the observation that adenosine absorption spectra shift to longer wavelengths upon the addition of Hg(II). No changes in the spectra were observed if formaldehyde was present in solution, so binding was assumed to occur to the amino nitrogen (5). The pH dependence of the spectra suggested a proton loss from the amino group. Later work suggested however that formaldehyde can block groups other than the 6-amino group in the purine ring (7,8), and thus the original suggestion has become less certain.

Nuclear magnetic resonance studies of the interaction of Hg(II) with adenosine in dimethylsulfoxide have demonstrated that N-1 is a binding site, and that additional binding occurs at N-7 (3,9). However, it has been shown that reactions in dimethyl sulfoxide are very different from those in water (2,9). Recent studies of interactions of methyl-

mercury(II) with adenosine in aqueous solutions by means of Raman difference spectrophotometry (2) and ^1H nuclear magnetic resonance (4) have shown that in alkaline solution mercury binds to the 6-amino group. Thus the original conclusion of Eichhorn and Clark (5) concerning aminomercuriation of adenine in aqueous alkaline solutions has been confirmed directly.

In recent years cathodic stripping voltammetry (CSV) has been applied more and more frequently for the determination of organic compounds (10-15). Its application is based on the ability of the substance being determined to accumulate at the electrode surface during a waiting time at a potential at which anodic current flows; the product of the anodic reaction is then reduced by scanning in the cathodic direction. Most of the applications of CSV reported so far have been carried out with the mercury electrode (10-17). The use of other electrode materials such as silver (18) may extend the capabilities of CSV in organic analysis.

Until recently it has been assumed that the use of CSV in organic analysis is limited mainly to sulphur-containing substances (10-14,16,17). Quite recently it has been shown (1,2,15,19-22) that there exists a large group of purine and pyrimidine derivatives not containing sulphur which form sparingly soluble compounds with mercury and which can be analyzed by CSV. Determination of very small quantities of nitrogen bases which are minor constituents of nucleic acids is important in research in molecular biology. With the sulphur-containing substances it is clear that the sulfur itself interacts with mercury groups.

However, it is not known to what group or groups mercury is attached during the electrode process involving nitrogen heterocycles.

In this paper we discuss the electrochemical behavior of adenine(I) (the purine base which is the usual constituent of nucleic acids) and its methylated derivatives (some of which represent rare nucleic acid constituents) in an attempt to (a) find the mercury binding site in adenine, (b) find out how methyl substitution influences the electrochemical behavior of adenine, and (c) determine whether CSV may be useful for the determination of some rare nucleic acid bases. Because the scope of this work is quite broad, necessarily some of the results suggest further experiments rather than answering clearly all the questions which might be posed concerning these complicated chemical systems.

EXPERIMENTAL SECTION

Adenine (Ade) and its derivatives 1-methyl-6-aminopurine (1MeAde), 3-methyl-6-aminopurine (3MeAde), N-methyl-6-aminopurine (6MeAde), and N,N-dimethyl-6-aminopurine (6Me₂Ade) were products of Sigma. All other reagents were of analytical grade. As supporting electrolytes either 0.05M borax or borate buffer were used.

Polarographic and voltammetric measurements were carried out with an IBM 225 voltammetric analyzer and with an EG&G PARC 174A polarographic analyzer with an Omnigraph Model 2000 X-Y Recorder (Houston Instrument Co.). Peak currents were integrated using a Model 2120 Bascom-Turner recorder. A three-electrode system was used, including a platinum-wire

auxillary electrode and a saturated calomel electrode (SCE). All potentials are reported vs SCE. Either a hanging mercury drop electrode (HMDE) Metrohm E-410 (for cyclic voltammetry (CV) and CSV) or a dropping mercury electrode (DME) were used as working electrodes. The four division drop of the HMDE had an area of 0.022 cm^2 . The conventional DME had a drop time of $t = 8.8 \text{ s}$ and flow rate of 0.686 mg/s at open circuit in 0.05M borax buffer at a mercury column height of 70 cm . For some measurements a Static Mercury Drop Electrode Model 303 (EG&G PARC) was used instead of the conventional DME. The mercury used for the working electrodes was triple distilled quality from Bethlehem Apparatus Co. Other details of the electrochemical measurements have been published elsewhere (15,19,20).

RESULTS AND DISCUSSION

Adenine, 1MeAde, 3MeAde, and 6MeAde all give anodic waves at mercury electrodes at pH 9.2. Representative DC and differential pulse (DP) polarograms are shown in Figure 1. Normal pulse (NP), DP and DC polarograms are also shown in Figure 2. The most significant finding is that 6Me₂Ade gives essentially no response in the pH range 8-12. The second significant point is that the polarograms generally display features characteristic of the involvement of adsorption in the reaction mechanism. This is most evident in Figure 1b and Figures 2a-d. These points taken together suggest at once that interaction of the ligand with the mercury surface involves specific binding at the amine nitrogen. This suggestion will be supported and discussed further below.

For adenine, 1MeAde, and 3MeAde the waves are not too badly distorted by adsorption. A detailed study of the time dependence of these currents was not undertaken. However evidence presented below suggests that these limiting currents are diffusion-controlled. On the basis of the known chemistry of mercury with nitrogen bases, and in particular with adenine (22), we assume that the anodic reaction is



in which $p = 1$ or $p = 2$. Using a reasonable value of the diffusion coefficient for adenine, $10 \times 10^{-6} \text{ cm}^2/\text{s}$ (23), we can calculate the magnitude of the currents to be expected for these experimental conditions. The limiting DC current is $1.74 \text{ } \mu\text{A}/\text{mM}$ for $p = 2$, the corresponding NP current is $5.20 \text{ } \mu\text{A}/\text{mM}$, and the ratio of the DP peak current to the DC limiting current is 0.31 for $p = 2$, 0.61 for $p = 1$. The limiting currents for adenine, 1MeAde, and 3MeAde are about right for $p = 1$ or $p = 2$ (recognizing the considerable uncertainty in D). The DP peak currents are also in the right range. These observations do not verify that eq 1 is correct, nor do they define the value of p . The examples of Figures 1 and 2 are, however, consistent with eq 1. It should be pointed out explicitly that because adsorption and multiple homogeneous equilibria are involved in these reactions, rather minor changes in conditions can change the behavior not only in a quantitative but also in a qualitative way. Several examples of this are reported below.

The behavior of 6MeAde illustrated in Figures 1 and 2 is rather unusual and different from that of 1MeAde, 3MeAde, and Ade. Figure 1 shows DC and DP polarograms for 6MeAde at a concentration of 0.1 mM. The

DC behavior is quite complex, but the general morphology is consistent with a mechanism involving product adsorption with some inhibition of the forward reaction due to film formation. The DP response is also consistent with this view. The same general features are displayed at slightly higher concentrations as shown in Figure 2c,d. However in the concentration range 0.5-1 mM the DC polarogram loses its complex structure, and a very narrow peak of half-width ca 10 mV appears in the NP mode. The position and height of this peak was determined as a function of concentration of 6MeAde with the results as shown in Figure 3. At concentrations of 6MeAde lower than 0.5 mM, the DC and DP polarograms changed markedly as already described, and the NP curves lost their needle-like character, although they retained the maximum. Normal pulse polarographic curves free of maxima were observed only at lower concentrations (0.05 mM).

The needle-like peak for 6MeAde is undoubtedly an adsorption phenomenon. It has been shown previously (24-28) that Ade is adsorbed at the mercury electrode over a wide potential range and is desorbed at negative potentials (around -1.2 V). However, little is known about its adsorption at potentials close to those at which the anodic currents due to formation of mercury compounds occur. In the NP mode, in contrast with the DC and DP modes, the response depends on the state of the electrode surface at the initial potential, E_i . Therefore we examined the dependence of the needle-like peak on E_i . Furthermore, in order to examine this dependence for potentials anodic of the wave and to see if the formation of adsorbed product influenced the peak, we performed

similar experiments in the reverse pulse (RP) mode (29). The results for both NP and RP experiments are presented in Figures 4 and 5. The peak appears unchanged in either shape or position not only in the NP mode but also in the RP mode. This is so even when the initial potential is maintained at potentials more positive than +0.05 V, in which case an additional, much broader stripping peak appears. In the absence of a detailed study it should not be assumed that the absolute magnitude of the needle-like peak has some fundamental significance. For example, the current may depend on uncompensated resistance as well as on the nature of the electrode surface (30). However the height of this peak as a function of initial potential is displayed in Figure 5.

The variety of behavior displayed in Figures 1-5 shows that methylation of Ade not only influences the ability of a given species to react with mercury electrodes, but also influences the exact nature of its adsorption characteristics. Adsorption at more negative potentials of Ade, its nucleosides and nucleotides, and some methylated bases has been studied by AC polarography (31-37) and by the maximum bubble pressure method (36). Ade and some of its derivatives at higher solution concentrations display broad, sharply defined minima (pits) in differential capacity curves. It has been suggested that in the range of potentials at which such a pit appears the adsorbed molecules are associated and form a film on the electrode surface. The area occupied by one Ade molecule on the electrode surface in this film is about 0.40 nm^2 , which is about 30% less than outside the region of the minimum. Apparently in these potential regions Ade molecules are adsorbed with the plane of

the molecules perpendicular to the surface, while outside this region the purine rings are parallel to the electrode surface. The shapes of the NP curves (Fig. 2) suggest that in the case of Ade and 6MeAde the reactant is adsorbed (38) while in the case of 1MeAde and 3MeAde no reactant adsorption occurs at the initial potentials. It has been shown previously (35,37) that 6MeAde and 6Me₂Ade are adsorbed in a manner similar to that of Ade. Apparently these methylated substances do not produce the pit in the differential capacity curve observed with Ade. No data concerning adsorption of 1MeAde and 3MeAde have been reported.

Although this is apparently the first report of an extremely narrow NP peak associated with adsorption, this phenomenon is not unique to 6MeAde. It has been observed previously by one of us (E.P.) also with 2,6-diaminopurine and with Ade at concentrations higher than those used here. With 2,6-diaminopurine a marked dependence on the initial potential was observed and the maximum NP peak height occurred at an initial potential corresponding to the potential of the pit in the differential capacity curve. It thus appears that the appearance of this needle-like NP peak is connected with the ability of the substance to associate at the electrode surface and to form a film.

In order to investigate this conjecture, we determined the dependence of the peak on the concentration and identity of neutral salts. Some results are shown in Figure 6. With increasing salt concentration up to about 1 M, NaNO₃ and NaClO₄ have similar effects. The peak diminishes in height and is shifted to more positive potentials. At higher concentrations of NaClO₄ the peak shape is changed dramatically, and the

peak completely disappears at a concentration of 2 M NaClO_4 . At high concentrations NaClO_4 is known to unstack purine and pyrimidine bases in solution (39) and to disturb association of bases at the mercury electrode surface (32,33). Thus the ability of NaClO_4 to eliminate the peak of 6MeAde agrees with the assumption about the surface film.

Cyclic and Cathodic Stripping Voltammetry.

Representative cyclic voltammograms for 1MeAde and 6MeAde are shown in Figure 7. In each case the potential is held at the most positive value for 20 s before reversing the direction of the scan. This is done in order to accumulate products of the anodic reaction at the electrode surface. The resulting voltammograms may be compared with the polarograms of Figure 2, which display the same general features. The peaks occurring at about 0 V can be identified with the waves of Figure 2 which are not well resolved from the background oxidation of mercury. These peaks depend strongly on the positive switching potential and on delay time at the switching potential, as described below. The sharp peaks N_a and N_c can be identified with the needle-like peak of Figure 2a. These peaks do not depend on initial potential, scan direction, or delay time at the switching potential. Addition of NaClO_4 caused the height of these peaks to decrease. The height was also decreased markedly by addition of $10^{-5}\%$ Triton X-100, and at a concentration of $4 \times 10^{-5}\%$ Triton X-100 the peaks were hardly visible. The peaks occurring at more positive potentials were affected only slightly by these changes in conditions. These effects show clearly that peaks N_a and N_c are connected with the

adsorption of 6MeAde at the electrode surface. The extreme narrowness of these peaks suggest that the phenomenon is purely capacitive, and thus is similar to the tensammetric peaks observed with polynucleotides (40), polyethyleneglycol (41), and other surfactants.

The general features of the cyclic voltammograms of 3MeAde are the same as those of 1MeAde, while, in agreement with the polarographic results, 6Me₂Ade produced no peaks in cyclic voltammetry in the range -0.5 to +0.13 V at a concentration of 1×10^{-4} M. The behavior of 1MeAde and 3MeAde is illustrated by the cathodic stripping (CS) voltammograms for 1MeAde of Figure 8. The CS peak heights increase with increasing deposition time and more positive deposition potential. The CS peak potential moves to more negative values with increasing concentration of base. As a consequence of the latter, measurements of the dependence of peak height or charge on the experimental parameters became difficult at concentrations below 0.1 mM at shorter deposition times, because the peaks were poorly resolved from the background oxidation of mercury. However, as shown in Figure 8, at higher concentrations a well-formed peak is obtained which has the features described above. At a deposition time of 120 s the charge density Q corresponding to the CS peak is about $700 \mu\text{C}/\text{cm}^2$. The charge density is linear in $\sqrt{t_d}$ ($\partial \log Q / \partial \log t_d = 0.50$ with $r = 0.98$) with intercept $-15 \mu\text{C}$ and slope $66 \mu\text{C}/\sqrt{s}$. The linear dependence of Q on $\sqrt{t_d}$ is to be expected for diffusion-controlled deposition from quiet solution.

As suggested by Figure 7 the CS voltammetric behavior of 6MeAde is quite different from that of 1MeAde and 3MeAde. At low concentration

and short deposition times (10-30 s) with deposition potentials near +0.1 V a single narrow peak appeared at a potential of +0.05 V (Figure 9, peak I). At a concentration of about 0.01 M a second peak (peak II of Figure 9) appeared at about 0 V. At higher concentrations or longer deposition times these very narrow peaks were obscured by the appearance of rather broad stripping peaks in the same potential regions. This is illustrated by the voltammogram on the right-hand side of Figure 9; the sharp peak II has been obscured by the broad peak III. The dependence of peak heights and shapes on deposition time (which is qualitatively similar to the dependence on concentration) is illustrated in Figure 10.

The dependence of the position and height of these peaks on concentration, deposition time, and deposition potential is complex. Proper choice of two of these parameters permits systematic study of the dependence on the third. Figure 11 shows the dependence of the height and position of peaks I and II on concentration of 6MeAde. In this range, for peak II i_p is linear in concentration with slope 2.7 $\mu\text{A}/\text{mM}$. Detailed investigation of the dependence of the charge under the stripping peak on experimental parameters was not undertaken. However, the values obtained were roughly those expected for a diffusion-controlled deposition process, that is, $Q = 2nFAC\sqrt{Dt/\pi} = 7.2 \text{ C}/\sqrt{t}$ for $n = 1$, $D = 9 \times 10^{-6} \text{ cm}^2/\text{s}$. Assuming that the rate of accumulation of oxidized product at the electrode surface during the deposition step is diffusion-controlled the corresponding sensitivity calculated from the equation of de Vries and Van Dalen (42) for thin layer stripping is 3 $\mu\text{A}/\text{mM}$. This is in remarkably good agreement with the experimental value given above.

Notice that $\underline{n}$ in the context of eq 1 is the value of $2/p$, so if $n = 1$, then $p = 2$. Thus it may be that peak II corresponds to formation of a thin film of a compound with the stoichiometry Hg(II)(6MeAde)_2 .

The sensitivity for peak I is about 10x that for peak II ($34 \mu\text{A}/\text{mM}$, $1-30 \mu\text{M}$). The maximum charge associated with peak I was found to be about $30 \mu\text{A}/\text{cm}^2$. The minimum surface area occupied by one Ade molecule on the electrode surface was given above as 0.40 nm^2 which corresponds to $40 \mu\text{C}/\text{cm}^2$ for $n = 1$. Note that although the peak currents for peak I are about 10x those for peak II, the values of charge are comparable. It might be expected that the minimum area per molecule for 6MeAde would be greater than for Ade and therefore the maximum charge density would be a bit less for 6MeAde. Thus $30 \mu\text{A}/\text{cm}^2$ is a reasonable value for monolayer coverage by 6MeAde. Also the stripping peak at more positive potentials should correspond to a larger value of n , that is, a smaller value of p . This is a consequence of the larger surface activity of Hg^{2+} required by the Nernst relation. This suggestion is supported by the fact that peak II appears only at higher concentrations and by dependence of peak height on deposition potential shown in Figure 12.

Adenine reacts in homogeneous solution with Hg(II) to form an insoluble product with composition Hg(Ade)_2 at higher concentrations of Ade; but in the equimolar concentration range the composition of the insoluble product is HgAde (22). The solubility product for $\text{Hg(Ade)}_2(\text{s})$ has been estimated to be $1.5 \times 10^{-13} \text{ M}^3$ (pH 8.5-8.9, borax buffer) (22). If the oxidation of Hg to form Hg(6MeAde)_2 occurs in the limiting current region, then only soluble product should form for bulk concentration of 6MeAde less than twice the solubility of Hg(6MeAde)_2 . If we use the

value of the solubility product of $\text{Hg}(\text{Ade})_2(\text{s})$ to estimate the solubility of $\text{Hg}(\text{6MeAde})_2$, we find the minimum bulk concentration of 6MeAde for which a cathodic stripping peak should be seen is $6 \times 10^{-5} \text{ M}$. This is close enough to the observed value of $1 \times 10^{-5} \text{ M}$ to lend credence to this hypothesis.

It appears, then, that the anodic oxidation of mercury in the presence of 6MeAde can form a monolayer film of composition HgL or HgL_2 ; stripping of the HgL film gives rise to peak II and stripping of the HgL_2 film to peak I. It should be emphasized that at pH 9.2 these bases are either neutral or carry a single positive charge. (The formation constant for HL^+ is given by $\log K = 9.8$ for adenine). We assume that the monolayer films are neutral in composition but the nature of the interaction with the necessary anions is unknown.

Peak III appears at higher concentrations, longer deposition times and more positive deposition potentials. The maximum charge density corresponding to this peak is about $180 \mu\text{C}/\text{cm}^2$. At pH 9.2 the hydroxide concentration is approximately $16 \mu\text{M}$, and $E_{1/2}$ for the oxidation of Hg to $\text{Hg}(\text{OH})_2$ (soluble) is $+0.145 \text{ V}$ at the HMDE. The sharp increase in peak height for peak III at potentials positive of $+0.11 \text{ V}$ and the equally sharp decrease beginning at $+0.14 \text{ V}$ suggest that this peak is associated with formation of a mixed complex of $\text{Hg}(\text{II})$ with 6MeAde and OH^- . Presumably the decrease in peak current for all peaks for deposition positive of $+0.14 \text{ V}$ is due to disruption of the deposition process by the oxidation of mercury at a rate determined by the buffer capacity of the solution. If mixed compounds are formed, especially if they are

non-stoichiometric, the effective value of n for 6MeAde could be very large. Therefore the maximum charge density observed of $180 \mu\text{C}/\text{cm}^2$ may still correspond to only a monolayer of 6MeAde at the electrode surface.

Although this study did not involve determination of detection limits, comparison of the behavior of 6MeAde with that of Ade (21) suggests that 6MeAde should be detectable by CSV down to concentrations in the 10^{-8} - 10^{-9} M range. The determination by CSV of 1MeAde should be comparable to that of thymine (19). Although 6Me₂Ade did not exhibit stripping peaks, it might do so in more acid solution.

The marked difference in behavior between Ade and 6MeAde on one hand and 1MeAde and 3MeAde on the other cannot be rationalized easily on structural grounds. These results do show that the differences in behavior are largely attributable to differences in adsorption. Apparently methyl substitution in the 1 or 3 position prevents adsorption in the potential range near 0 V. Methylation of uracil in position 5 has a similar effect (19,20).

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CREDIT

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FIGURE CAPTIONS

- Figure 1. Sampled DC and DP polarograms of adenine derivatives at a concentration of 0.1 mM in 0.05 M borax (pH 9.2).
(a) Ade, (b) 6MeAde (c) 6Me₂Ade, (d) 3MeAde.
Upper row: DC; lower row: DP, pulse amplitude 10 mV.
Scan rate 2 mV/s, drop time 1 s, IBM 225. Background curves are shown also in frame (a).
- Figure 2. Sampled DC, DP, and NP polarograms of 6MeAde and 1MeAde.
(a) 0.5 mM 6MeAde, NP; (b) 0.5 mM 6MeAde, DC;
(c) 0.125 mM 6MeAde, DP; (d) 0.125 mM 6MeAde, DC;
(e) 0.25 mM 1MeAde, NP; (f) 0.25 mM 1MeAde, DC.
Other conditions as in Figure 1.
- Figure 3. Dependence of the height and position of the NP peak on concentration of 6MeAde. Initial potential -0.13 V.
Other conditions as in Figure 1.
- Figure 4. RP (a-c) and NP (d,e) polarograms for 6MeAde. Initial potential:
(a) +0.120, (b) +0.050, (c) 0.000, (d) -0.300,
(e) -1.200 V. Other conditions as in Figure 1.
- Figure 5. Dependence of NP and RP peak heights on initial potential.
() as (d,e) of Figure 4; (x) as (a-c) of Figure 4, narrow peak; (|□|) as (a) of Figure 4, broad stripping peak.
- Figure 6. Dependence of the NP peak of 6MeAde (Figure 2a) on salt concentration. 0.5 mM 6MeAde in 0.05 M borax (pH 9.0-9.2)
(—) NaClO₄, (---) NaNO₃. Initial potential -0.10 V, PARC 174.

FIGURE CAPTIONS (continued)

- Figure 7. Cyclic voltammograms for 0.5 mM 1MeAde (left) and 6MeAde (right) in 0.05 M borax, pH 9.2. HMDE, scan rate 25 mV/s, initial potential - 0.2 V, delay time at switching potential 20 s, IBM 225.
- Figure 8. Dependence of CSV response for 1 mM 1MeAde on deposition time, t_d .
 t_d = (a) 10, (b) 30, (c) 60, (d) 120 s. E_d +155 mV. Other conditions as in Figure 7.
- Figure 9. Cathodic stripping voltammograms of 6MeAde.
(a) 0.057 mM, t_d = 20 s, (b) 0.107 mM, t_d = 30 s.
 E_d = +125 mV. Other conditions as in Figure 7.
- Figure 10. Cathodic stripping voltammograms of 0.13 mM 6MeAde at various deposition times.
 t_d = (a) 0, (b) 3, (c) 5, (d) 7, (e) 10, (f) 40 s.
 E_d = +130 mV. Other conditions as in Figure 7.
- Figure 11. Dependence of heights and positions of CSV peaks of Figure 7 on concentration of 6MeAde.
____, peak I; x—x, peak II. Deposition time 30 s.
Other conditions as in Figure 7.
- Figure 12. Dependence of height of CSV peaks for 6MeAde on deposition potential.
x—x, peak I, _____, peak II, 0.03 mM 6MeAde, t_d = 20 s;
 Δ — Δ , peak III, 0.12 mM 6MeAde, t_d = 30 s. Other conditions as in Figure 11.

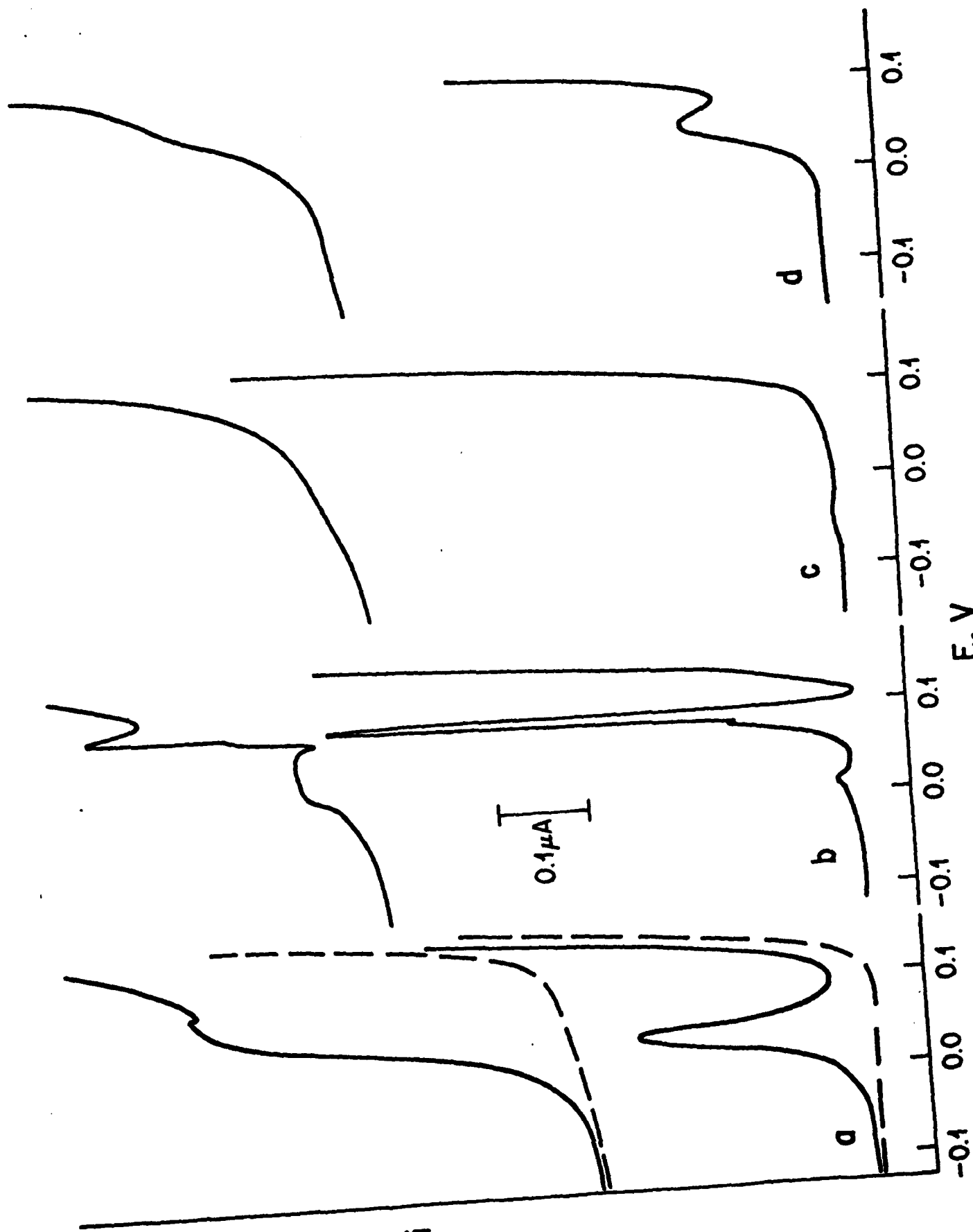


FIGURE 1

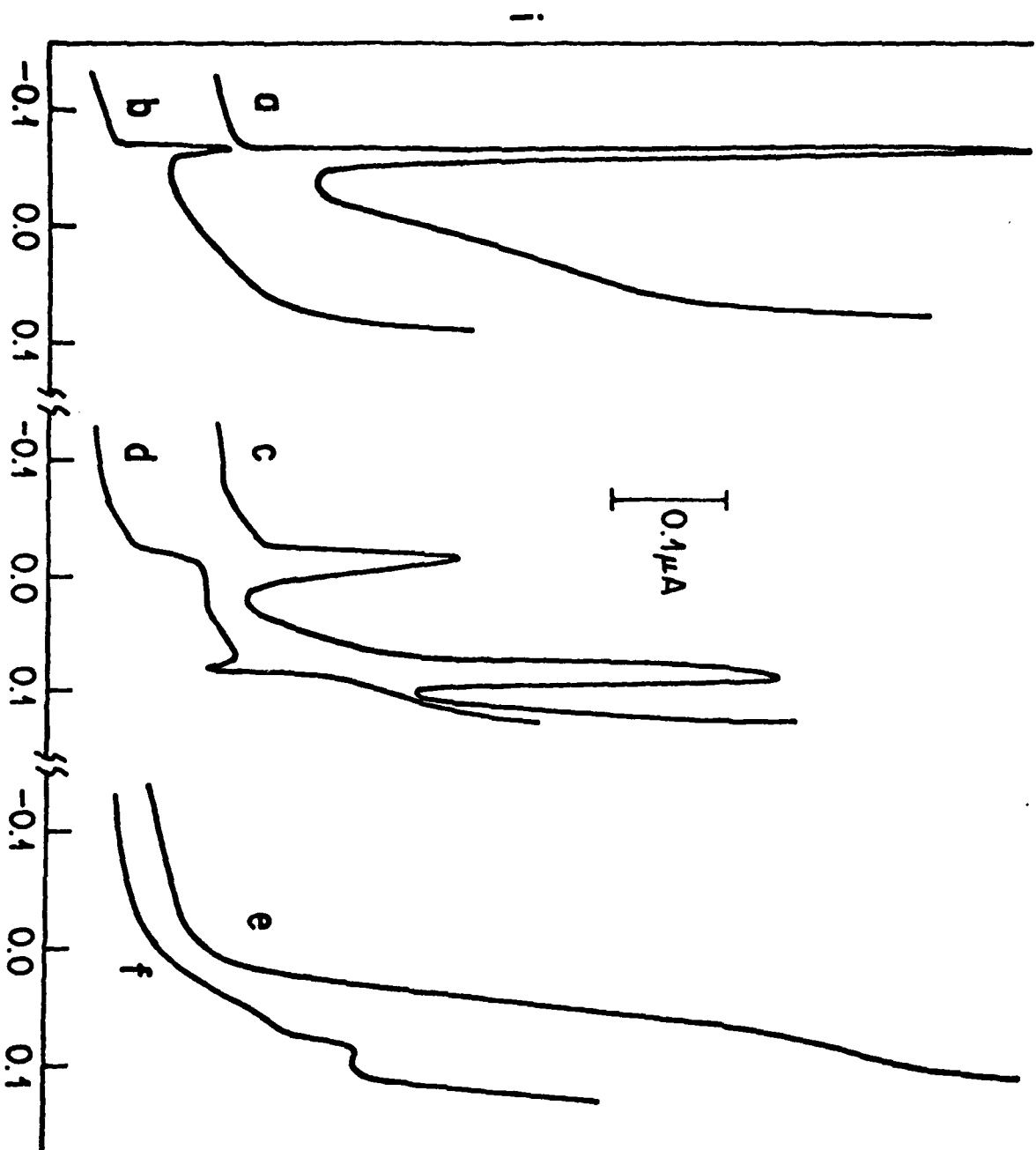


FIGURE 2
 E, V

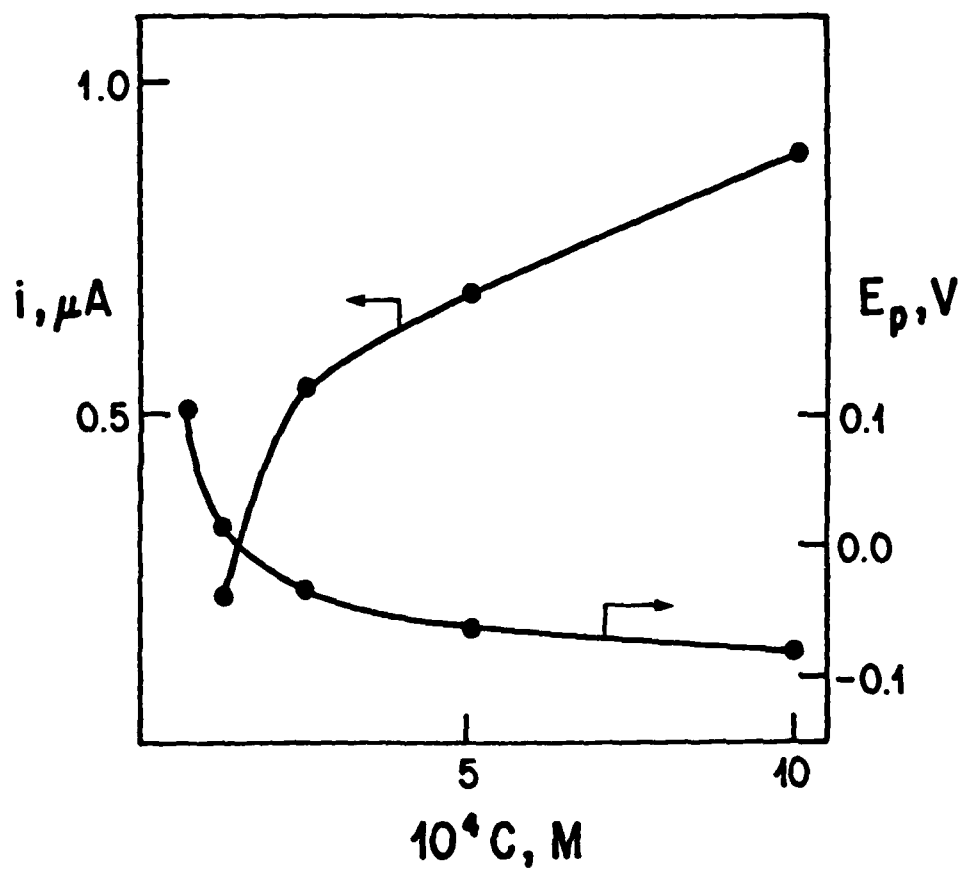
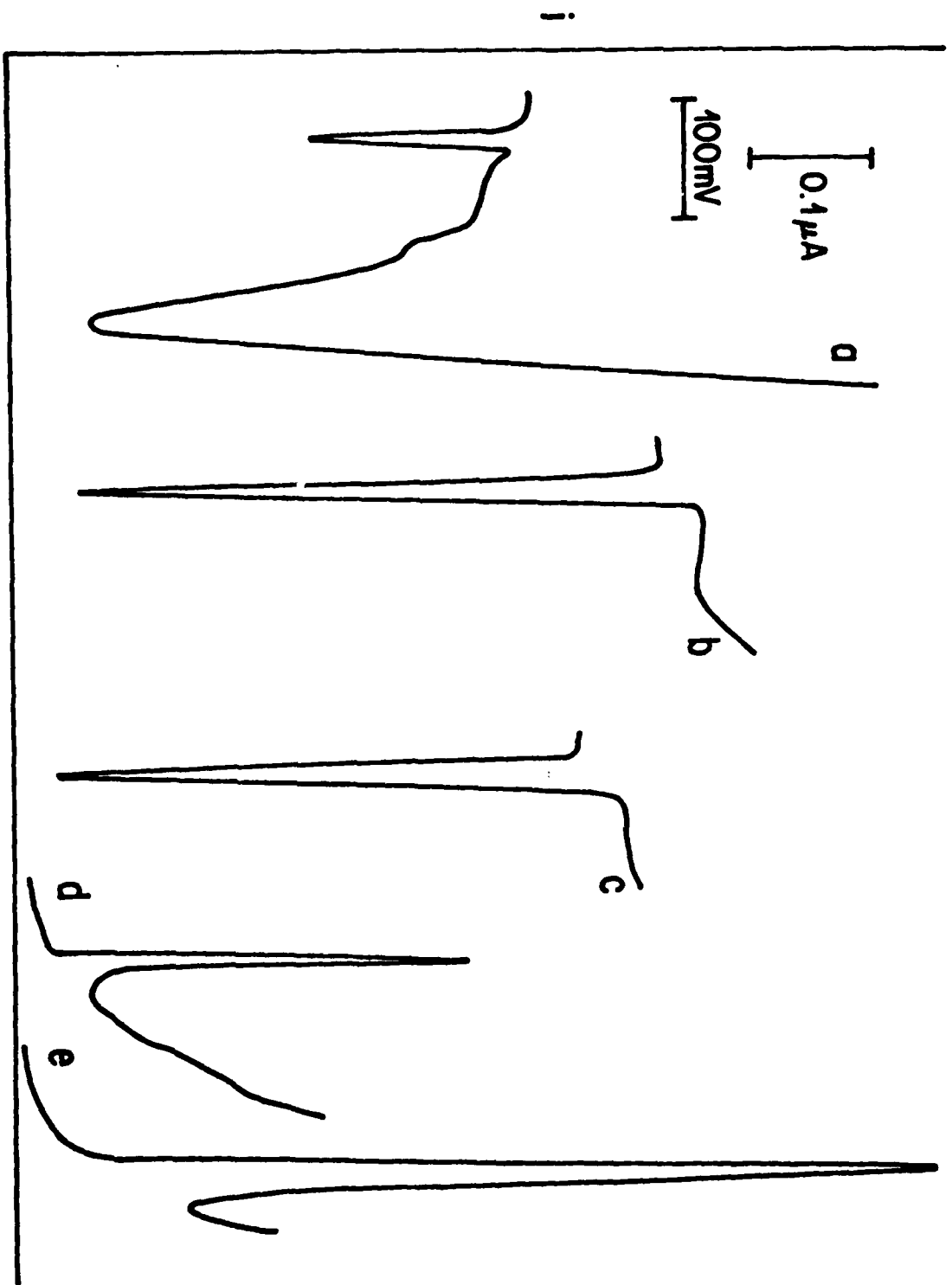


FIGURE 3



E
FIGURE 4

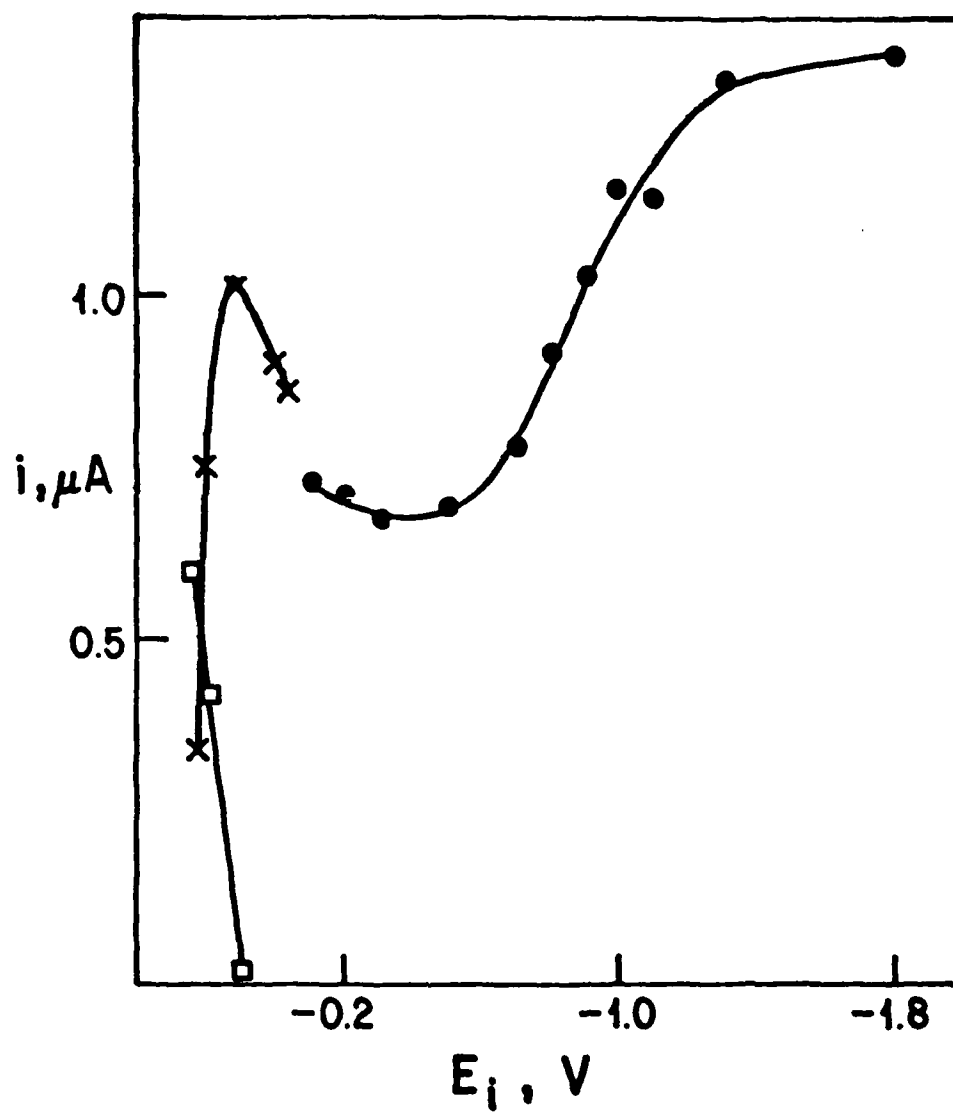


FIGURE 5

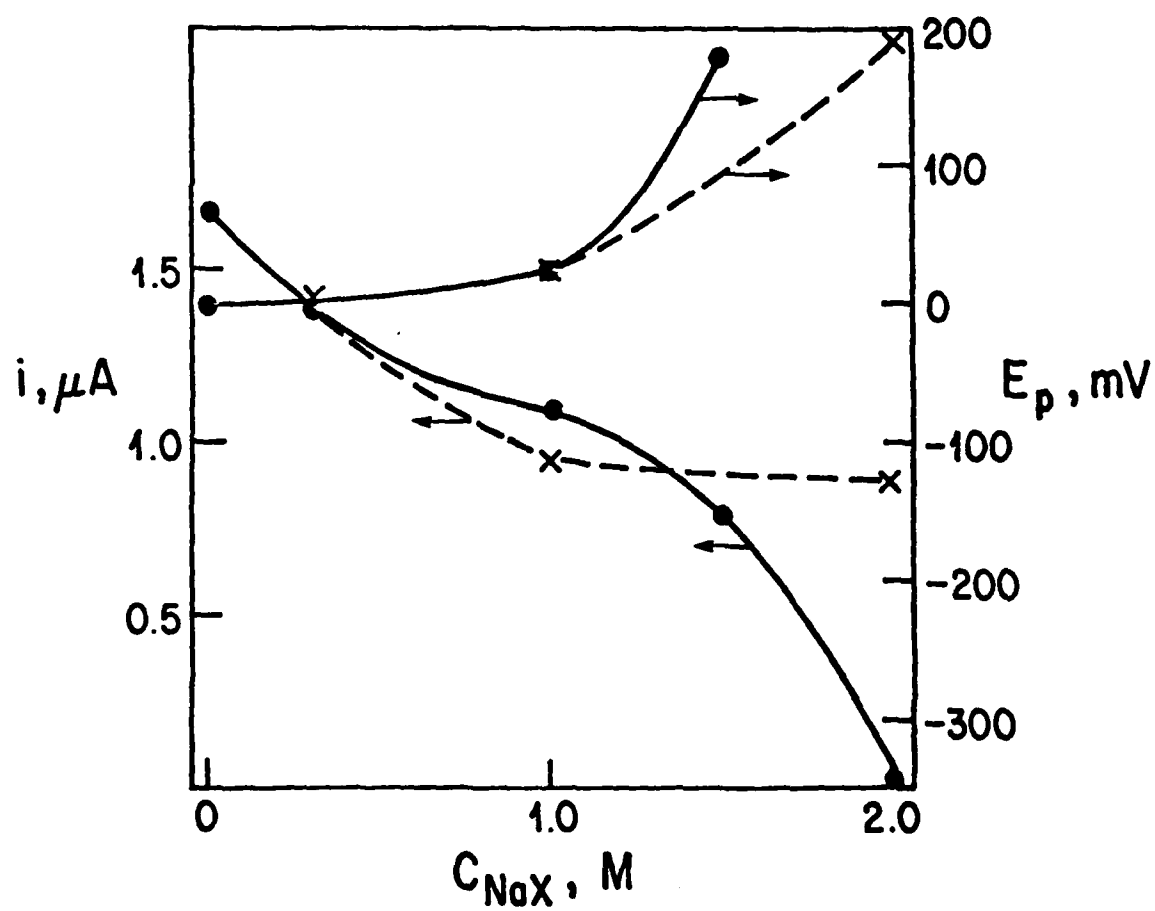


FIGURE 6

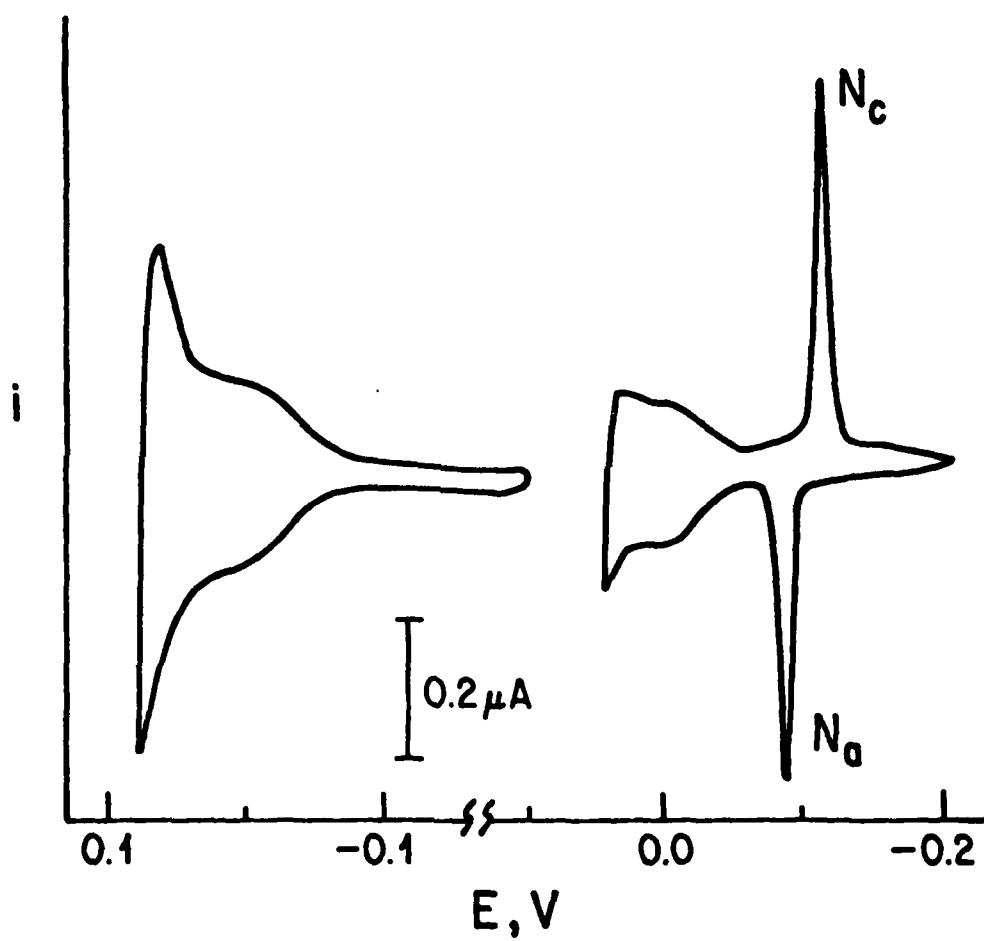


FIGURE 7

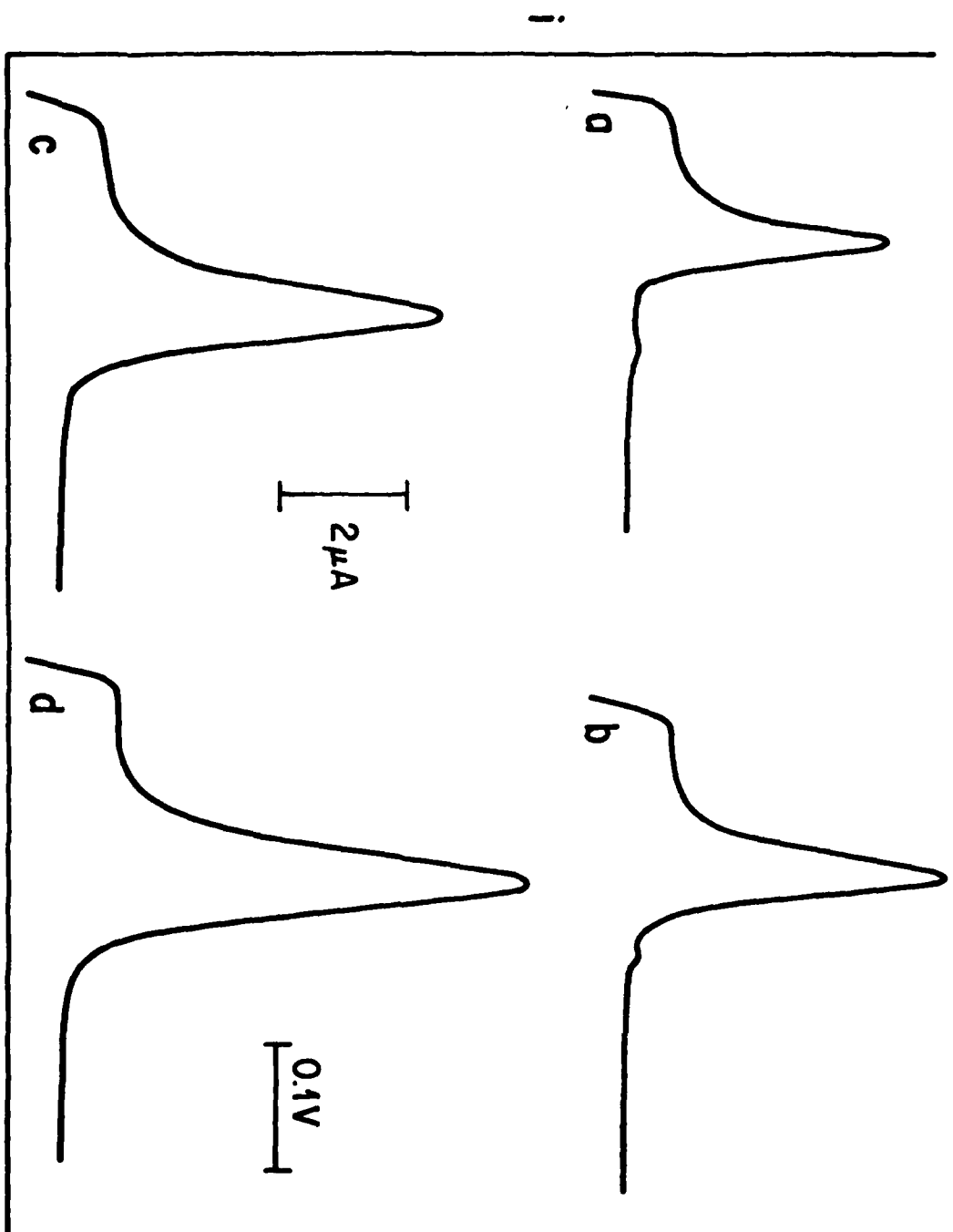


FIGURE 8

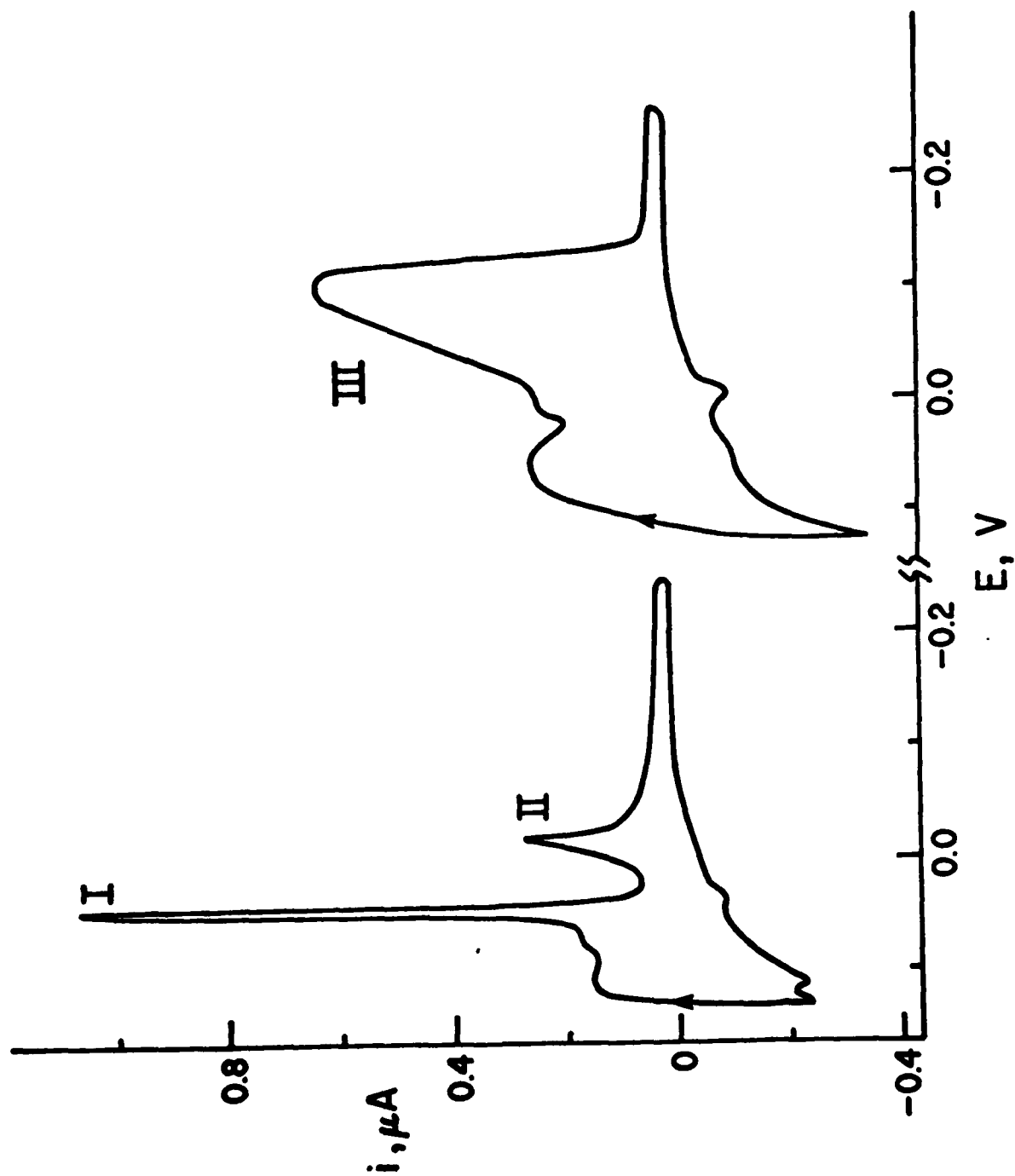
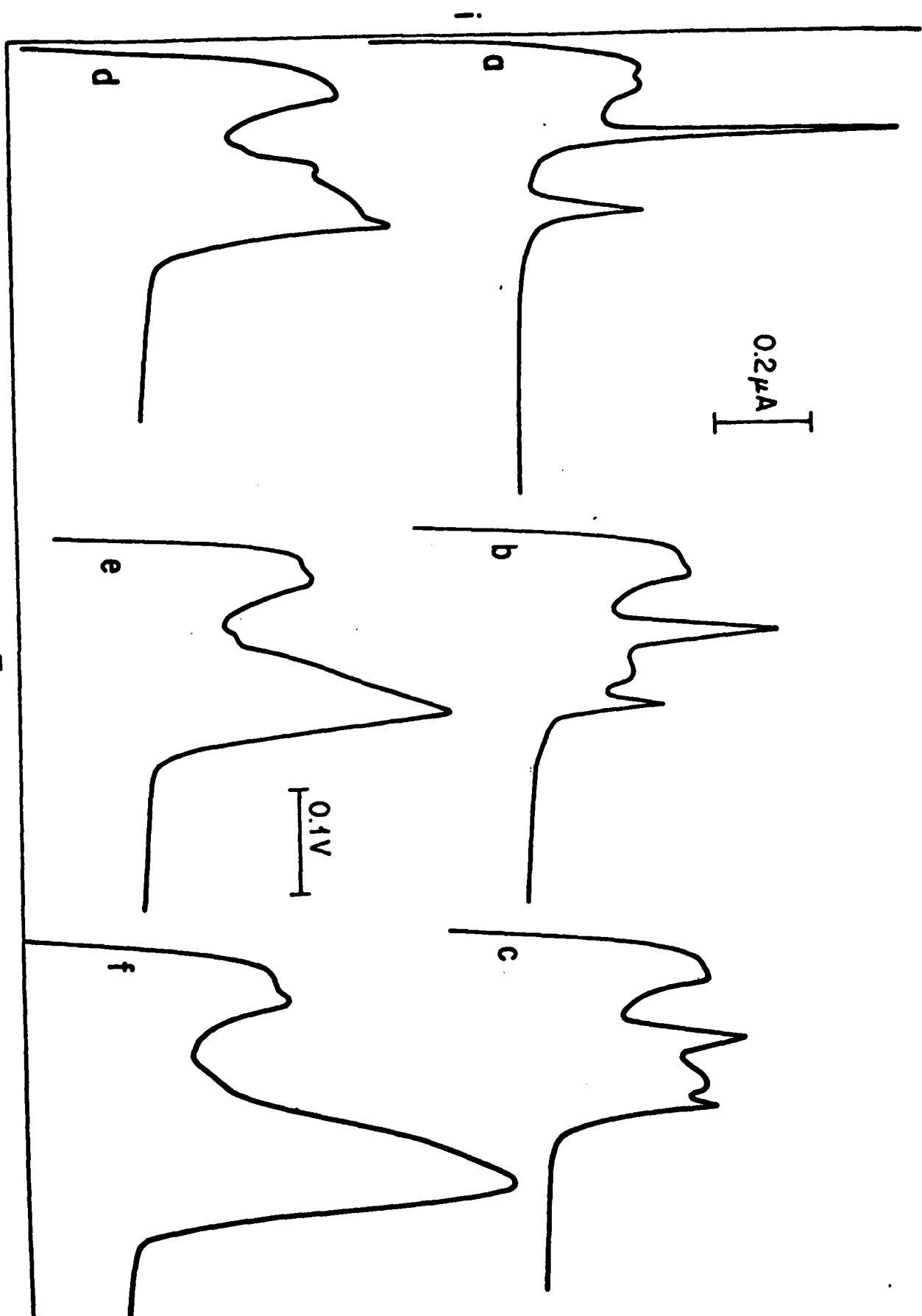


FIGURE 9



E
FIGURE 10

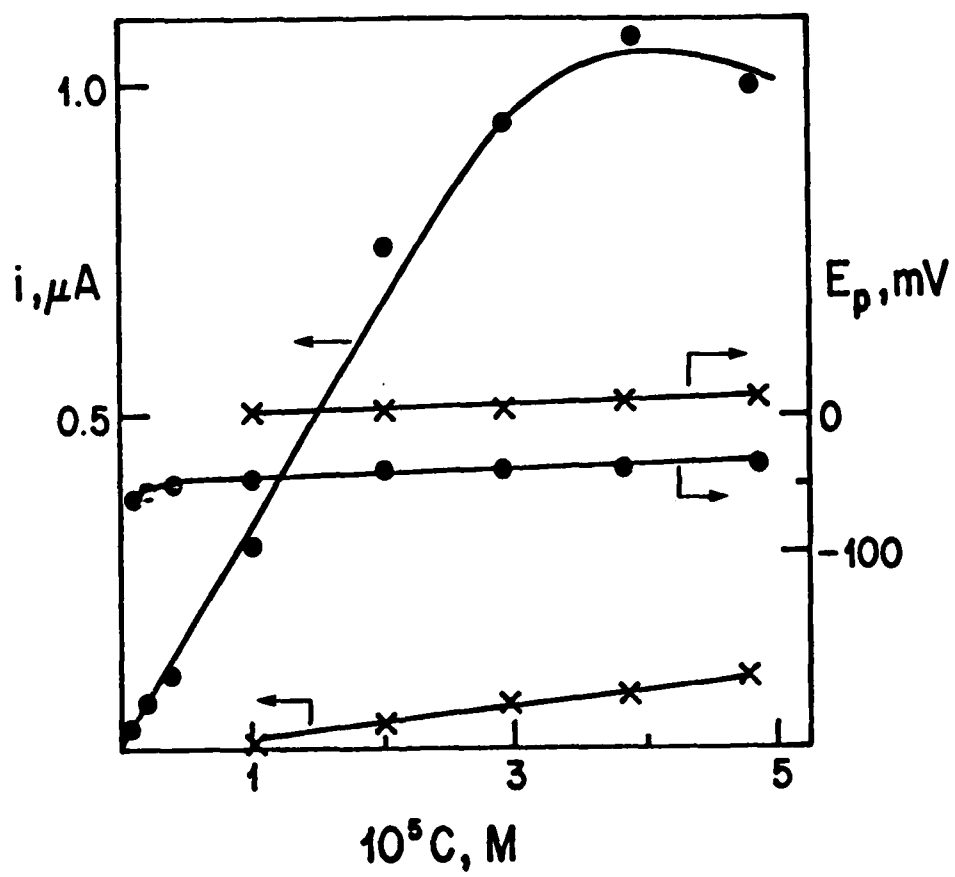


FIGURE 11

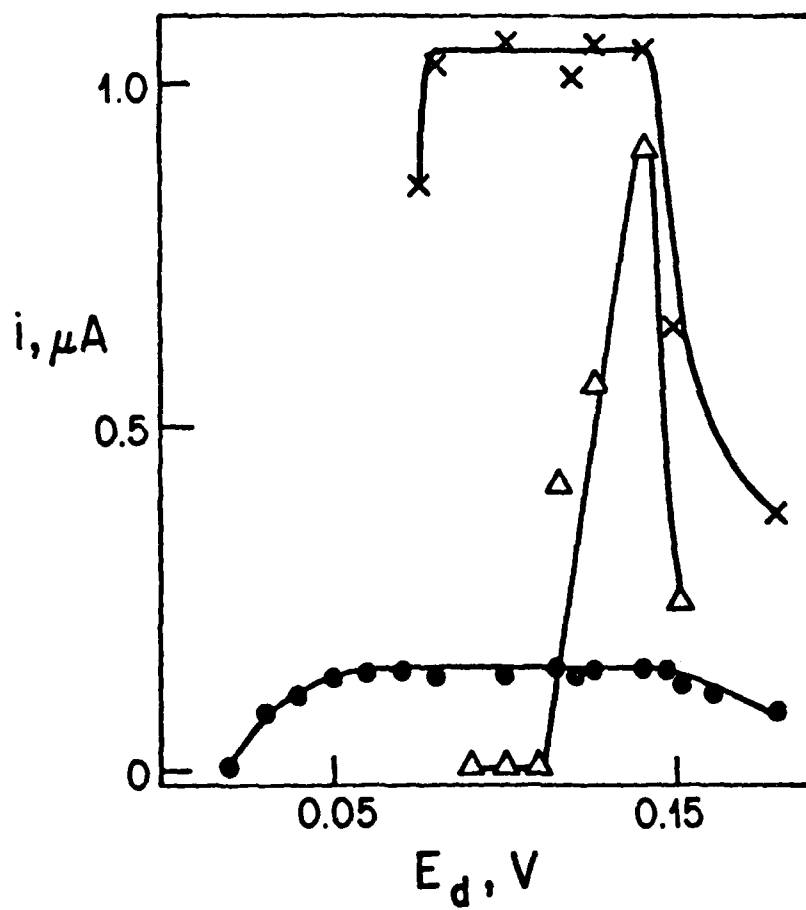


FIGURE 12

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