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A new method of interpretation of cathodic stripping peak current data is proposed where slow adsorption/desorption of the solution species to be determined is involved. Mechanisms of processes taking place during deposition and stripping steps which are complicated by adsorption/desorption are considered. As an example of such a system, the electrodeposition and stripping of a 2-thiouracil silver compound at the rotating silver disk electrode have been investigated at physiological pH = 7.2. Two concentration regions for the determination of 2-thiouracil, which appear in nature as a pyrimidine base [cont'd]

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[handwritten annotations:] micro c/sq. cm ; cu m ; 10 to the -8th power

Cathodic Stripping Analysis Complicated

by Adsorption Processes:

Determination of 2-Thiouracil at a Rotating

Silver Disk Electrode

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Abstract

A new method of interpretation of cathodic stripping peak current data is proposed where slow adsorption/desorption of the solution species to be determined is involved. Mechanisms of processes taking place during deposition and stripping steps which are complicated by adsorption/desorption are considered.

As an example of such a system, the electrodeposition and stripping of a 2-thiouracil silver compound at the rotating silver disk electrode have been investigated at physiological pH = 7.2.

Two concentration regions for the determination of 2-thiouracil, which appear in nature as a pyrimidine base of nucleic acid, have been found. The first region involves microphase deposition which occurs if the total charge passed through the electrode during cathodic stripping of the most easily removed material is less than 70 $\mu C/cm^2$. The second region, for charges greater than 200 $\mu C/cm^2$, corresponds to macrophase stripping. The effect of concentration, potential sweep rate, rotation speed, deposition potential and other parameters on the shape and height of the stripping peaks have been determined.

The lowest concentration of 2-thiouracil determined was 6×10^{-8} mol/dm^3.
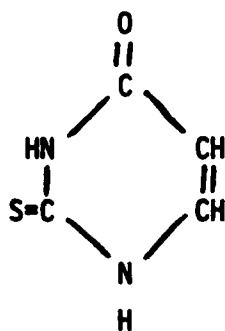
Introduction

Application of the rotating disk electrode for cathodic stripping voltammetry (CSV) is advantageous compared to a hanging mercury or stationary solid electrodes [1,3-6] because of the increased rate of mass transport to the electrode surface and well defined hydrodynamic conditions [2,7,8]. At high electrode rotation speeds it is possible to obtain a very thin diffusion layer adjacent to the electrode and to calculate its thickness [9]. Improved sensitivity can also be obtained as a result of the greater surface area of a solid electrode compared to a dropping mercury electrode. Cathodic stripping voltammetry at a rotating silver disk electrode was recently employed by Shimizu and Osteryoung for determination of sulfide [10]. Although linear-scan voltammetry is the common technique employed for the stripping step, much higher sensitivity can be achieved by applying fundamental a.c. [11-13], second harmonic a.c. [14], pulse polarography [15-22], square wave [23,24], staircase [25] or symmetric double-step waveforms [26].

Voltammetric methods for the determination of organic compounds of biological significance were described by Smyth and Smyth [43]. Thiols and disulfides can be determined by CSV by utilizing the formation of surface films of insoluble mercury-sulfur compounds. Cathodic stripping for a number of substances, among them cysteine and cystine, at mercury electrodes has been published by Florence [27]. The CSV behavior of cysteine/cystine in the presence of cupric ions was investigated by Forsman [28]. The electrochemistry of this system was described by Stankovich and Bard [29].

The electrochemical behavior of 4-thiouracil and its derivatives on mercury electrode was investigated by Wrona et al. [35,36]. Thiouracils are minor components of transfer RNA, and their interactions with metal ions can be of particular biological interest because of the possible role played by metal complexes of thio bases in protein synthesis. 2-thiouracil and its 6-methyl derivative, have been used for treatment of hyperthyroidism in man. It has been found that these compounds block thyroid hormone formation [37].

The structure of thiouracil is:

$$
\begin{array}{c}
O \\
\parallel \\
C \\
HN \diagup \quad \diagdown CH \\
\mid \qquad\qquad \parallel \\
S{=}C \diagdown \quad \diagup CH \\
N \\
H
\end{array}
$$

Thus, an elaboration of an analytical method at physiological pH for the determination of 2-thiouracil, appearing in nature as a pyrimidine base of nucleic acid, seemed useful.

Experimental

Chemicals. Analytical grade 2-thiouracil was obtained from Sigma Chemical Co. Stock solutions of 2×10^{-3} mol/dm^3 2-thiouracil of pH 7 to 8 and in 0.1 M NaOH were prepared independently for each measurements series and were refrigerated in a hermetic vessel. No changes in concentration and voltammetric behavior during a one week storage were found in tests performed using CSV. Buffer stock solutions were prepared from chemicals of reagent grade purity.

Buffer capacity was calculated for each case and was adjusted to be at least 50 times greater than the 2-thiouracil concentration. The solution pH was measured before and after each experiment and showed no significant changes.

Solutions were prepared with deionized water (18 Mohm) obtained using a Milli-Q purification system.

Electrolytic cell and apparatus. A pyrex glass electrolytic cell of 250 cm^3 capacity, equipped with a glass thermostatted water jacket was used. A teflon cell cover had holes for various inserts. A fritted glass tube was used to separate the platinum-foil counter electrode from the main cell compartment. A commercial rotating silver disk electrode mounted on a Model ASR rotator (Pine Instrument Co., Grove City, PA) was used as a working electrode. Rotation speed of the disk electrode was adjusted by changing the voltage supplying the rotator and was stabilized by a negative feedback from a tachometer. The geometric surface area of the rotating disk was 0.442 cm^2. Potentials were measured with respect to a saturated calomel electrode (SCE).

A Model EG&G PARC 173 potentiostat, equipped with a Model 179 digital coulometer and Model 175 universal programmer were used for coulometric studies and voltammetric measurements were performed with an IBM Model 225 Voltammetric Analyzer. A Hewlett-Packard Model 7046 A XY plotter, was used for recording voltammograms. Details of automatic control of the deposition charge will be described elsewhere [38]. This was employed for those experiments where the effect of sweep rate was studied.

Argon was passed through the solution to remove oxygen, and the cell was thermostatted to $\pm$0.1°C.

Experimental procedure. Except for those experiments where the effect of accumulation was studied, the electrode surface was wet polished before each experiment with 0.3 µm alumina, next 0.05 µm alumina (Fisher Scientific Co.) on a polishing cloth, washed with acetone or ethanol and etched in 1 mol dm^{-3} ammonia solution for 30 seconds. The electrode was then washed with deionized water and dried at room temperature and immersed into the deaerated background solution, where it was conditioned at potentials negative of -450 mV vs. SCE. Argon was again bubbled through the solution for 20 minutes, which was then covered by an argon purge (the oxygen reduction wave occurs at potentials where the CSV stripping peaks are examined, Figure 1).

After background stripping voltammograms were obtained, aliquots of 2-thiouracil standards were introduced and the resulting solution was mixed by argon bubbling and electrode rotation. The potential was then stepped to the deposition potential in the range 0 to 180 mV vs. SCE. This resulted in deposition at the electrode surface of insoluble silver compounds. The charge passed during deposition was measured. The compound was then stripped by scanning the potential in a cathodic direction: LSCSV (linear scan cathodic stripping voltammetry) or DPCSV (differential pulse cathodic stripping voltammetry) were used. The electrode was rotated during both deposition and stripping.

RESULTS AND DISCUSSION

Theoretical Treatment

In general, the height of the stripping peak current, i_p, depends on the product of the potential sweep rate, v, and the electric charge, Q, passed during deposition of the surface film. For a simple stripping reaction:

$$MeX + ne \rightleftharpoons Me + X^{n-}_{(aq)} \tag{1}$$
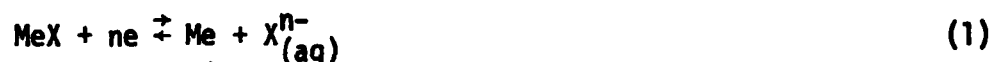
and

$$i_p = bvQ \tag{2}$$

where b is a proportionality coefficient which can be determined for stripping of a microphase, generally 1 to 2 monolayers, on the basis of the theory developed by Brainina [39]. For a rotating disk electrode and diffusion controlled deposition one obtains:

$$i_p = kv\omega^{1/2}C\,\tau_d \tag{3}$$

The values of b and k depend on the reversibility of the system under investigation. For a reversible system b is given by the equation:

$$b = nF(RT)^{-1} \exp\{RT(nFv\tau_d)^{-1} -1\} \tag{4}$$

and for irreversible stripping:

$$b = \alpha_c nF(RT)^{-1} \exp\{\frac{RTk_s\gamma}{\alpha_c v} \exp[\frac{-(E_d-E^\theta)\alpha_c nF}{RT}] -1\} \tag{5}$$

where τ_d is the deposition time, k_s the heterogeneous standard rate constant, α_c the cathodic charge transfer coefficient, E_d the deposition potential, E^θ the standard potential, and γ the parameter describing

properties of the deposited substance as in equation (6) for "a" which was assumed by Brainina as the activity of the substance on the electrode surface:

$$a = a_0(1 - \exp\{-\gamma Q\}) \tag{6}$$

where a_0 stands for the activity of the macrophase. When the stripping reaction is more complicated and involves the formation of intermediates, equation (6) no longer holds. The expressions for i_p for a few reaction mechanisms were derived and are collected in two monographs [39,40]. If the reaction mechanism is not known, equation (2) can be assumed as a basis for an empirical determination of the parameter b; the value of b may change with the experimental conditions.

In the analysis of many organic species, the solution species to be determined, say X^{n-}, as in equation (1), may adsorb on the electrode surface and then CSV may not give accurate results. Reasons for this are presented below.

Let us consider a sub-monolayer deposit formed as a result of a fast surface reaction:

$$MeX + ne \underset{\text{deposition}}{\overset{\text{stripping}}{\rightleftarrows}} Me + X^{n-}_{(ads)} \tag{7}$$
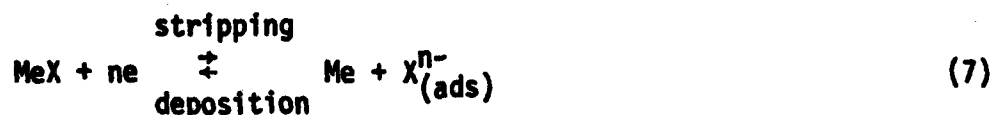
for which the Nernst equation can be written as:

$$E = E^{\theta} - RT \, (nF)^{-1} \, \ln(a_{X_{ads}} a_{Me}/a_{MeX}) \tag{8}$$

where a's are the surface activities. The total amount of charge (in electrical units) of the electroactive species is equal to the sum of three components Q_X, Q_{Me} and Q_{MeX}.

Model I. In this analysis it is initially assumed that charge passed in the deposition process equals that during the stripping process.

Suppose, in the conditioning step, $Q_{MeX} = Q_{MeX}^O$ and $Q_X = Q_X^O$; i.e., a certain amount of MeX (Q_{MeX}^O), is initially present at equilibrium, together with an amount Q_X^O, of X^{n-}, on the electrode surface. Then, during the deposition step in which charge Q_d passes at the electrode surface, Q_{MeX} will change to the value $Q_{MeX}^O + Q_d$ by conversion of both adsorbed X^{n-} (Q_X^O) and X^{n-} which diffuses to the electrode surface, reacting to form MeX. Q_X will be changed to $Q_X^O - Q_d$ by conversion of the adsorbed X^{n-} to MeX, or to zero if it all is converted. During the stripping step charge Q_d is again passed, but in the opposite sense, the electrode restored to its initial condition, and the peak height is proportional to Q_d.

Since this model assumes that the surface reaction, (Equation (7)), forming MeX is much faster than the deposition from solution, (Equation (1)), if $Q_d \leq Q_X^O$ then the peak height will not be proportional to the concentration of X^{n-} in solution since most of Q_d during deposition will go to transferring X_{ads}^{n-} to MeX.

If Q_d is greater than Q_X^O, only the difference $Q_d - Q_X^O$ gives a component (signal) to the cathodic peak proportional to $C_X n-$. That is, coulombs passed during the deposition step, Q_d, result from film formation as a result of MX formed from $X_{(ads)}$ and $X_{(soln)}$. The signal-to-noise ratio is $(Q_d - Q_X^O)/(Q_X^O + Q_i)$ when Q_i is "background", and is small if Q_d is not significantly greater than Q_X^O. This means that although we can observe high cathodic peaks due to the reduction of MeX, under these

conditions only a part of the peak height delivers information about the concentration of X^{n-} in the solution.

Suppose we now assume that the desorption step

$$X^{n-}_{(ads)} = X^{n-}_{(aq)} \tag{9}$$

does not take place. This results in accumulation of $X^{n-}_{(ads)}$ on the electrode surface if the experiments are repeated with increasing deposition time under conditions where the electrode is not cleansed after each stripping experiment. We are considering here increasing the deposition time, τ_d, and associated with each deposition time will be a charge, $Q_{d(1)}$ for the first experiment, $Q_{d(2)}$ for the second, etc., which will be composed of charge arising from the formation of MX as a result of X^{-n}_{ads} and X^{-n} which diffuses to the electrode to react. After the first stripping experiment (for $Q_{d(1)} > Q^0_{X(0)}$), the charge $Q_{X(1)}$ at the conditioning potential will be greater than $Q^0_{X(0)}$ by the value $Q_{d(1)} - Q^0_{X(0)}$ and after j experiments it will be:

$$Q^0_{X(j)} = Q^0_{X(0)} + \sum_{i=1}^{j} (Q_{d(i)} - Q^m_{X(i-1)}) = Q_{d(j)} \tag{10}$$

Equation (10) describes a maximum effect of accumulation, i.e. when no desorption of $X^{n-}_{(ads)}$ from the electrode takes place. If the rate of the desorption step (9) is considered then equation (10) can be expressed as:

$$Q^m_{X,j} = Q^m_{X,0} + \sum_{i=1}^{j} (Q_{d,i} - Q^m_{X,i-1} - \Delta Q^{des}_{X,i}) = Q_{d,j} - \Delta Q^{des}_{X,j} \tag{11}$$

where the terms $\Delta Q^{des}_{X,i}$ stand for the electric charge accompanying the desorption of $X^{n-}_{(ads)}$. Equation (11) shows how the electrode history changes the initial charge Q_X at the conditioning potential from $Q^0_{X(0)}$

to $Q_{X(j)}^0$ under the condition of progressively increasing deposition time.

Model II. Another mechanism can be considered which results in accumulation of $X_{(ads)}^{n-}$ on the electrode surface but gives a stripping peak whose height is proportional to the solution concentration $C_X n-$. In this mechanism, reactions (1) and (7) are considered to occur in parallel. Reaction (1) prevails during deposition and (7) during stripping, i.e., the film forms solely as a result of the reaction of X^{n-} from solution but when it is reduced X^{n-} is maintained at the electrode. For the charge $Q_{X,j}^m$ we then obtain:

$$Q_{X,j}^m = Q_{X,0}^m + \sum_{i=1}^{j} (Q_{d,i} - \Delta Q_{X,i}^{des}) \qquad (12)$$

where the term $\Delta Q_{X,i}^{des} = 0$.

In both mechanisms repetition of stripping experiments with the same deposition charge, Q_d, leads to unchanged stripping peaks (provided that $\Delta Q_{X,i}^{des} = 0$). Note that for the first mechanism, constant charge does not imply constant deposition time, whereas in the second instance, constant deposition time is implied. However in the second mechanism the electrode is poisoned more and more by $X_{(ads)}^{n-}$ and repetition of stripping experiments lead to a current peak change due to saturation effects. Thus, reproducibility of stripping peak current for the same Q_d is not proof that accumulation does not occur. Note that for fixed deposition time the first mechanism would result in increasing i_p values on stripping due to the accumulation of X_{ads}^{n-} at the electrode surface, and its oxidation to MeX, followed by reduction during the stripping step.

A diagnostic criteria for stripping complicated by adsorption-
desorption processes of the electroactive species to be determined
involves performing consecutive stripping experiments first with
progressively increasing deposition times followed by progressively
decreasing deposition times. Stripping is carried out after each
deposition, and the electrodes are not physically cleansed between runs.
Note that this might correspond to the situation where cathodic stripping
techniques are employed in electrochemical detectors in liquid chroma-
tography.

If no accumulation occurs, plots of the stripping peak current
versus the deposition time give one straight line. The maximum effect
of accumulation effect for Model I for initially clean surface ($Q = 0$)
is shown in Figure 2. In Figure 2 it is assumed that no desorption
takes place; hence the stripping peak increases by the amount of
material previously deposited. For instance, point d is the sum of
points a and b, and point e is the sum of points d and c. The upper
curve (2 in Figure 2), i.e. for decreasing τ_d, lies above the forward
line. If the rate of desorption is taken into account, the forward line
(curve 1) will tend to line 3 characteristic of ideal stripping behavior
without accumulation, and at the same time, the upper curve 2 will move
down and in ideal cases will trace the forward line. When the accumulation
process proceeds according to Model II, no effect (curve 3) is expected
until saturation phenomena are involved.

The case of Model II is illustrated in Figure 3. The curves 1-3
show increasing saturation effect for increasing (from curve 1 to 3)
initial surface coverage Q_χ. All the curves pass through the origin but

the linear current response is significantly diminished at higher initial coverages Q_X.

The influence of the initial values of Q_X on the relation between the peak current and the deposition time is much stronger when the surface reaction is fast under deposition conditions, i.e. in the case of Model I. This situation is presented in Figure 4, where the curves 2 to 6 are drawn for increasing initial coverages Q_X. It is assumed here that initial coverage Q_X is the same for all points on a given curve. For $Q_X > 0$, the stripping peak currents have non-zero values but they do not depend on the deposition time (region over the dotted line) until τ_d reaches some critical value at which $Q_d - Q_X$ is comparable with Q_X (region between the dotted line and curve 1). When $Q_d - Q_X \gg Q_X$, the dependence of $\log i_p$ vs $\log \tau_d$ is linear.

Note that the accumulation Model I, although here described in terms of charge, must reflect a similar behavior if τ_d is considered. For example, consider the case of very low concentration of material in solution where a fixed deposition time is employed. If the material formed on the electrode is reduced without desorption, a second experiment, performed for the same deposition time, would have a stripping peak twice the height of the first, but equation 3 would not be obeyed, since it refers only to material which must diffuse to the electrode to react. If the second experiment were performed for, say, 1/5 of the time of the first, the peak current would be six times greater than it should be. That is, it would change 20 percent from the first experiment, but would not give information, based on equation 3, relating the peak current to the concentration of X^{n-} in solution. This would correspond to the region between the two straight lines of Figure 4.

Experimental Evidence of Adsorption of 2-thiouracil on Silver Electrode

It was observed that the LSV characteristics of a silver electrode immersed in 2-thiouracil solutions show a decrease in the hydrogen discharge wave that can only be explained by a blocking action of adsorbed 2-thiouracil molecules. The adsorption process is relatively slow but can be "activated" by deposition of 2-thiouracil silver compound that occurs at sufficiently positive electrode potentials, +140 to +180 mV vs. SCE at pH 7-8 to 0 mV in alkaline solutions (these potentials also depend on the 2-thiouracil concentration) and subsequent cathodic stripping of the deposit. After stripping, some 2-thiouracil remains on the electrode surface and influences the following deposition-stripping experiments.

Figure 5-a shows i_p/i_p^0 vs τ_d/τ_d^0, where i_p^0 and τ_d^0 correspond to the peak current and deposition time for monolayer coverage. These values were experimentally obtained for the first stripping peak at approximately -200 mV (Figure 5) and correspond to the point where the peak current on stripping does not increase with further deposition time. τ_d^0 for the condition of the experiments is 90 seconds. The concentration of 2-thiouracil was 6.6×10^{-7} mol dm^{-3} at pH 6.8. The electrode was not cleansed between runs. The accumulation-hysteresis method discussed above can be used to verify this observation. When the deposition time increases, the stripping peak current increases linearly. However, when these experiments are continued at decreasing deposition times, the peak current values deviate above the forward solid line indicating an accumulation mechanism with a slow desorption step.

Similar experiments performed in alkaline solutions showed no hysteresis (Figure 5-b), and the departure from linearity takes place at a point where surface coverage approaches a monolayer.

For an explanation of this behavior, consider that the first dissociation constant of 2-thiouracil, pK_1, is 7.75 and the second is ~12.7 [41]. Thus, we can assume that in the lower pH region, 2-thiouracil (H_2TUR) adsorbs as the neutral species or an anion. During formation of the 2-thiouracil silver compound a hydrogen atom is lost.

$$Ag^0 + H_2TUR_{(aq)} - e = AgHTUR + H^+ \qquad (13)$$
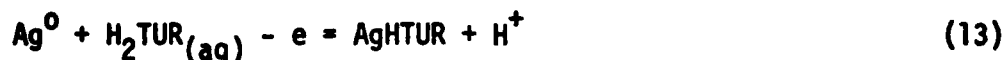
However, it is difficult to determine whether the adsorbed species remaining at the electrode surface are the neutral molecule $H_2TUR_{(ads)}$ or an anion $HTUR^-_{(ads)}$. The effect of pH is also a variable in building thicker, multilayer films of the 2-thiouracil silver compound. In the low pH region (pH < 8.5) we obtained deposits (second stripping peak) whose thickness was over 40 monolayers, but only a few monolayer deposits would be formed in alkaline solutions for concentration of KOH greater than 0.1 mol dm^{-3}. It is probable that hydrogen bonds play an important role in the structure of deposits [42].

Cathodic Stripping Voltammetry

1) <u>Higher concentration region.</u> The equilibrium potential of a
silver electrode covered with a sparingly soluble silver salt becomes
more negative as the concentration of the anion of this salt in solution
increases. The higher the concentration of 2-thiouracil in solution,
the greater the available deposition potential range and the lower the
risk of silver oxide formation. Typical stripping voltammograms obtained
for different concentrations of 2-thiouracil are presented in Figure 6.
Peak I in Figure 6 represents a surface layer that grows to a monolayer
thickness; experiments performed at varying concentrations of thiouracil
show that this peak forms initially and is then followed by peak II at
higher concentrations of thiouracil or greater electrode coverage -
i.e., more film formed on the surface (38). The deposition potential E_d
was +150 mV vs. SCE. The background voltammograms in solutions not
containing thiouracil were examined for deposition times τ_d up to 6
minutes and they showed no current increase in the region of the stripping
peaks. The oxide stripping peaks appear if a more positive deposition
potential is applied and no diffusion limited stripping peak for the
formation of the silver-thiouracil is achieved. The diagram in Figure 7
illustrates the region of overlapping oxide deposition and the 2-
thiouracil silver (I) compound formation. This concerns the peak II on
Fig. 6.

The concentration dependence of the stripping peak current (peak
II, Figure 5) is presented in Figure 8. Such a dependence is typical of
pyrimidine derivatives and, in general, for nucleosides and nucleotides
forming sparingly soluble compounds with mercury [30]. Unfortunately,

none of these species has been investigated on a silver electrode. However, the same reasons for a relatively narrow region of determination may also hold for silver electrodes. Estimation of film thickness was possible under the assumption that the charge corresponding to a mono-layer is not very different from those of other pyrimidine derivatives which were determined from capacitance data obtained on mercury electrodes [42]. The value for uracil which is quite similar in structure and size to the 2-thiouracil seems to be the best approximation. In higher concentration regions (perpendicular orientation of uracil molecules on the electrode surface) the area occupied by one molecule is 63 $\overset{\circ}{A}{}^2$ (i.e. 6.3×10^{-5} cm^2). Coulometric determinations of the cathodic charge consumed during stripping (peak II, Figure 6) show that the deposited films are multilayer macrophases, from 3 monolayers up to about 40 monolayers in the neutral pH region. A more detailed description of the deposited film structure will be presented elsewhere [38]. Physico-chemical data for bulk phases of 2-thiouracil silver compounds do not exist. If multilayer deposits are considered, a possible explana-tion of an upper limit in the increase of stripping peak (see Figure 8) with increasing concentration may be that based on (1) a weak adhesion of the deposited films to the electrode surface, (2) relu· ɾvely high solubility of the deposit so that its chemical dissolution cannot be ignored and (3) low electrical conductivity of the film causing an increase of the ohmic overvoltage.

The determination of 2-thiouracil by LS CSV has been examined in KOH solutions (Figure 9). Very good results were obtained in 10^{-3} mol dm^{-3} KOH, where the charge calculated by integration of the area under

stripping peak current indicates formation up to 40 monolayers of the 2-thiouracil silver compound. Excellent reproducibility has been found in 0.3 mol dm^{-3} KOH, but the stripping peak stopped increasing after deposition of a few monolayers of the salt.

A comparison of the anodic charge, Q_d, passed during the deposition step and the charge consumed during stripping, Q_c, showed that only about 1/3 of the anodic charge is used for building the film which is then electrochemically stripped. The difference $Q_d-|Q_c|$ is mainly due to the anodic dissolution of silver. In case of thicker films, as discussed earlier, some part of this difference may correspond to mechanical stripping of the deposit, though chemical dissolution may also play some part.

2) Sub-monolayer deposits. At the 2-thiouracil concentrations lower than about 7×10^{-6} mol/dm^3 and at high rotation speed of the RDE, one broad stripping peak is observed with the peak potential -50 mV to -200 mV (dependent on the experimental conditions) peak I, Figure 6. Typical linear scan stripping voltammograms are presented in Figure 10 for 2-thiouracil, the concentration 8.8×10^{-7} mol/dm^3 and a rotation rate of 10,000 rpm. As follows from coulometric measurements, the deposit forms a submonolayer film of the 2-thiouracil silver salt. Concentration dependence of the peak current is linear until the electrode surface becomes entirely covered by a full monolayer. This dependence is shown in Figure 11 for ω = 10,000, rpm and v = 100 mV/s.

Other characteristics for LPS CSV were also examined. In particular, an expected linear relation between the peak current and the potential

sweep rate was observed at a stationary disk electrode as well as at higher rotation speeds of the RDE. An example illustration of these relations is given in Figure 12 for stripping peak II, Figure 6. The dependence of the peak current on the potential scan rate is linear indicating a reaction of surface reactant.

Although the mechanism of the cathodic reduction of the film formed is rather complicated and probably more than one reaction occurs (the reaction mechanism and effect of other parameters on the stripping characteristics will be discussed elsewhere [38]), the linear dependence i_p-C_b may be useful for determination of 2-thiouracil at low concentrations.

Experimental data used for determination of parameter "k" in eq. (3) for submonolayer deposits of 2-thiouracil silver compound are presented in Table I. The parameter "k" was determined in the concentration range (0.62-25.7) x 10^{-10} mol cm^{-3} and its average value is 7.07.

Comparison of the analytical concentration of 2-thiouracil with those calculated from eq. (3) is shown in Table II.

Table I

Determination of the coefficient k in eq. (3) for submonolayer deposits of 2-thiouracil silver compound.

C_{TUR}, 10^{-10} mol cm^{-3}	E_d, mV vs. SCE	τ_d, s	$\bar{\omega}$, rpm	k	a_c, 10^{-6}C
0.62	150.9	540	10000	–	15.5
4.40	150.2	180	5000	7.03	26.0
4.40	150.2	120	5000	7.28	17.3
8.80	150.3	90	4000	7.15	23.3
8.80	150.3	150	2000	6.89	27.4
10.3	149.4	80	4000	7.05	24.2
18.5	150.8	105	1000	6.97	28.5
25.7	153.2	60	1000	7.12	22.6

Conditions: pH = 7.2, temp. 35°C, v = 100 mV/s

C_{TUR} stands for concentration of 2-thiouracil

Table II

Comparison of the analytical concentration of 2-thiouracil (C_{TUR}^{*}) with that calculated ($C_{TUR}^{calc.}$) from the equation (3) for k = 7.07.

C_{TUR}^{*}, 10^{-10} mol cm^{-3}	Q_c, 10^{-6}C	τ_d, s	i_p, μA	$C_{TUR}^{calc.}$, 10^{-10} mol cm^{-3}
0.62	15.8[a]	600	0.80[a]	0.65[a]
1.80	22.9	540	1.14	1.85
4.40	24.7	240	1.25	4.55
8.80	24.3	120	1.21	8.81
15.6	25.2	70	1.19	14.9
31.9	29.3	40	1.41	30.8

Conditions: pH = 7.3, E_d = +160 mV vs. SCE, v = 100 mV/s, $\bar{\omega}$ = 2500 rpm.

[a] C_{TUR} determined from the calibration curve, $\bar{\omega}$ = 10000 rpm.

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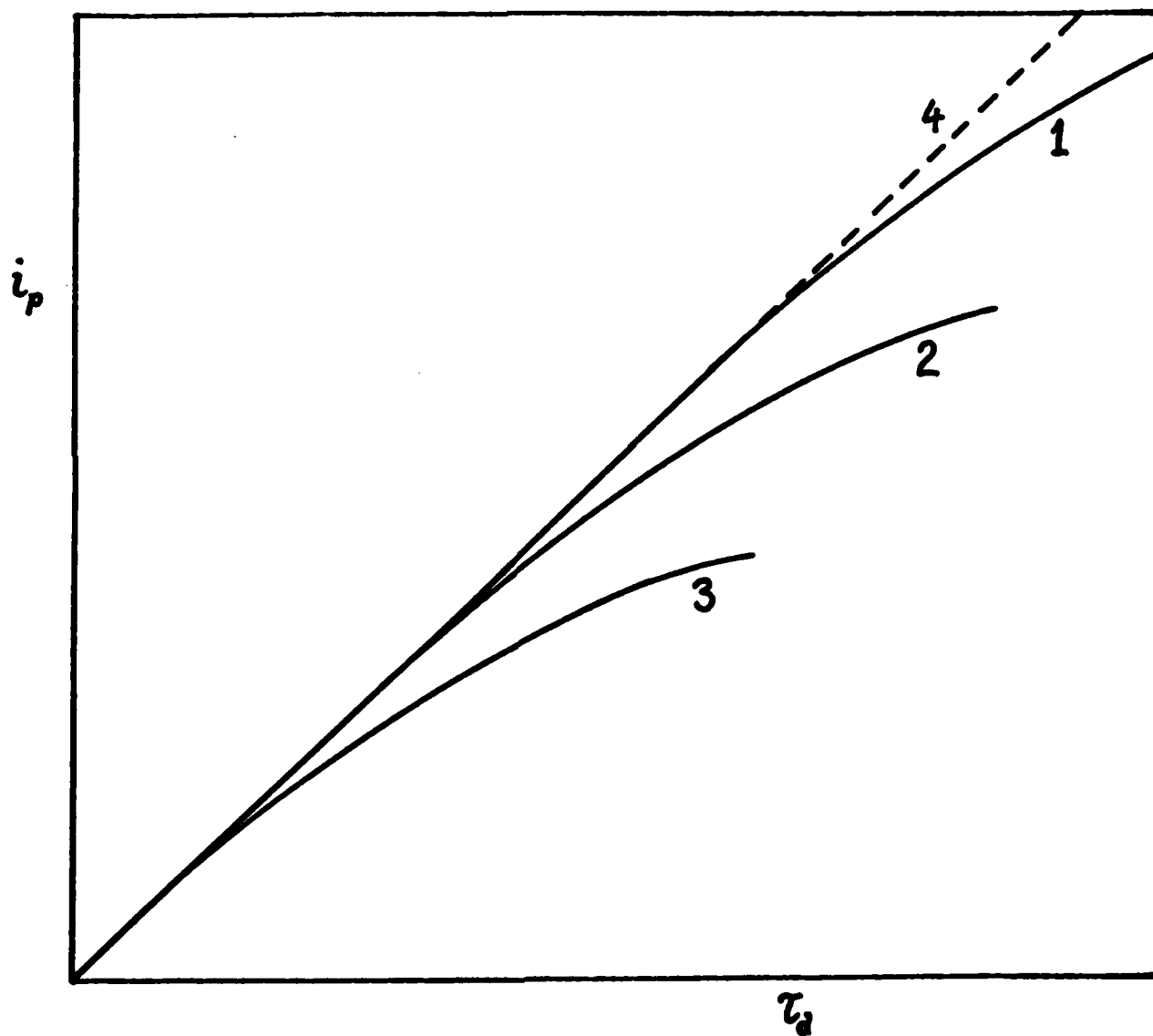## Credit

Figure Captions

Figure 1.   Background LS CSV characteristic (curve 1) and oxygen
               reduction wave (curve 2) obtained in 0.1 NH_4NO_3 buffer
               of pH 7.8 with E_d = +166.4 mV vs. SCE; τ_d = 300 s; v = 200 mV/s.

Figure 2.   Schematic representation of accumulation effects in stripping
               analysis which correspond to Model I (curves 1,2) and Model II
               (curve 3). Stripping peak currents i_p and deposition times
               τ_d are in arbitrary units; for other conditions see text.

Figure 3.   The dependence between i_p and τ_d for accumulation model II
               when surface saturation is reached; increasing initial
               surface coverage Q_X from curve 1 to 3. Curve 4: ideal
               behavior.

Figure 4.   The log i_p - log τ_d plot for Model I with slow desorption.
               Initial Q_X constant for particular curves; increasing values
               of Q_X for curves from 2 to 6. Curve 1: ideal behavior.

Figure 5.   Dependence of the ratio of the stripping peak current i_p to
               $i_{p,o}$ (corresponding to monolayer deposit) on the deposition
               time τ_d divided by the deposition time necessary for deposition
               of monolayer film (a) and on the deposition time τ_d (b) for:
               (a) microphase stripping, c = 6.6 x 10^{-7} mol cm^{-3}, pH = 6.8,
               $E_{cond.}$ = -500 ml vs. SCE, v = 100 mV/s; (b) macrophase,
               C = 4.1 x 10^{-5} mol/dm^3, pH = 11.8, $E_{cond.}$ = -1000 mV vs. SCE,
               v = 100 mV/s at 10000 rpm.

Figure 6.   The LS CSV characteristics for multilayer deposits of the
               2-thiouracil silver compound. Concentration of 2-thiouracil
               C x 10^{-5} (mol dm^{-3}): (1) 8.2, (2) 10.5, (3) 12.7, (4) 14.8;
               E_d = +147.9 mV vs. SCE, ω = 2500 rpm, v = 100 mV/s, pH = 7.28,
               τ_d = 40s.

Figure 7.   Dependence of the stripping peak current i_p on the deposition
               potential E_p, showing region of silver oxide formation; pH =
               8.23, concentration of 2-thiouracil: 1.62 x 10^{-5} mol dm^{-3};
               τ_d = 90 s; v = 50 mV/s, ω = 1500 rpm.

Figure 8.   Dependence of the peak current at the stripping peak potential (peak II, Figure 6) on the concentration of 2-thiouracil in the solution. E_d = +140 mV, τ_d = 60 s, v = 50 mV/s, pH = 7.8, ω = 500 rpm.

Figure 9.   The LS CSV characteristics obtained for the multilayer deposits of 2-thiouracil silver compound (a) in solution: 5×10^{-4} mol dm^{-3}, 2-thiouracil + 10^{-3} mol dm^{-3} KOH, pH = 7.83; E_d = 165 mV vs. SCE; v = 20 mV/s; $\tau_{(s)}$: (1) 20, (2) 50, (3) 80, (4) 100, (5) 140, (6) 180. (b): linear potential scan voltammograms obtained in the same solution at v = 100 mV/s, τ_d = 200 s, E_d = 160.4 mV vs. SCE.

Figure 10.   Effect of the potential scan rate v on the LS CSV characteristics; v (mV/s): (1) 10, (2) 20, (3) 30, (4) 40, (5) 50, (6) 60, (7) 80, (8) 100, (9) 120, (10) 140, (11) 160, (12) 180, (13) 200, (14) 220, (15) 250, (16) 275, (17) 300. Concentration of 2-thiouracil: 8.8×10^{-7} mol/dm^3; pH = 7.23; ω = 10,000 rpm; E_d = +180.2 mV vs. SCE,

Figure 11.   Concentration dependence of the total current at the stripping peak potential for submonolayer deposits, pH = 7.17, E_d = +140.8 mV vs. SCE, τ_d = 600 s, ω = 10,000 rpm, v = 100 mV/s.

Figure 12.   Effect of the potential scan rate on the stripping peak current (peak I, Figure 6) obtained in 1.62×10^{-5} mol dm^{-3} solution of 2-thiouracil at different rotation speeds of the RDE: ω = (1) 3000, (2) 1200, (3) 600, (4) 200 rpm, τ_d = 90 s.
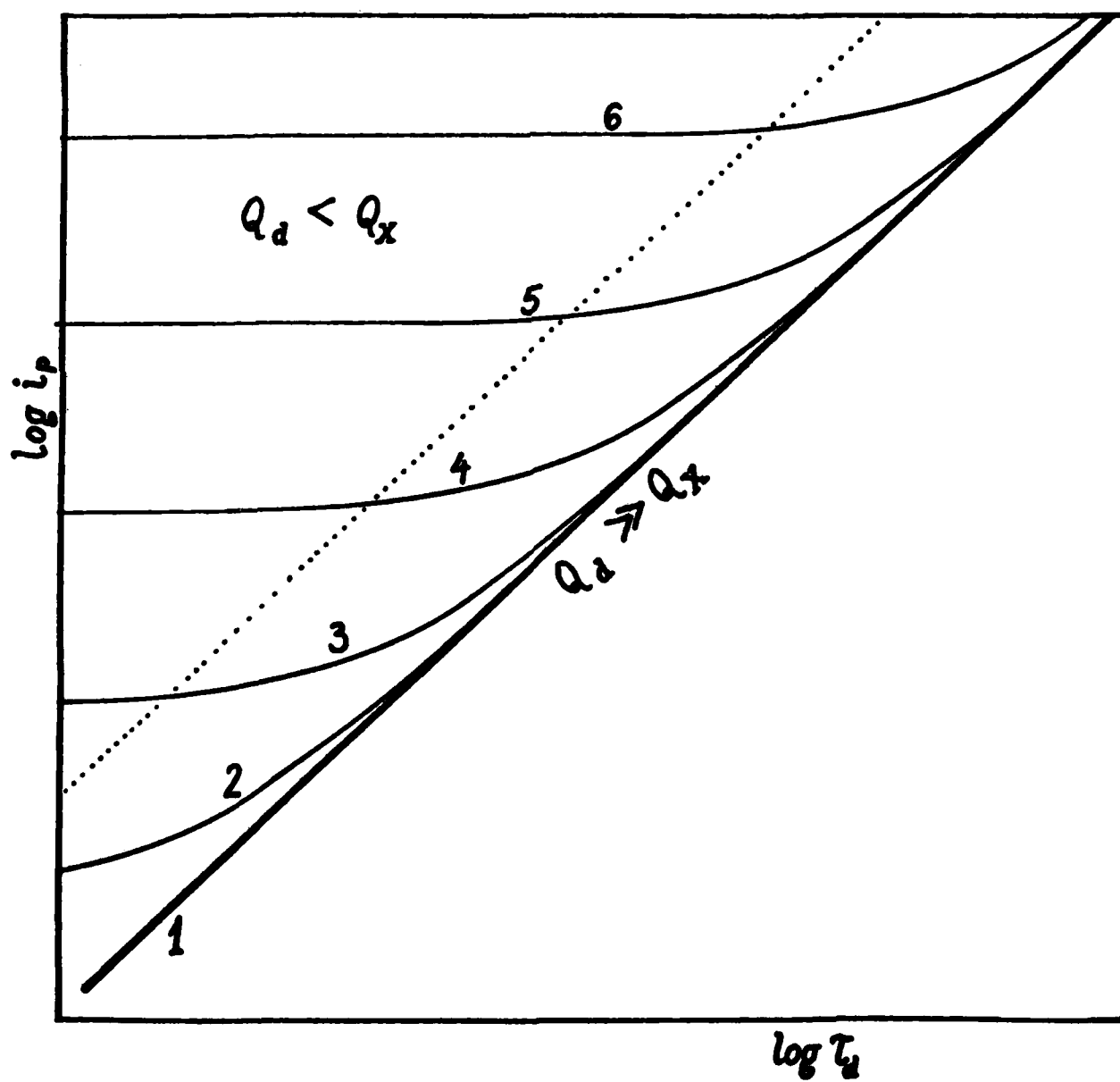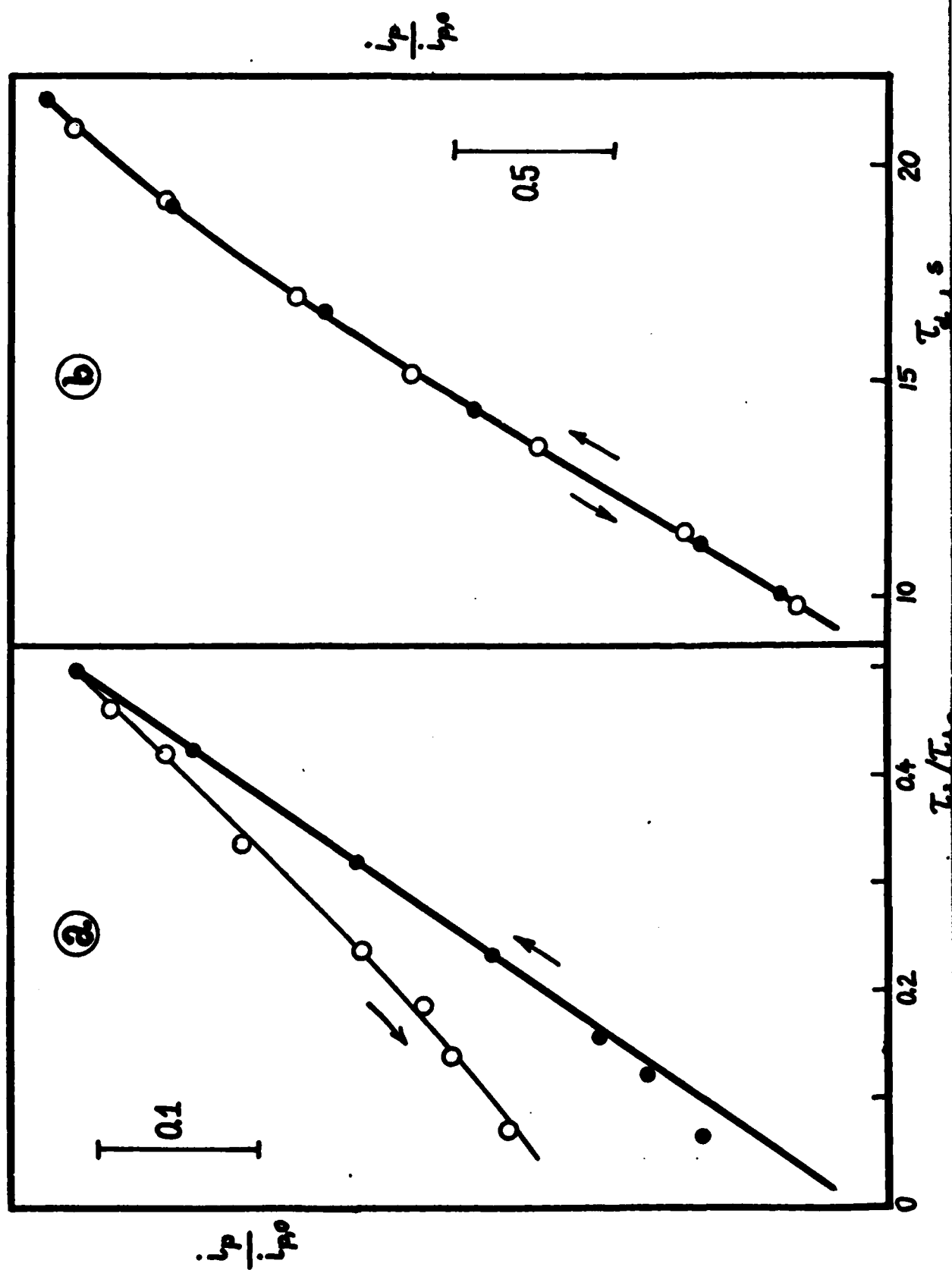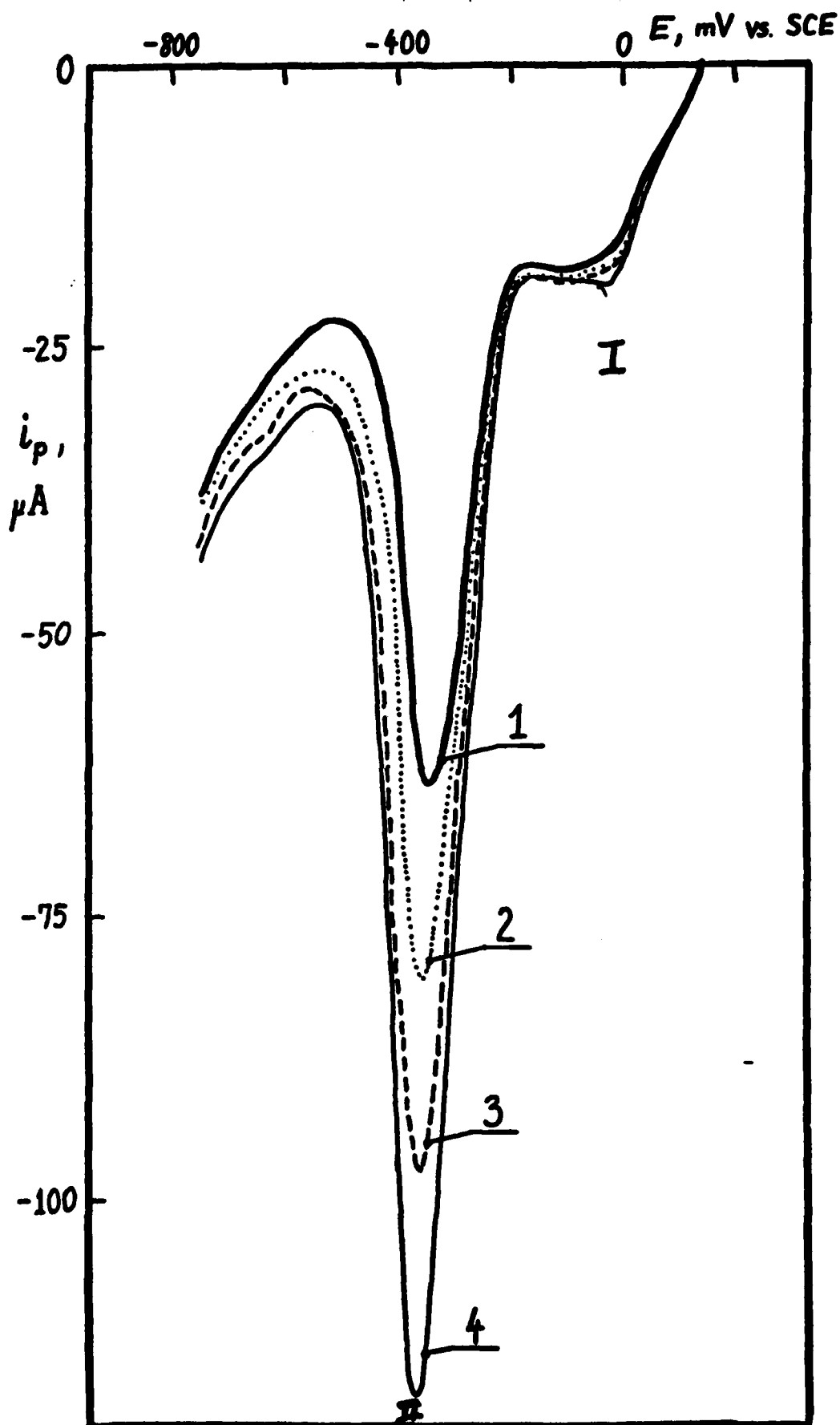
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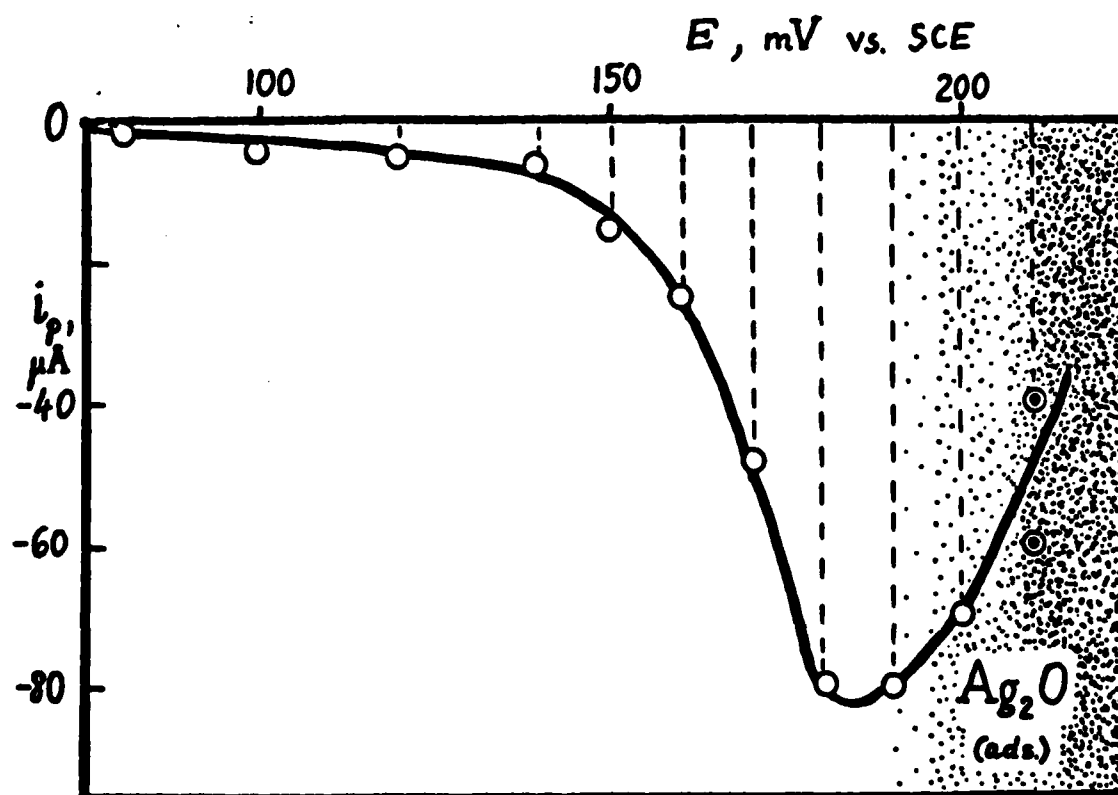
i_{d, O_2}

$i, \mu A$

E/mV vs. SCE

-1-

$\log i_p$

6

$Q_d < Q_x$

5

4

$Q_d > Q_t$

3

2

1

$\log \tau_d$

-7-
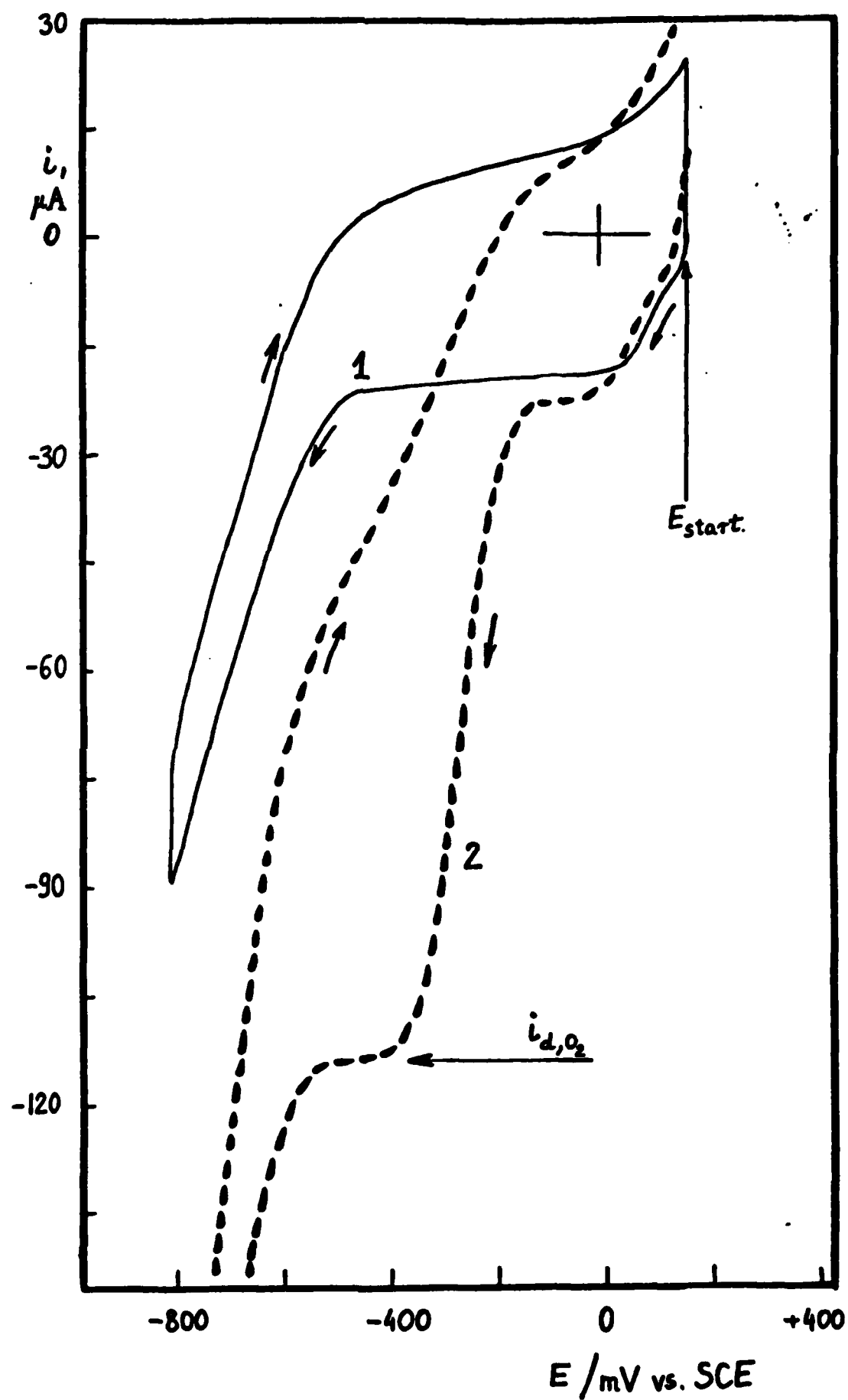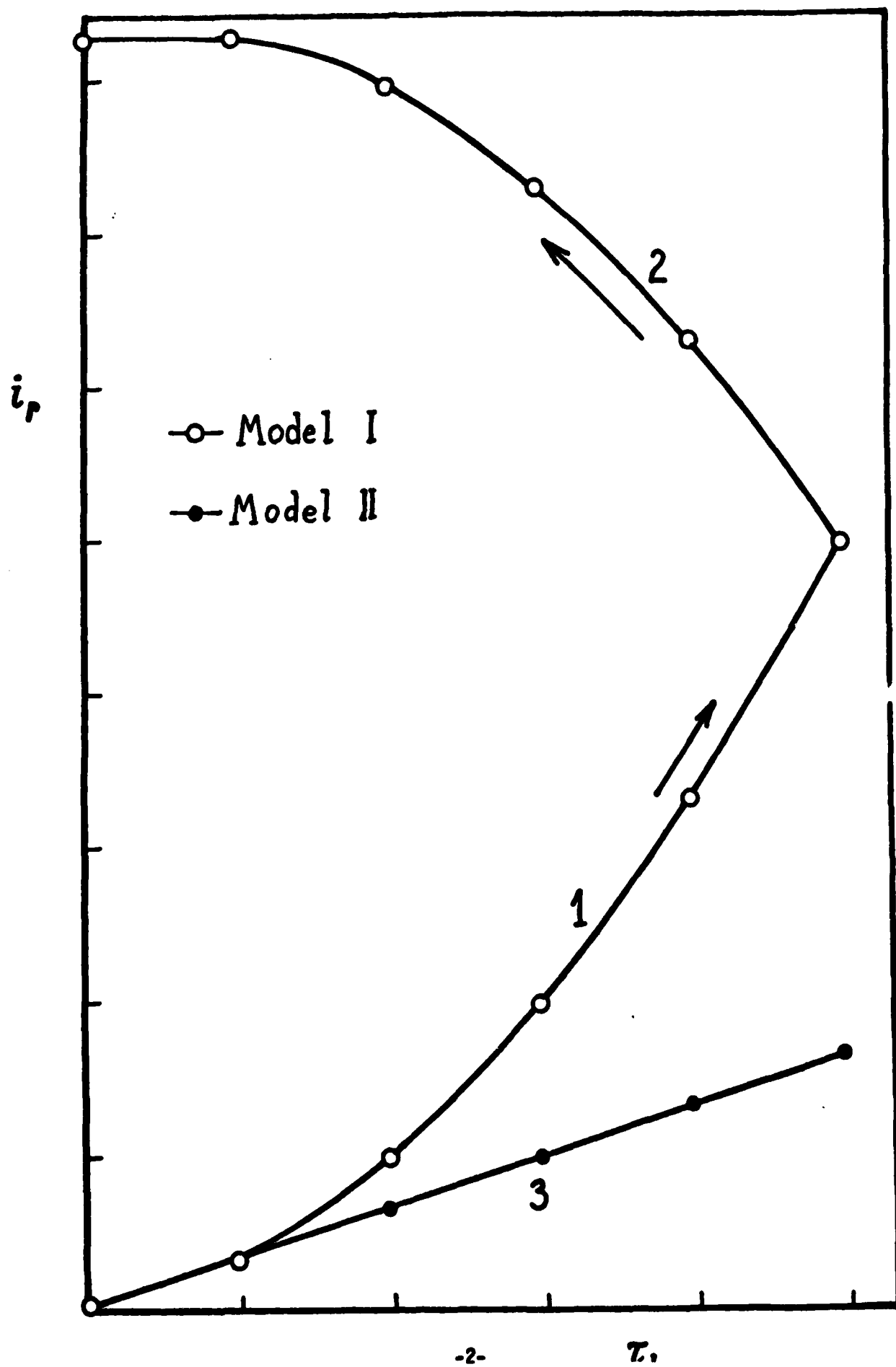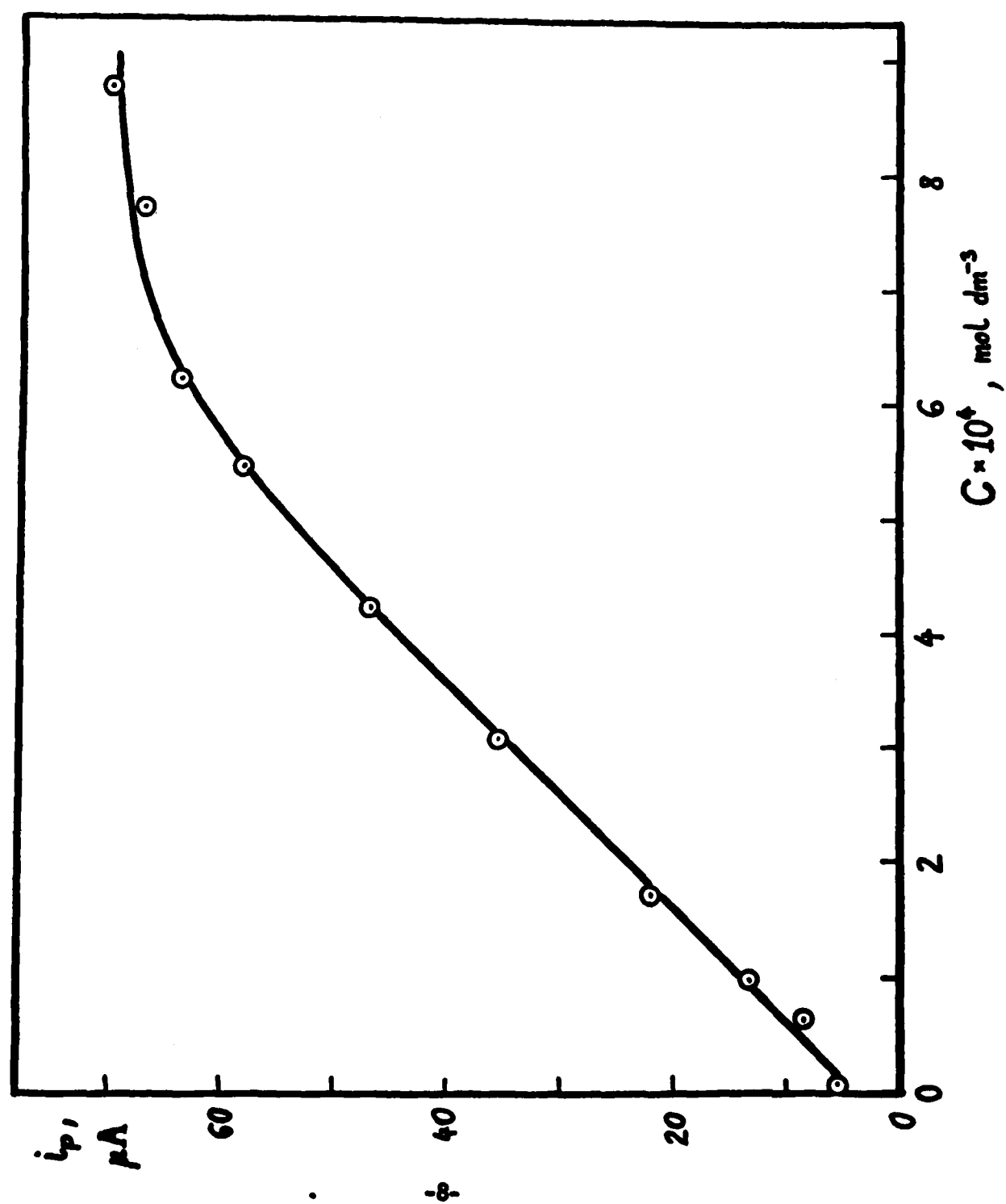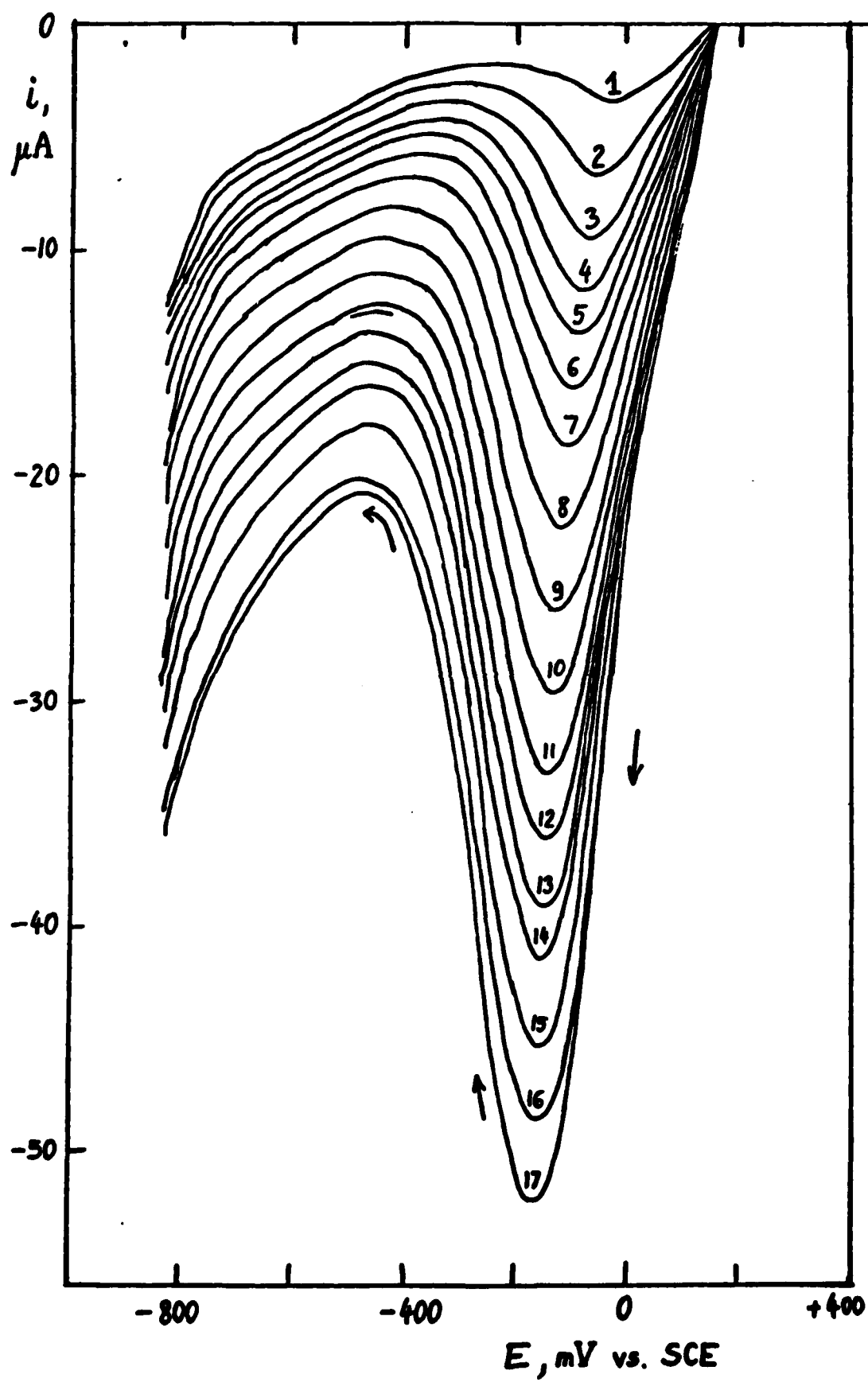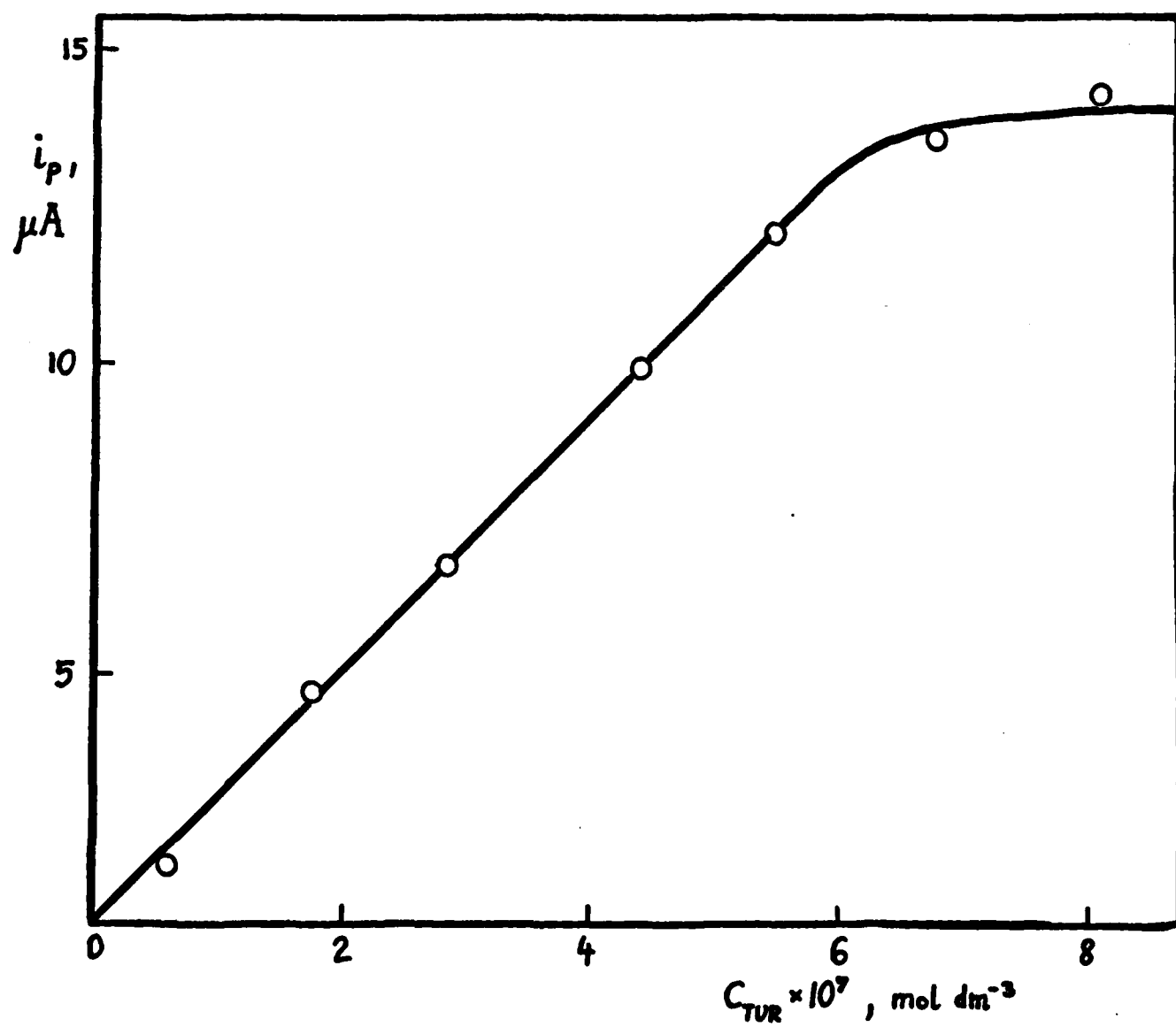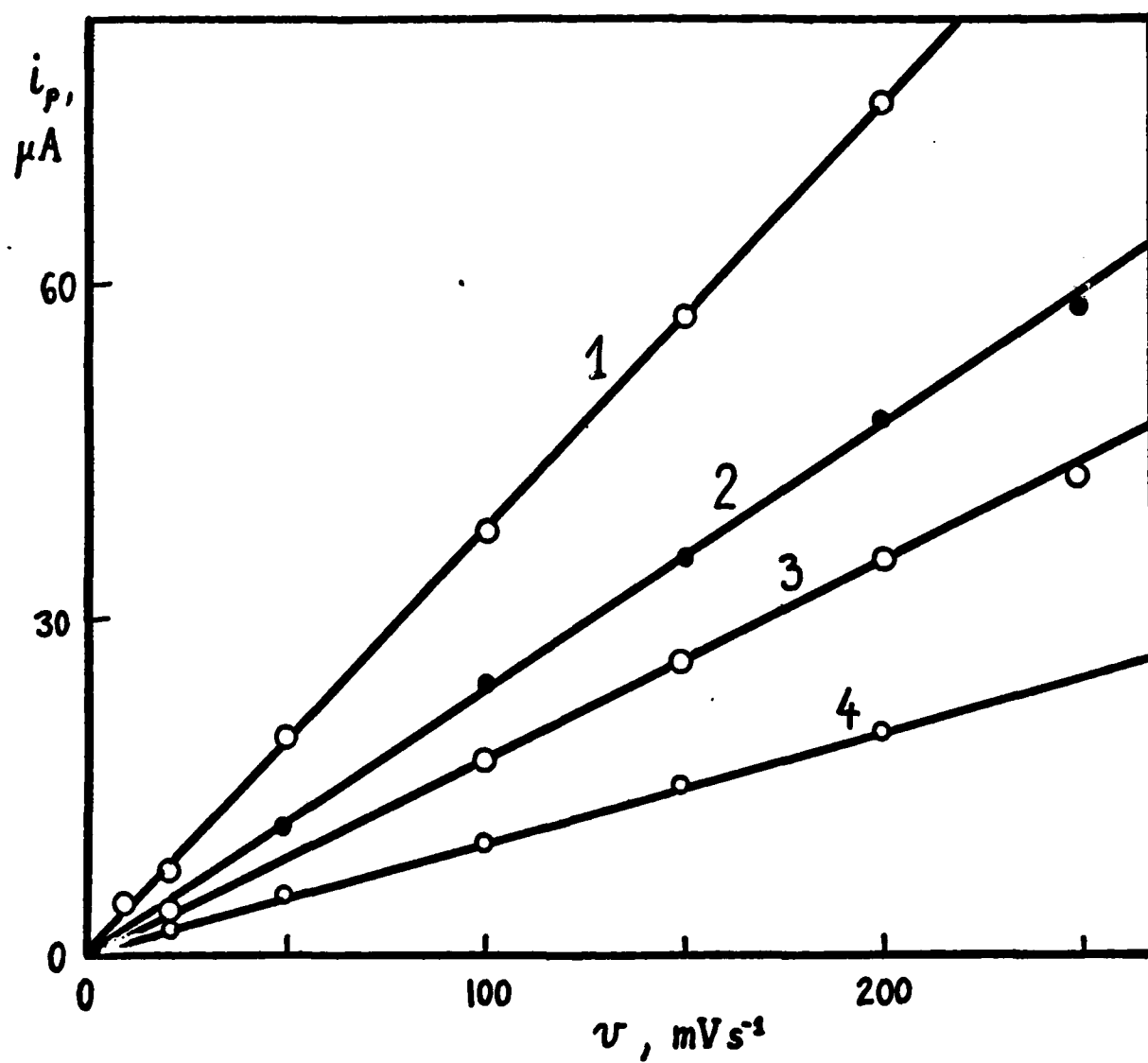
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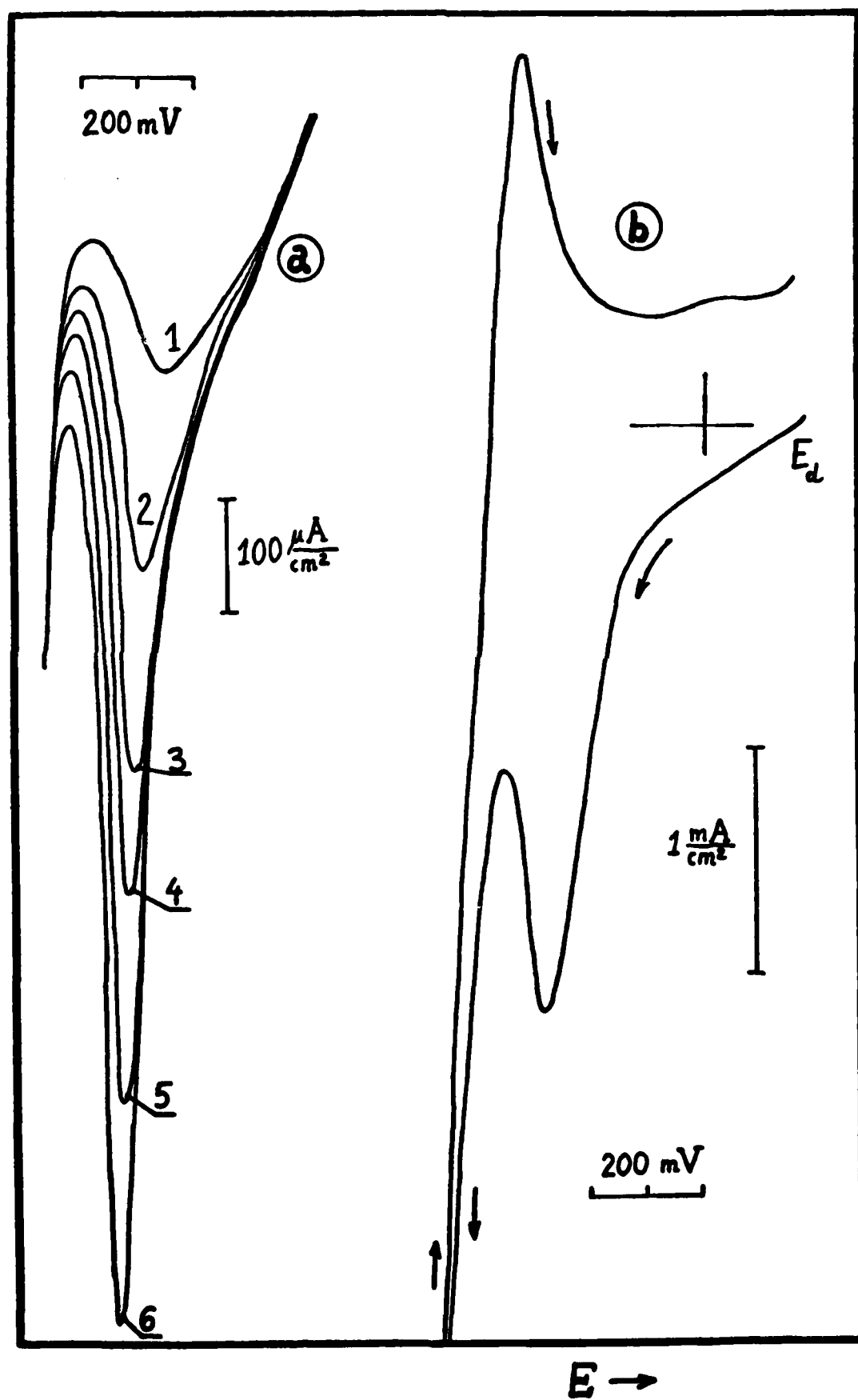|	No. Copies		No. Copies
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