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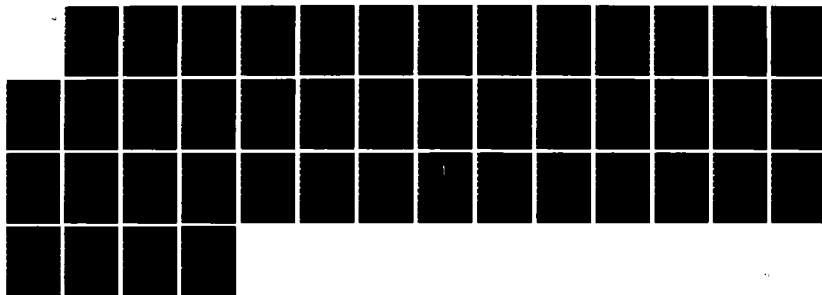
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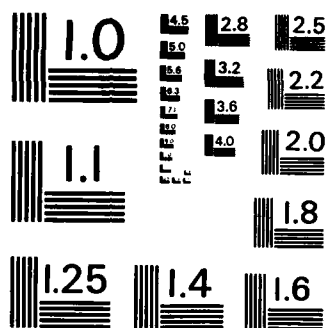
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9.2 borate buffer. Stripping peaks appeared at ~ -0.76 V vs SCE, approximately identical to that for S^{2-} , which, however, produces an oxidation wave at -0.66 V vs SCE. It is suggested that the insoluble compounds formed in the electrode surface are converted to Ag_2S . Linear cathodic stripping peak currents were found over a concentration range of $\sim 10^{-7}$ M to 10^{-5} M.

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TECHNICAL REPORT NO. 17

CATHODIC STRIPPING VOLTAMMETRY OF THIOAMIDES
ON A ROTATING SILVER DISK ELECTRODE

by

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Prepared for Publication in
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Abstract

Cathodic stripping voltammetry at a rotating silver disc electrode has been applied for the determination of five thioamides; thioacetamide (TAA), thiourea (TU), thionicotinamide (TNA), ethionamide (ETNA), and thiosemicarbazide (TSC). Well defined oxidation waves limited by convective diffusion were found at -0.29, -0.12, -0.27, -0.15 and -0.105 V vs SCE for the five amides in a pH 9.2 borate buffer. Stripping peaks appeared at ^{approx} -0.76 V vs SCE, approximately identical to that for S²⁻, which, however, produces an oxidation wave at -0.66 V vs SCE. It is suggested that the insoluble compounds formed in the electrode surface are converted to Ag₂S. Linear cathodic stripping peak currents were found over a concentration range of ^{approx} 10⁻⁷ M to 10⁻⁵ M.

approx
10⁻⁷ M to 10⁻⁵ M
0.0000001 0.000001

Introduction

Cathodic stripping voltammetry (CSV) has been employed for analysis of inorganic anions and organic materials which form sparingly soluble compounds with the electrode. Species which have been determined by CSV include halides, sulfide, etc. (1) and oxalate, succinate, dithizonate, diethyldithiophosphate, cysteine, ruheanic acid, thioanilide, dimercaptothiodiazide (2), thiourea (3) 2-mercaptohenzo⁺thiazole (4) diethyldithiocarbamate (5) and 2-mercapotpyridine N-oxide (6). Recently the CSV behavior of a wide range of organic sulphur compounds, flavins and porphyrins were surveyed by Florence (7). Several extensive reviews covering CSV for the determination of biological compounds have appeared (8,9).

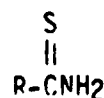
Most applications reported have been carried out at hanging mercury drop or mercury pool electrodes. Stripping voltammetry at solid electrodes has been performed on platinum (10), gold (11) and graphite or carbon (12).

Silver electrodes have been applied for the determination of trace amounts of halides (13) and thiocyanide (14). We have used a silver rotating disk electrode (AgRDE) for the determination of sulfide (15), with detection limits exceeding those of ion selective electrodes. Recently, the CSV of thiouracil on a AgRDE accompanied by complicated adsorption processes has been studied (16). The use of a AgRDE in CSV has the following advantages; 1) sparingly soluble compounds (similar to those on Hg) might be formed during anodic oxidation of solutes at silver electrodes; 2) rotating disk electrodes provide increased mass transport to the electrode surface and well defined hydrodynamic conditions compared

to a stationary electrode in a stirred solution (17,18); 3) solid electrodes for CSV are advantageous when compared to Hg which has both handling and toxicity problems.

The polarographic and voltammetric behavior of several thioamides on Hg, e.g. thiourea (3,19), thioacetamide (20), ethionamide (21) and other thioamides of pharmaceutical importance (22), have been studied, and some of these studies have involved CSV (3,21,22).

The purpose of the present work is to ascertain if CSV at a AgRDE can be utilized for compounds of biological importance. Five thioamides, thioacetamide (TAA), thiourea (TU), thionicotinamide (TNA), ethionamide (ETNA) and thiosemicarbazide (TSC), were investigated:



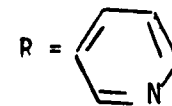
Thioacetamide (TAA)

R = -CH₃

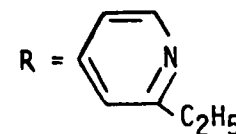
Thiourea (TU)

R = -NH₂

Thionicotinamide (TNA)



Ethionamide (ETNA)



Thiosemicarbazide (TSC)

R = -NHNH₂

Experimental

Reagents

Thioacetamide (TAA), thionicotinamide (TNA), ethionamide (ETNA), and thiosemicarbazide (TSC) were obtained from Sigma Chemical Co., and thiourea (TU) from Fisher Scientific. Stock solutions of 1×10^{-2} M TAA, TSC and TU and 1×10^{-3} M TNA and ETNA were prepared with deionized water and were stored in a refrigerator. Possible changes in concentration from hydrolysis of the thioamides were monitored by measuring the UV spectra. Analytical grade $\text{Na}_2\text{B}_4\text{O}_7$ was obtained from Fisher Scientific. 0.05 M buffer solutions were prepared and adjusted to be at least 100 times greater in concentration than the thioamides. The solution pH, adjusted to 9.2, was measured before and after each experiment.

Apparatus

A Pine Instrument's rotating silver disk electrode was mounted on a Pine Model ASR rotator. The geometrical surface area of the rotating disk was 0.442 cm^2 . The electrode surface was polished prior to immersion in the electrolyte solution with $0.3 \text{ }\mu\text{m}$ and $0.05 \text{ }\mu\text{m}$ alumina (Dry Power, Type A, Fisher Scientific Co.) for at least 15 minutes on a Minimet Polisher (Buehler Ltd.). The surface condition and preparation of the silver electrode were extremely important to the cathodic stripping peaks of the thioamides. The silver surface was polished with $45 \text{ }\mu\text{m}$, $15 \text{ }\mu\text{m}$ and $6 \text{ }\mu\text{m}$ diamond, and $1 \text{ }\mu\text{m}$, $0.3 \text{ }\mu\text{m}$ and $0.05 \text{ }\mu\text{m}$ alumina to remove scratches. This surface was examined through a microscope to ascertain if scratches were still noticeable. A satisfactory electrode surface was taken as one where the background current was about $10 \text{ }\mu\text{A}/\text{cm}^2$ at approximately -1V. If the background current had a value greater than $25 \text{ }\mu\text{A}/\text{cm}^2$ and gave a hydrogen

evolution current which increased steeply at potentials more negative than -1.2 V, the possibility of electrode leakage at the disc was suspected. A small leak affects CSV of the thioamides for concentrations less than 10^{-6} M.

An EG&G PARC Model 173 potentiostat/galvanostat equipped with a Model 179 digital coulometer and Model 175 universal programmer was used for voltammetric measurements. An Omnigraph Model 2000 X-Y recorder (Houston Instrument Co.) was used for recording voltammograms. All potentials were measured against a saturated calomel electrode (SCE). A large platinum counter-electrode was used.

Procedure

Buffer solution poured into a 250 cm³ pyrex glass electrolytic cell was deaerated by bubbling with argon for 30 minutes at a constant potential of -1.0V until a current less than 10 μ A was obtained. After background voltammograms were obtained, the thioamide solution was added to the background solution with an Eppendorff pipet. The potential was then stepped to the deposition potential; the electrode was rotated during the deposition of thioamide. During deposition and stripping processes the solution was covered by an argon purge. The temperature was $25 \pm 0.5^\circ\text{C}$.

The deposited film was cathodically stripped by means of a linear potential scan. The charge passed during deposition was measured by the coulometer and the charge passed during stripping was determined by integrating the recorder chart paper by cutting out the stripping current-potential (time) curve and weighing.

Results and Discussion

Cyclic Voltammograms at AgRDE

Cyclic voltammograms at a AgRDE for TAA, TU, TNA, ETNA and TSC at $\sim 10^{-4}$ M in pH 9.2 borate buffers are shown in Figs. 1-5. The thioamides give anodic currents (process 1 in Fig. 1-5) corresponding to the formation of sparingly soluble silver compounds (see below) at half-wave potentials ($E_{1/2}$) of: TAA) -0.29 V; TU) -0.12 V; TNA) -0.27 V; ETNA) -0.15 V and TSC) -0.105 V vs. SCE, respectively. Limiting currents plotted against the square root of rotation rate ($\omega^{1/2}$) showed linear behavior (Fig. 6), passing through the origin, and were proportional to concentration, indicating control by convective diffusion of the thioamides from the bulk solution. Figure 7 shows anodic current at less than limiting current values plotted vs $\omega^{1/2}$ for TAA for various potentials. The convex curves indicate chemical and/or electrochemical complications but were not investigated further.

Thiourea produces a second wave at potentials more positive than +0.15V (process 2 in Fig 2), which is due to oxidation of TU to the disulfide (19). In the cases of ETNA and TNA, a spike "peak" appears prior to the limiting current, which may correspond to nucleation of the Ag compound on the electrode surface. The $E_{1/2}$ of ETNA on anodic scan is more positive than that on the reverse, cathodic scan, indicating that the formation of a Ag-ETNA compound is inhibited by a strong adsorption of ETNA on the Ag surface. TSC gives less-defined anodic waves with hysteresis, suggesting more complicated electrode reactions.

All the thioamides studied show clear cathodic stripping peaks suitable for determination of each thioamide (process 3 in Figs. 1-5) with

peak potentials (E_p) of -0.70 to -0.80 V. ETNA and TNA show a reduction current at about -1.0 V which is independent of the anodic deposition (process 4 in Fig. 3 and 4). The limiting reduction current of ETNA is proportional to its concentrations. These reduction currents may result from catalytic hydrogen evolution of the primary thioamide (22).

A comparison of the anodic charge (Q_a) passed during the deposition to cathodic charge (Q_c) consumed during stripping is shown in Table I. Q_c for TAA, TU, TNA and ETNA are almost the same as Q_a in 10^{-4} M solutions. The results indicate that at a high concentration of these four thioamides anodically deposited silver-thioamide compounds at a silver electrode do not dissolve chemically and are not removed mechanically during deposition; deposits are completely stripped during the cathodic scan. Contrary to this, Q_c of TSC is $\sim 1/3$ of Q_a even in 10^{-4} M solution. Hence, the Ag species deposited initially on the electrode, probably a Ag-TSC compound, appears soluble in the bulk solution.

Voltammograms of sulfide at the AgRDE were compared to those of thioamides (Fig. 8). Although anodic current corresponding to formation of Ag_2S appears at much more negative potential ($E_{1/2} = -0.66$ V) than those of the thioamides, its stripping peak potential is very close to that of the thioamides. For deposits of the same amount of silver-thioamide compounds, the stripping peak potentials are the same as for sulfide; for example, E_{p_c} for Q_c of 4×10^{-3} C is about -0.84 - 0.86 V for the thioamides and sulfide. This suggests the cathodic stripping process for these thioamides is similar to that of sulfide.

These preliminary studies indicate the possibility of cathodic stripping voltammetric analysis using deposition of these thioamides at

potentials more positive than -0.25 V for TAA, TNA and ETNA and -0.10 V for TU and TSC respectively.

Cathodic Stripping Voltammetry

As the pH decreases, the potential of Ag compound formation shifts to positive potentials close to that of silver oxide formation. TAA, TU and TNA gave sharp stripping peaks, in pH 4.6 acetate buffer, but the sensitivity decreased because of a decrease in the recovery of Q_c and of the positive shift of the anodic waves. In very alkaline solutions, thioamides are unstable and tend to hydrolyze. Thus, a pH 9.2 borate buffer was chosen as the electrolyte for detailed study.

Fig. 9 shows the effect of the deposition potential (E_d) on the stripping peak current (I_p) in the range of 10^{-7} M TAA, TU, TNA, ETNA and 10^{-6} M TSC. At deposition potentials more positive than $+0.1$ V a decrease in the stripping peak current occurs as a result of overlapping oxide deposition. The optimum deposition potential (E_d) is -0.05 V for TAA, TNA and ETNA, and 0 V for TU and TSC. The plots of I_p against time (t_d) for TU and TAA in the 10^{-6} - 10^{-7} M range are shown in Fig. 10. At concentrations of $\sim 10^{-7}$ M, TAA and TU show an induction period; other thioamides behave in a similar manner. At greater than 5×10^{-6} M, the plots pass through the origin. Although the cathodic stripping charge (Q_c) is smaller than the anodic deposition charge (Q_a) calculated theoretically from the Levich equation at a concentration showing an induction period, Q_c is almost the same as Q_a at higher concentrations which display no induction period. This induction period may depend on the solubility and formation constant of the Ag compound and/or adsorption of thioamides. Thus, deposition times (t_d) greater than 600 s were employed

for CSV of the thioamides in concentration ranges less than 10^{-7} M.

I_p is proportional to scan rate and to the square root of the rotation rate during deposition. In this work, scan rates of 50 mV/s and rotation rates of 2500 or 3000 rpm were employed.

Stripping peaks for the same amount of deposited silver-thioamide compounds are independent of electrode rotation during stripping, indicating that the cathodic stripping process of the Ag compounds is not controlled by diffusion of thioamides from the electrode surface and that the overall process for the stripping is irreversible.

Typical cathodic stripping voltammograms of TAA in the range of 10^{-7} - 10^{-6} M are shown in Figs 11. The stripping peaks for all the thioamides are very similar and reproducible. Plots of I_p against concentration for TAA, TU and TNA are shown in Fig. 12. However, these calibration curves do not pass through the origin presumably because of the solubility of the Ag-thioamide compound, kinetics of film formation and other complicated anodic processes of thioamides on Ag electrodes. The analytical data for determination of TAA, TU, TNA, ETNA and TSC is listed in Table II. I_p is proportional to Q_c at coverages corresponding to less than $5.5 \times 10^{-3} \mu\text{C}/\text{cm}^2$, and the linearity in the plots of I_p vs. C is maintained to 5.0×10^{-5} M at various deposition times. Thus, the application of the silver RDF for CSV permits thioamides to be determined in the range 5×10^{-8} M - 10^{-5} M.

An important interfering ion for the determination of sulphur containing organic molecules is chloride. Concentrations of Cl^- in the range of 10^{-5} - 10^{-4} M have no effect on the stripping peaks of 1×10^{-6} M solutions of TAA and TU. The potential at which Cl^- forms AgCl

at the Ag electrode at pH 9.2 is +0.2 V, which is more positive than the deposition potential for the thioamides.

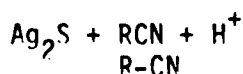
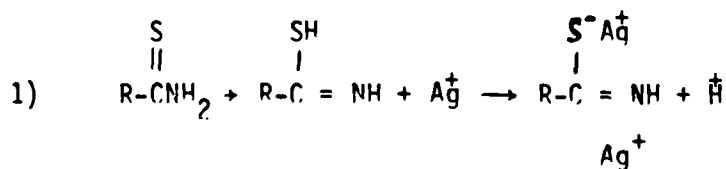
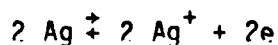
Suggested Mechanism for Anodic Deposition of Thioamides on Ag Electrode.

The mechanism for deposition of these thioamides appears different from that of thiol-type sulfur compounds like thiouracil. E_p values for the CSV of thiobarbituric acid and thiouracil (5) are about -0.25 V in pH 9.2 and -0.35 V at pH 8.3 in 10^{-5} M solutions, respectively, which are more positive than E_p for thioamides. The previous work (20-24) on anodic processes of the primary thioamides (thiourea, thioacetamide, thiosemicarbazide and ethionamide) on Hg concluded that HgS is produced in the anodic polarographic process of such compounds along with nitrile. E_p values for CSV of thioamides on Ag are very close to that of sulfide at both pH 9.2 and 4.6 (Table II). Solutions of the five thioamides and S^{2-} gave only one stripping peak at a given deposition time, but at deposition time shorter than 60 s the stripping peak split in two. It is suggested that Ag compounds formed initially on anodic deposition turn to Ag_2S with increasing deposition time.

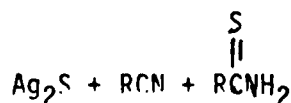
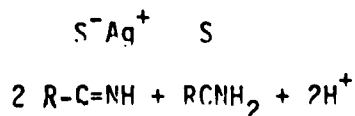
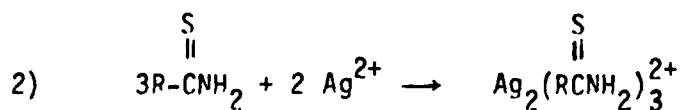
Some chemical reactions of five thioamides were examined and gave the following results: 1) at pH 9.2 the addition of thioamide solution to silver nitrate solution gave a dark gray-brown precipitate similar to that in sulfide solution for all thioamides, TAA, TU, TNA, ETNA and TSC; 2) the same treatment in neutral medium led to the same precipitate as pH 9.2 for TAA, TNA and ETNA but a white precipitate for TSC. As for TU, a white precipitate formed initially but turned black within several seconds. After the measurement of CSV for 10^{-4} M thioamide solutions, a dark gray

precipitate remained on the electrode surface.

TU and TSC form sparingly soluble 2:3 complexes in acidic solutions (26,27) and then the complexes decompose, more or less readily to silver sulphide with increasing silver ion concentration. The decomposition usually begins as the molar ratio of silver(I) to ligand approaches 1:1 with increasing silver ion concentration. An excess of ligand leads to the complex species $[Ag(SR)_n]^+$ which are soluble in aqueous solution (27). Thus, it is assumed that at a Ag electrode the anodic reactions of the thioamides proceed to a final product of Ag_2S through silver-thioamide compound formation, i.e.



or



The values of the diffusion coefficients (D) for TAA, TU, TNA and ETNA were calculated by using the anodic limiting currents (Table I) and the Levich equation, assuming $n = 2$ for the anodic reaction (Table III). The value of D for TU, $1.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ is in good agreement with the published value of $1.33 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (28) and the values for other thioamides are quite reasonable considering the differences in molecular structure.

The reaction rate leading to Ag_2S formation appears to depend on the concentration of thioamide, the applied potential and deposition time. More work is needed to completely characterize the behavior of the anodic deposition of thioamides on Ag electrodes.

CREDIT

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Table I. Comparison of anodic charge (Q_a) and cathodic charge (Q_c).
 $\omega = 2500$ rpm, scan rate = 50 mV/s

	$[C]/10^{-4}$ M	$I_d/10^{-4}$ A	I_d/C AM $^{-1}$	$Q_a/10^{-3}$ C	$Q_c/10^{-3}$ C
TAA	1.00	1.00	1.00	3.43	4.00
$E_d = -0.15$ V	2.00	1.95	0.975	6.46	6.31
$t_d = 30$ s	2.99	2.98	0.997	10.3	10.2
	3.98	3.95	0.992	13.5	13.2
	4.98	5.00	1.01	17.3	16.5
TU	1.00	1.06	1.01	4.22	4.17
$E_d = +0.050$ V	2.00	2.02	1.01	7.91	7.89
$t_d = 30$ s	2.99	3.08	1.03	11.8	11.4
	3.98	4.11	1.03	15.8	16.0
	4.98	5.11	1.02	19.8	19.1
TNA	0.594	0.480	0.808	1.50	1.59
$E_d = -0.15$ V	0.990	0.760	0.797	2.42	2.40
$t_d = 30$ s	1.40	1.10	0.786	3.55	3.45
	1.90	1.51	0.795	5.55	5.62
	2.68	2.10	0.784	6.82	6.75
ETNA	0.690	0.510	0.739	2.03	2.40
$E_d = 0$ V	1.35	1.00	0.741	3.70	3.83
$t_d = 30$ s	1.99	1.55	0.754	5.41	5.44
	2.60	1.96	0.754	7.50	7.15
	3.20	2.37	0.741	8.14	7.93
TSC	1.00	2.00	2.00	6.40	2.29
$E_d = -0.15$ V	2.00	3.80	1.90	11.1	4.14
$t_d = 30$ s	2.99	3.90	1.31	16.8	6.14
Na ₂ S	0.40	0.41	1.025	1.30	1.40
$E_d = -0.5$ V	0.80	0.79	0.988	2.70	3.00
$t_d = 30$ s	1.20	1.20	1.000	3.90	4.30

Table II. Cathodic Stripping Voltammetric Data for Determination of Thioamides

$t_d = 15$ s ~ 900 s, $\omega = 3600$ rpm, scan rate = 50 mV/s. Potentials are in V vs SCE.

thioamide	pH 9.2			pH 4.6		
	$E_{1/2}^a)$ anodic waves	E_d	$E_p^b)$ stripping peak	linear range/M	$E_{1/2}^a)$	$E_p^b)$
TAA	-0.29	-0.05	-0.76	$5.1 \times 10^{-8} - 6.0 \times 10^{-5}$	+0.02	-0.54
TU	-0.12	0	-0.78	$6.8 \times 10^{-8} - 6.0 \times 10^{-5}$	>+0.1	-0.56
TNA	-0.27	-0.05	-0.76	$7.5 \times 10^{-8} - 6.0 \times 10^{-5}$	+0.03	-0.55
ETNA	-0.15 (-0.26) ^{c)}	-0.05	-0.77	$9.0 \times 10^{-8} - 6.0 \times 10^{-5}$		
TSC	-0.105	0	-0.78	$7.5 \times 10^{-7} - 1.0 \times 10^{-4}$		
S ²⁻	-0.66		-0.76		-0.63	-0.53

a) in 10^{-4} M solution

b) at cathodic charge (Q_c) of 450 $\mu\text{C}/\text{cm}^2$

c) on cathodic scan

Table III. Diffusion coefficients for thioamides in 0.05 M borate buffer.

Thioamide	$(I_d/C)/A \text{ M}^{-1}$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	lit. value
TAA	0.995	1.25	$1.329 \times 10^{-5} \text{ cm s}^{-1}$ (28)
TU	1.02	1.31	
TNA	0.788	0.891	
ETNA	0.746	0.813	

Figure Captions

1. RDE voltammogram (solid line) of 2×10^{-4} M TAA; AgRDE; $\omega = 2500$ rpm; $\nu = 10 \text{ mV s}^{-1}$; pH 9.2 borate buffer. Background in the absence of TAA (dashed line).
2. As Fig. 1; 2×10^{-4} M TU.
3. As Fig. 1; 1.4×10^{-4} M TNA.
4. As Fig. 1; 1.35×10^{-4} M ETNA.
5. As Fig. 1; 1.4×10^{-4} M TSC.
6. $I_d - \omega^{1/2}$ plots of a) 4×10^{-4} M TAA; b) 2.8×10^{-4} M TNA; c) 1.99×10^{-4} M ETNA; d) 4×10^{-4} M TU and e) 1.0×10^{-4} M TSC. $\nu = 10 \text{ mV s}^{-1}$.
7. Dependence of anodic current of 4.0×10^{-4} M TAA at various potentials vs square root of rotation rate. a) -0.1 V; b) -0.2 V; c) -0.25 V; d) -0.3 V; e) -0.35 V. $\omega = 2500$ rpm; $\nu = 10 \text{ mV s}^{-1}$.
8. As Fig. 1; 1.24×10^{-4} M Na_2S .
9. Effect of deposition potential (E_d) on stripping peak current (I_p) for thioamides. (-○-) 8.8×10^{-7} M TAA; (-●-) 6.8×10^{-7} M TU; (-△-) 7.6×10^{-7} M TNA; (-▲-) 7.3×10^{-7} M ETNA; (-■-) 3.6×10^{-6} M TSC. $t_d = 300$ s (180 s for TSC); $\omega = 3600$ rpm; $\nu = 50 \text{ mV s}^{-1}$.
10. Plots of stripping peak currents (I_p) against deposition time (t_d) for: a) 5.4×10^{-7} M TU; b) 8.0×10^{-7} M TAA; c) 8.1×10^{-7} M TU; d) 2.0×10^{-6} M TAA; e) 3.0×10^{-6} M TU; f) 5.2×10^{-6} M TU; g) 6.1×10^{-6} M TAA. $E_d = -0.05$ V for TAA; 0 V for TU; $\omega = 3600$ rpm; $\nu = 50 \text{ mV s}^{-1}$.

11. Cathodic stripping peaks at various concentrations of TAA.
a) 1.27; b) 2.54; c) 3.80; d) 5.06; e) 6.36; f) 8.83×10^{-7} M.
 $t_d = 600$ s; $E_d = 0$ V; $\omega = 3600$ rpm; $v = 50$ mV s⁻¹.
12. Concentration dependence of stripping peak current (I_p) for
a) TAA; b) TU and c) TNA. $t_d = 900$ s; $E_d = -0.05$ V for TAA and
TNA; 0 V for TU; $\omega = 3600$ rpm; $v = 50$ mV s⁻¹.

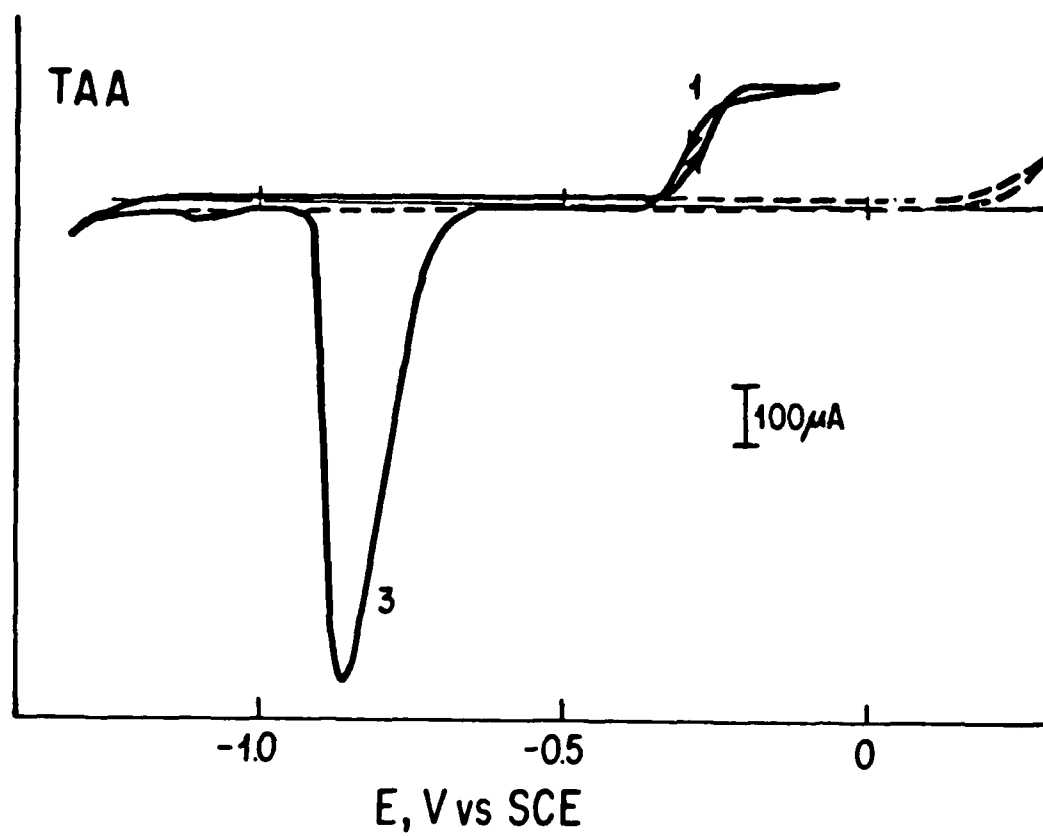


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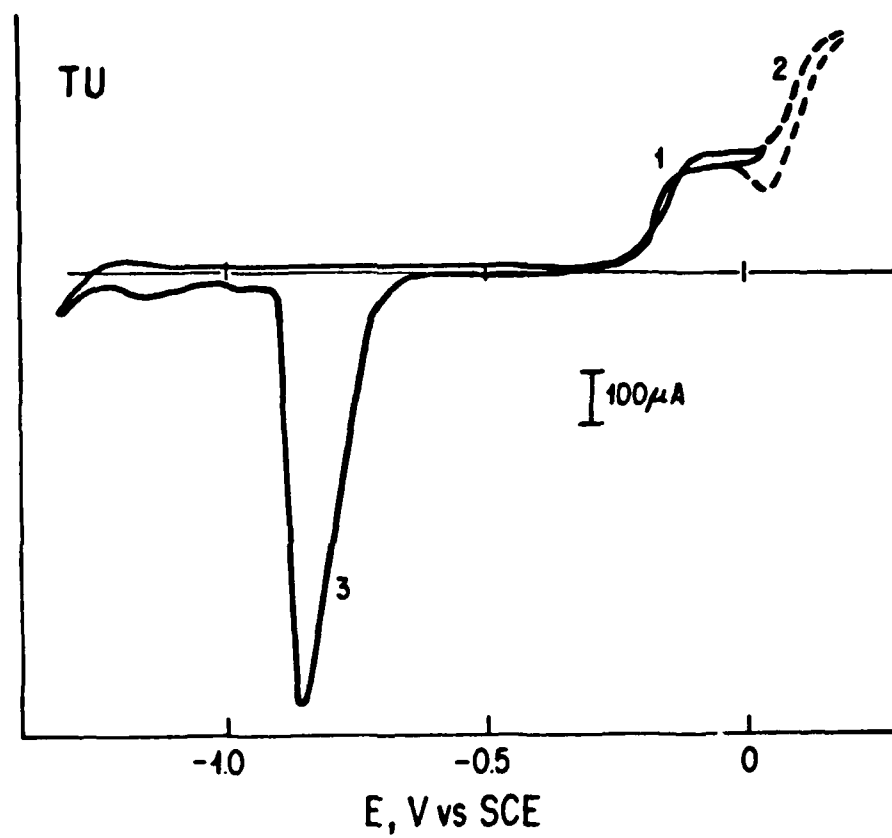


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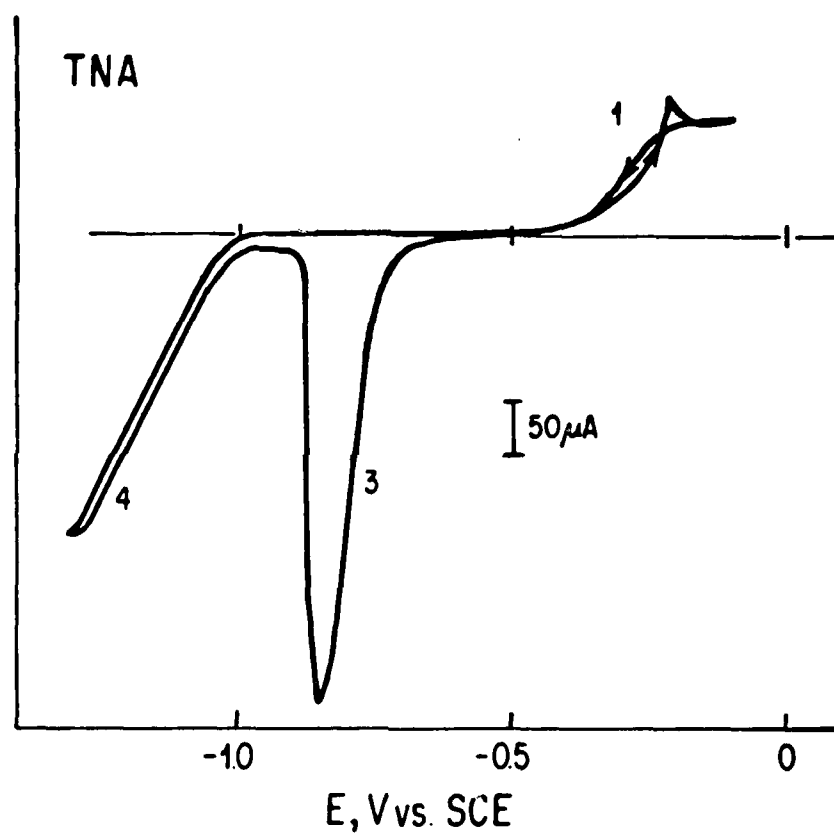


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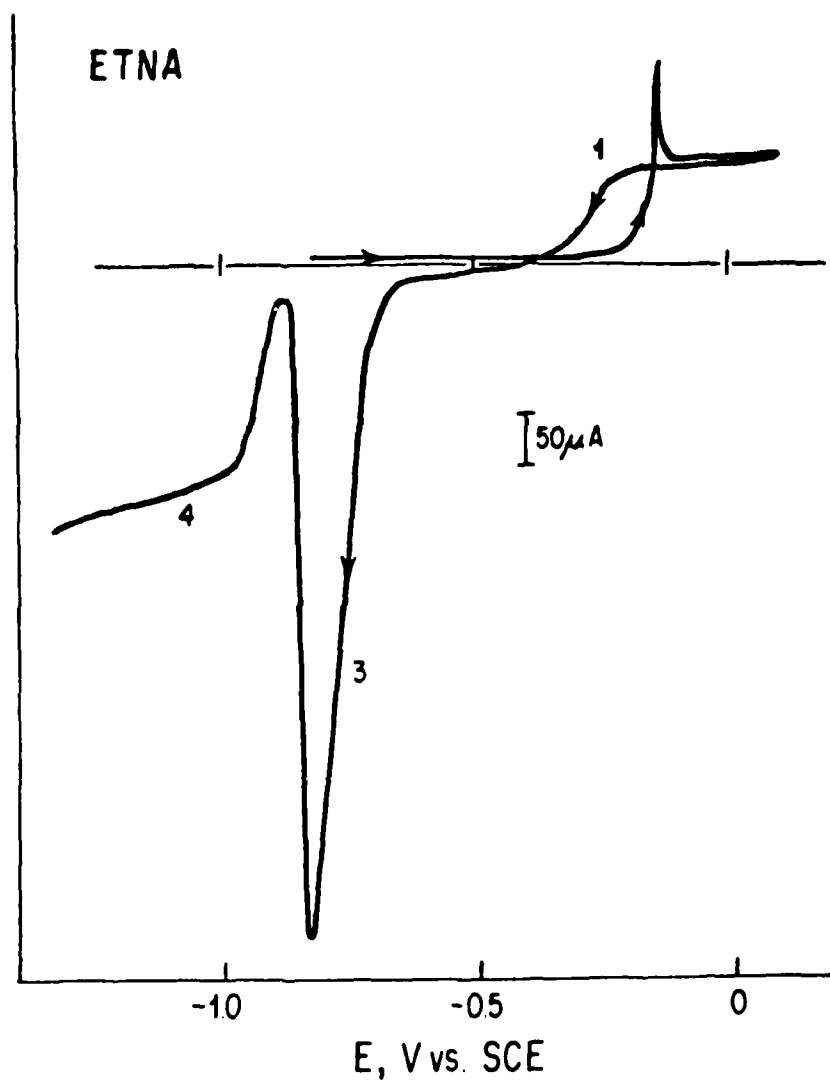


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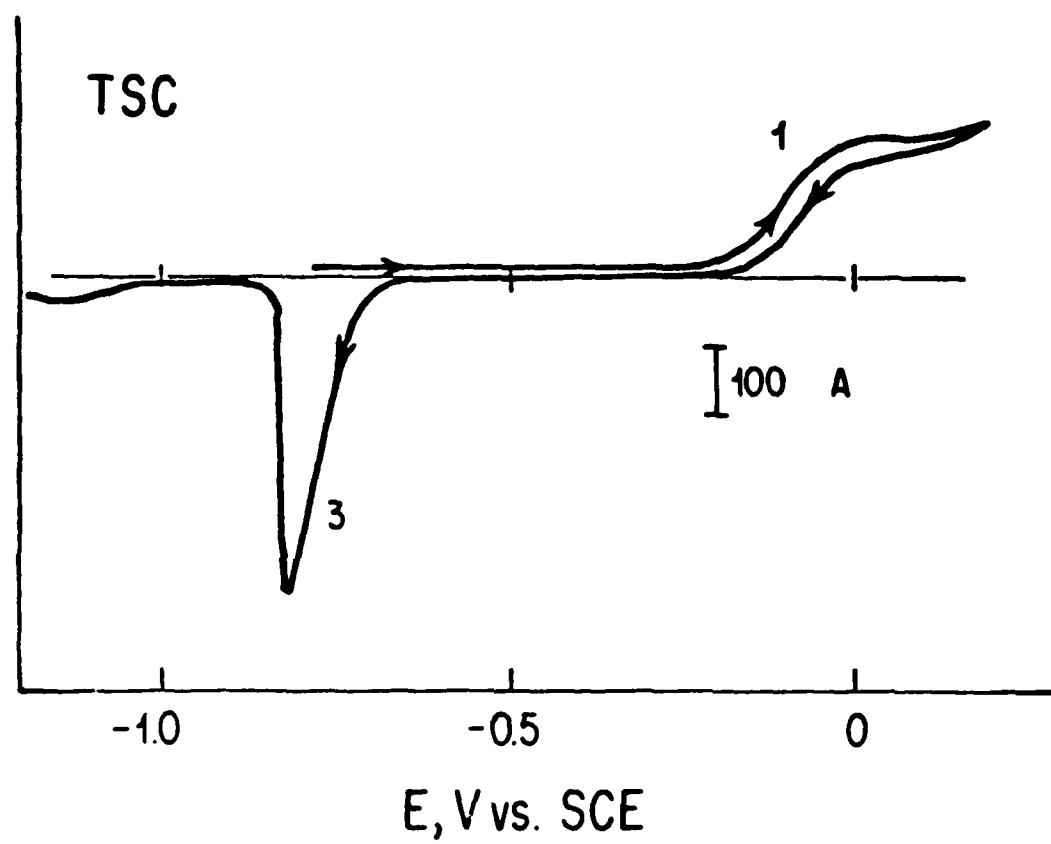


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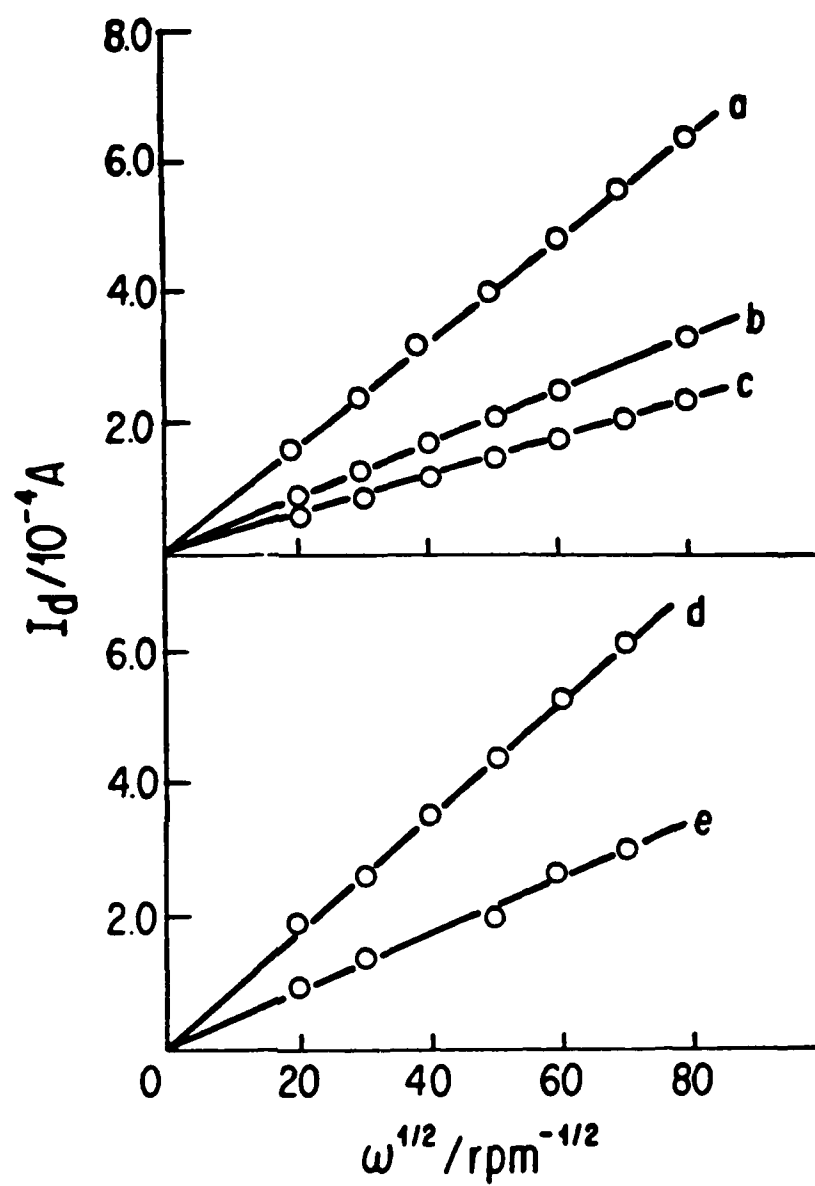


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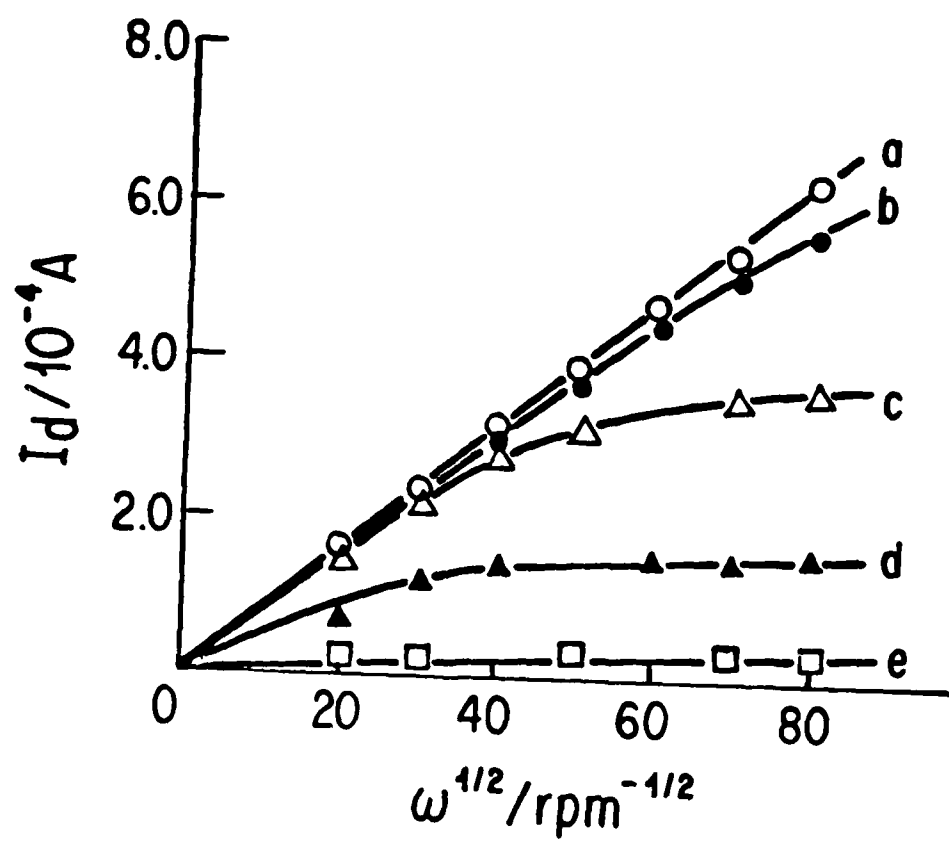


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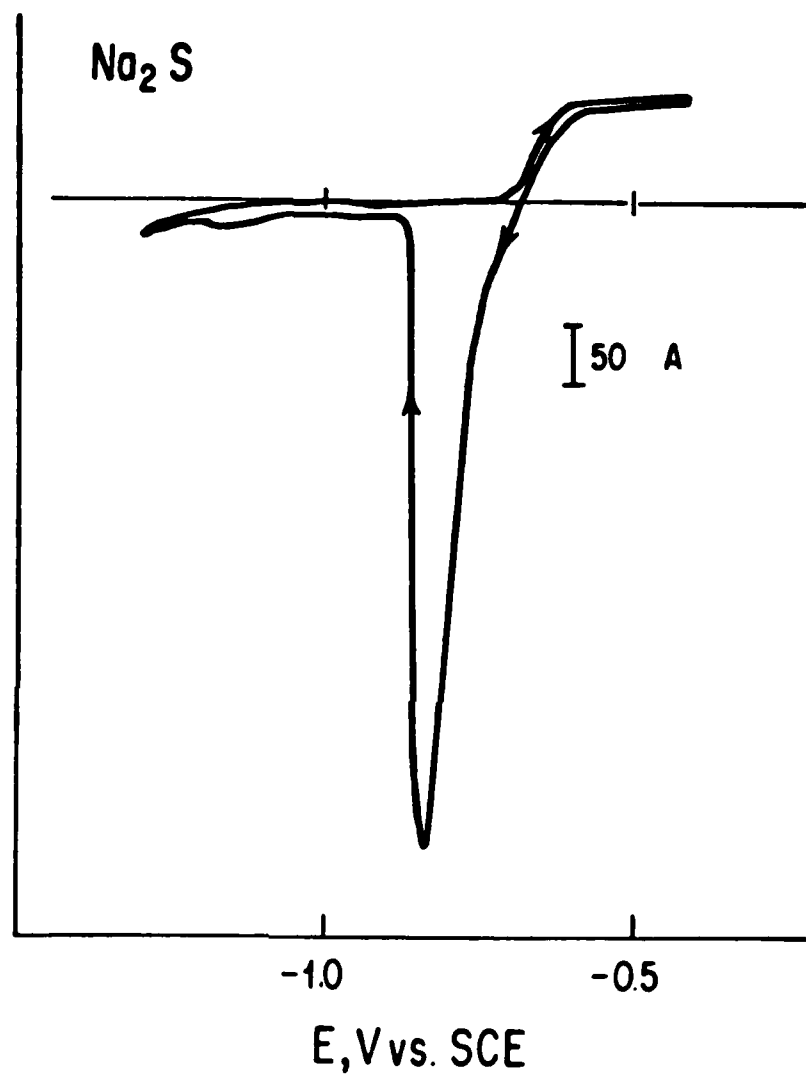


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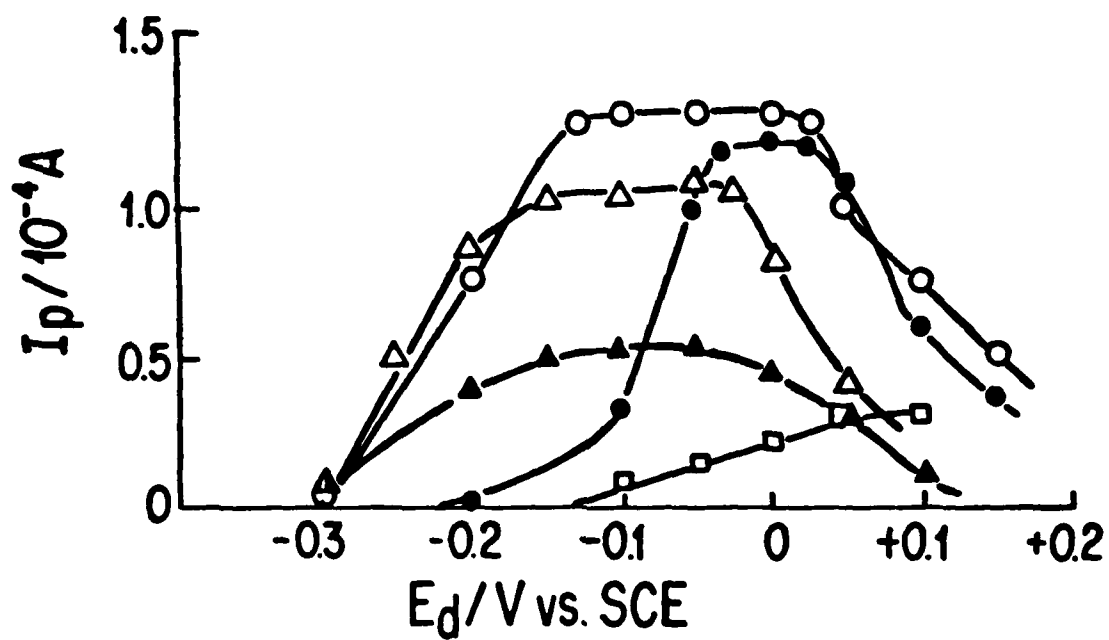


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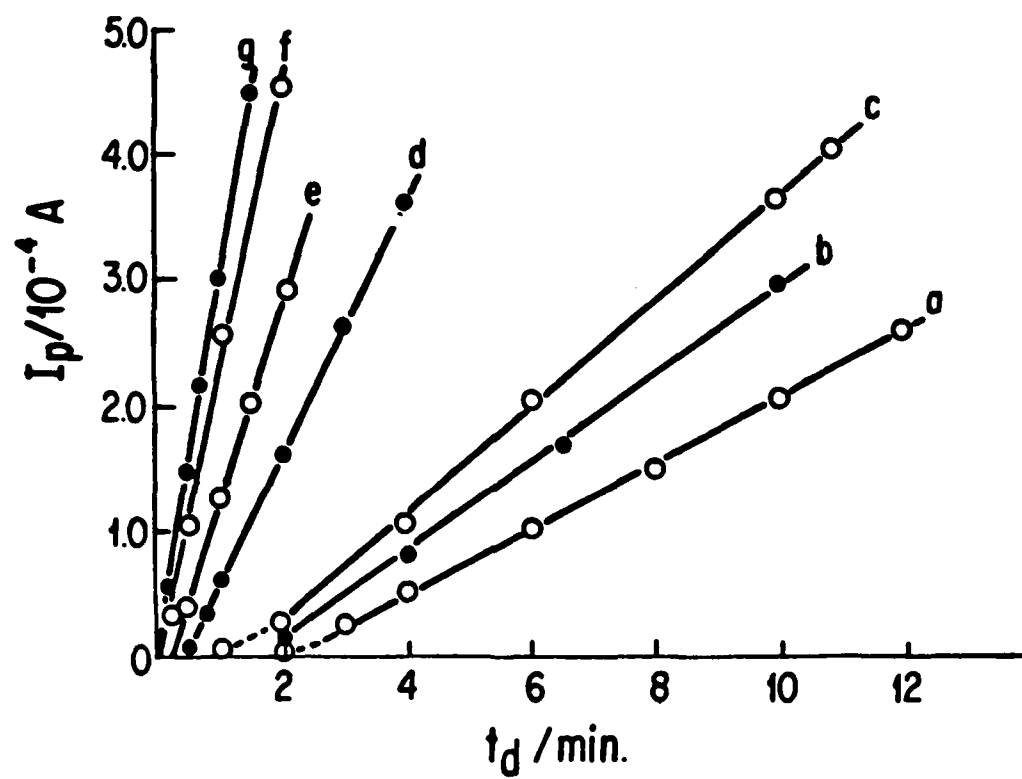


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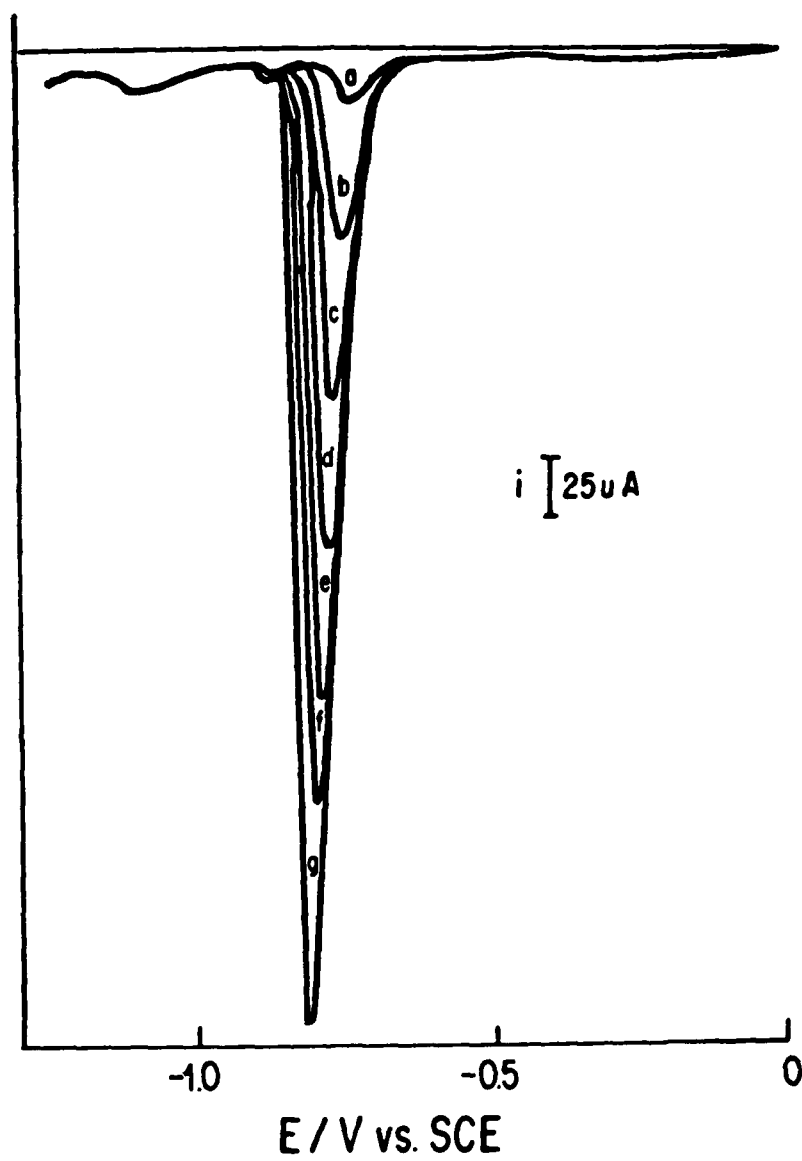


Figure 11

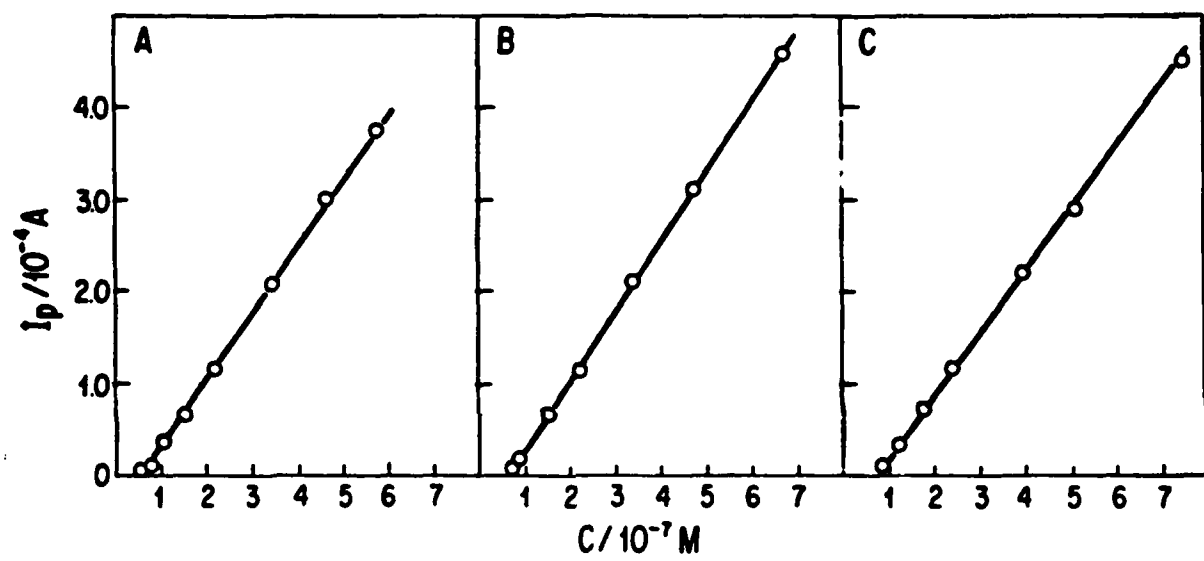


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