



Unclassified

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12 14 TR-4

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER 9 Technical Report No. 4 - AD-A099214	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 Electrochemical Behavior of Sulfide at the Silver Rotating Disc Electrode. I. Polarization Behavior of Silver Sulfide Films.	5. TYPE OF REPORT & PERIOD COVERED	
7. AUTHOR(s) 10 Kunio/Shimizu, Koich/Aoki, Robert A. Osteryoung	8. CONTRACT OR GRANT NUMBER(s) 15 N00014-79-C-0682 ✓	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research/Chemistry Program Arlington, VA 22217	12. REPORT DATE 11 May 1981	13. NUMBER OF PAGES 32
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 42 LEVEL II	15. SECURITY CLASS. (of this report) Unclassified	
15a. DECLASSIFICATION DOWNGRADING SCHEDULE		

16. DISTRIBUTION STATEMENT (of this Report)  
Approved for Public Release: Distribution Unlimited

DTIC ELECTRIC  
MAY 21 1981

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  
C

18. SUPPLEMENTARY NOTES  
Prepared for publication in The Journal of Electroanalytical Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  
Silver sulfide formation; silver disc electrodes; depolarization of silver by sulfide

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  
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→ tively reduced to silver during a cathodic potential scan.

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Contract N00014-79-C-0682

TECHNICAL REPORT NO. 4

ELECTROCHEMICAL BEHAVIOR OF SULFIDE  
AT THE SILVER ROTATING DISC ELECTRODE:  
I. POLARIZATION BEHAVIOR OF SILVER SULFIDE FILMS

by

KUNIO SHIMIZU, KOICHI AOKI AND ROBERT A. OSTERYOUNG

Accepted for Publication in  
The Journal of Electroanalytical Chemistry

Department of Chemistry  
State University of New York at Buffalo  
Buffalo, New York 14214

May 1981

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ABSTRACT

A rotating silver disc electrode in a sodium hydroxide solution containing sodium sulfide was used to study the anodic polarization, passivation and cathodic polarization of silver sulfide films on the silver disc electrode. Anodic limiting currents are controlled by convective diffusion of sulfide ions at potentials more anodic than the equilibrium potential for silver sulfide/sulfide ion. The anodic depolarization of silver by sulfide is diffusion limited until the deposited film develops an appreciable thickness. All silver sulfide produced during anodic polarization is quantitatively reduced to silver during a cathodic potential scan.

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## INTRODUCTION

There has been increased attention to the electrochemistry of sulfides partly because froth floatation of sulfide ores, involving heterogenous reactions in nature, has been studied successfully by electrochemical techniques (1) and because metal sulfides are useful for ion selective electrode (2, 3) and sulfur batteries (4). The electrochemistry of sulfides has been reviewed in the areas of mineral processing science (1, 5), metal sulfide electrodes (6) and sulfur electrodes in nonaqueous media (7). One of the most attractive metal sulfides is silver sulfide, which has been developed as an ion selective electrode. Early work on silver sulfide involved thermodynamics of electrodes of the second kind, (8), the electrical double layer (9) and composition of silver sulfide (10). Since solid ionic conductors have been recognized as useful material for power generation and storage, several workers have reported on the kinetics of the formation of solid silver sulfide (11-15). In such investigations, complications often arose at the solid/solid interface between a silver electrode and silver sulfide as a solid electrolyte as well as at the solid/ liquid interface between silver sulfide and sulfide solution.

We are interested in the behavior of the solid/solution interface composed of a silver electrode and an aqueous sulfide solution, which may function as an electrode of the second kind if silver sulfide is deposited. Although such half cells as reference electrodes have been fully discussed, (techniques of assembly of electrodes and appropriate conditions for usage of electrodes) (16), basic studies on the kinetics

of formation of electrodes of the second kind have been limited to calomel (17, 18), silver sulfide (19), silver chloride (20,21) and silver iodide (22) to our knowledge. There is also a review of kinetics of anodic film formation (23). These experiments were generally conducted in such high concentrations of anions forming a film on an electrode that diffusion of anions to the electrode could be ignored; i.e., the conditions were such that concentration polarization could be neglected.

However, when the deposited film on an electrode is porous, mass transport may be a rate determining step. Thus, it is necessary to determine if mass transport is rate determining or not in the case of reactions forming films. When the concentration of the anion is low, as in polarographic conditions, a limiting current is normally observed which is controlled by diffusion of the anion (24). One can then attempt to deduce a reaction mechanism from the current-voltage curve and sometimes estimate the order of kinetic parameters from currents at less than the limiting value if the reaction involves electrochemical or chemical complications. This corresponds to the normal process of analyzing voltammograms. However, most of the studies (11 - 15, 19, 25, 26) were carried out under conditions where no limiting current was obtained. For instance, an electrochemical study of the silver sulfide system has been performed by Jaenicke et al (19). Their experiment did not result in a limiting current, which they ascribed to ohmic drop in the deposited film of silver sulfide. However, no supporting evidence was presented. Sufficiently high concentrations of sodium sulfide were employed so as to cause anodic potential shifts, but no diffusion plateau.

In the course of anodic polarization of an electrode of the second kind, a new phase is produced on the metal surface or replaced by another solid phase, and voltammograms are often complicated by kinetics related to properties of the film deposited on the electrode. One source of complication is a variation of capacity at the interface with a change in the amount of deposit (19). This can be circumvented by employing a rotating disc electrode (RDE) technique under steady state conditions. It is worth noting that even though constant currents are observed at the RDE, they occur while the amount of deposit is continuously changing as current passes at the interface. However, such steady state currents, without a capacitive component, are expected to contain much information about mass transport and kinetics of film formation. This report describes the anodic depolarization of a silver disc electrode immersed into sodium sulfide in basic aqueous solutions and the cathodic stripping of the deposited silver sulfide.



## EXPERIMENTAL

### Reagents

Analytical grade sodium sulfide and reagent grade sodium hydroxide were used. Solutions were prepared with water purified using a Milli-Q Purification system. Stock solutions of ca  $0.6 \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{S}$  in  $1.0 \text{ mol dm}^{-3}$   $\text{NaOH}$  were prepared and standardization of sodium sulfide was performed iodimetrically (27, 28). The calibration curve of the anodic limiting current vs the concentration of sodium sulfide in  $0.2 \text{ mol dm}^{-3}$   $\text{NaOH}$  at a silver RDE was obtained at a rotation rate of 2500 rpm. The concentration of sodium sulfide in the stock solution was redetermined occasionally using the calibration curve.

### Apparatus

All measurements were performed in a jacketed glass cell having a volume of ca  $400 \text{ cm}^3$ . The temperature in the cell was controlled to  $25 \pm 0.2^\circ\text{C}$  by circulation from an external thermostat. The top of the cell was fitted with a grooved Teflon cap. The cap had a hole in the center 2 cm in diameter for inserting the RDE, and four  $14/35$  tapered holes around the center hole, which were employed as inlets for reference and counter electrodes, for passing purified argon through the solution and adding the solutions. A helical platinum plate (4 cm x 5 cm) electrode was used as counter electrode and was isolated from the RDE by a glass tube with a single junction glass frit. The reference electrode was connected through a solution of the same concentration as that of the background solution in a narrow tube with a stop cock to avoid the diffusion of chloride ion into the test solution. All potentials were measured against a saturated calomel electrode (SCE). The tip of the

Luggin capillary probe was as close as 0.3 cm to the center of the RDE to minimize the error in the measured potential associated with the ohmic drop.

Silver disc electrodes were prepared from a silver rod (99.999 %) and were 0.38 cm in diameter and 0.3 cm thick. The disc electrode was mounted on Teflon and electrical connective made to the stainless steel shaft with silver paste. The procedure for the fabrication of the silver disc electrode was based on the work of Bruckenstein and Albery (29). The surface of the disc electrode was ground and polished by common metallographic techniques, and finally polished with 0.3  $\mu\text{m}$  alumina powder (Dry Powder, Fisher Scientific Co., Type A) on a polishing cloth (Fisher Polishing Cloth, 12 - 28, 2B) with water.

A model EC 225, Voltammetric Analyzer (IBM Instruments, Inc.) was employed for cyclic voltammetry and normal pulse voltammetry. A model EC 220, Stripping Voltammeter (IBM Instruments, Inc.) was employed for linear potential sweep and chronoamperometry. A PARC model 173 Potentiostat/Gavanostat was also used for chronopotentiometry. An Omnigraph, model 2000-XY Recorder (Houston Instrument Co.) was used to record the voltammograms, chronoamperograms and chronopotentiograms. A Pine Instrument ASR Rotator was employed.

#### Experimental procedure

The silver electrode surface was renewed prior to each measurement by a brief polish with 0.3  $\mu\text{m}$  alumina on the wet polishing cloth. The solution to be measured was deaerated by bubbling argon which had been passed through acidic vanadium (II) solution and water. The stock solution of sodium sulfide was added to the background solution with an

Eppendorff  $5 \times 10^{-5} \text{ dm}^3$  pipet.

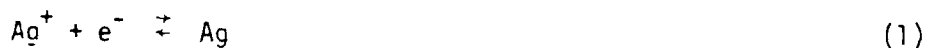
In these experiments the electrode surface was first conditioned at a constant potential of  $-1.20 \text{ V}$  with rotation until a constant current ( $\sim 10 \mu\text{A}$ ) was obtained. Potentiometric measurements at the silver-silver sulfide electrode were carried out as follows. Silver sulfide electrodes on the rotating silver disc were prepared by polarizing the silver disc anodically at  $-0.6 \text{ V}$  at a rotation rate of  $2500 \text{ rpm}$  for  $320 \text{ s}$  in a solution containing  $8.85 \times 10^{-6} \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{S}$  and  $0.20 \text{ mol dm}^{-3}$  of  $\text{NaOH}$ . The equilibrium potentials were measured by the voltage follower in the Model EC 225 Voltammetric Analyzer.

RESULTS AND DISCUSSION

A cyclic voltammogram at the silver RDE in  $0.2 \text{ mol dm}^{-3}$  sodium hydroxide is shown in Figure 1. Silver in basic solution has a relatively flat base line in the potential region of + 0.1 to -1.3 V.

Figure 2 shows anodic and cathodic voltage scans at the silver RDE in  $0.852 \times 10^{-3} \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{S}$ . The waves are almost independent of scan rate ( $\underline{v}$ ) as well as the potential at which the scan is reversed. The quantity of electricity passed during the anodic scan ( $Q_a$ ) is the same as that during the cathodic scan ( $Q_c$ ), independent of the time of electrolysis ( $t_d$ ), rotation rate ( $\underline{\omega}$ ), concentration of sodium sulfide (see Table 1) and sodium hydroxide. Therefore, all the anodic reaction product is held on the electrode surface and the deposited film is completely stripped during cathodic polarization. During the cathodic potential scan, the current crossed the zero current axis at a potential independent of rotation and scan rate but varying with the concentration of sodium sulfide.

One possible interpretation for this zero crossing potential is to consider the equilibrium potential for reaction (1).



The equilibrium potential of reaction (1) is given by Equation (2) assuming the overall electrode reaction (3).

$$E = E^{\circ'} + \frac{RT}{nF} \ln \left( \frac{K_{sp}}{(\underline{c}^{\ominus})^2 \underline{c}_{\text{S}^{2-}}} \right) \quad (2)$$



where  $\underline{c}_S^{2-}$  is the concentration of  $S^{2-}$  which is in equilibrium with  $HS^-$  in the bulk,  $\underline{c}^\ominus$  the standard concentration ( $1 \text{ mol dm}^{-3}$ ),  $\underline{E}^\ominus$  the formal potential for reaction (1) and  $\underline{K}_{sp}$  the solubility product of silver sulfide. To investigate the dependence of the zero-current potential in the cyclic voltammogram on sulfide concentration, a silver sulfide electrode, formed by deposition of silver sulfide on the rotating silver electrode, was used for potentiometric measurements. Plots of the potentials against the logarithm of concentration of sodium sulfide ( $\underline{c}_O$ ) are shown in Figure 3 and give a straight line with a slope of 34 mV, indicating an  $n$  value of two. The formal potential for reaction (3) obtained by the potentiometric data and using  $10^{14.0} \text{ mol}^{-1} \text{ dm}^3$  (30) as the formation constant ( $\underline{K}_1$ ) for  $S^{2-} + H^+ \rightleftharpoons HS^-$  was  $-0.934 \text{ V}$ . The value is in good agreement with that ( $-0.914 \text{ V}$ ) calculated from Equation (2) using  $1.6 \times 10^{-50} \text{ mol}^3 \text{ dm}^{-9}$  for  $\underline{K}_{sp}$  (31) and  $0.555 \text{ V}$  for  $\underline{E}^\ominus$  (32). This value is very close to the standard potential ( $-0.93 \text{ V}$ ) (33) for reaction (3). Thus, reaction (3) above takes place at the silver sulfide covered electrode, and that the electrode formed in this manner behaves thermodynamically.

Reaction (3) describes the voltammogram in Figure 2 quite well as described below. The anodic reaction gives a limiting current controlled by convective diffusion of sulfide to the electrode (see below). Silver sulfide produced on the electrode is stripped during a cathodic scan to silver and sulfide ions. All the silver sulfide produced anodically remains on the electrode.

The electrode surface gradually blackens as anodic polarization

proceeds. It is difficult to remove the black film on the electrode by polishing with alumina powder. The color of the electrode is still black following cathodic stripping but loses its luster. The thick film of Ag formed following reduction of deposited  $\text{Ag}_2\text{S}$  is mechanically so weak that the film often spontaneously peeled off immediately after completion of a cathodic scan in the form of a thin disc with the same diameter as the electrode. This may result from the high porosity of silver generated as a consequence of the removal of sulfide ion from the silver sulfide film. The poor luster of the cathodic product may also result from the high porosity of the silver film.

The next three sections discuss the anodic polarization, passivation after prolonged anodic polarization and cathodic stripping of silver sulfide.

#### Anodic polarization

Highly reproducible anodic limiting currents ( $I_d$ ) were obtained in the potential region from -0.65 V to -0.20 V. Since the values of the limiting currents are proportional to the concentrations of sodium sulfide (Figure 4, Table 1), except at high concentrations, the reaction order is unity with respect to sodium sulfide. Limiting currents for the formation of  $\text{Ag}_2\text{S}$  plotted against the square root of rotation rate are shown in Figure 5, which indicates the limiting currents are controlled by convective diffusion. Thus, the formation of  $\text{Ag}_2\text{S}$  film on the limiting current plateau is controlled by diffusion of sulfide ion from the bulk of solution. Under the experimental conditions there may be two sulfide species participating in the diffusion,  $\text{S}^{2-}$  and  $\text{HS}^-$ .

Here,  $H_2S$  is ignored in view of the high pH. Since  $S^{2-}$  and  $HS^-$  can be considered to be in equilibrium at the electrode surface as in the bulk even if current is flowing, the limiting current can be represented by the Levich equation as

$$\bar{I}_d = 6.2 \times 10^{-4} n F A \bar{D}^{-2/3} c_0 v^{-1/6} \omega^{1/2} \quad (5)$$

where  $\bar{D}$  is the mean diffusion coefficient for  $S^{2-}$  and  $HS^-$  and is given as

$$\bar{D} = \left\{ (D_S^{2/3} + K_1 [H^+] D_{HS}^{2/3}) / (1 + K_1 [H^+]) \right\}^{3/2},$$

$D_S$  and  $D_{HS}$  are the diffusion coefficient for  $S^{2-}$  and  $HS^-$  respectively, and the other variables have their usual meaning. The plots of limiting currents against  $c_0 \omega^{1/2}$  in 0.2 mol  $dm^{-3}$  NaOH solution are straight lines (Figure 5). Values of  $\bar{D}$  for three concentrations of sodium hydroxide calculated from the slopes of these plots using values of the kinematic viscosity corresponding to each sodium hydroxide solution (Table 2). Since a diffusion coefficient is inversely proportional to the viscosity of the medium by the Stokes - Einstein equation, Table 2 shows corrected values of  $\bar{D}$  which are multiplied by  $\eta/\eta_0$  where  $\eta$  and  $\eta_0$  are the viscosity of sodium hydroxide solutions and pure water respectively. These values are almost the same, and indicates reasonable adherence to the Stokes - Einstein equation.

Figures 6 shows anodic currents at less than limiting current values plotted vs  $\omega^{1/2}$  at a given concentration of sodium sulfide and for various constant potentials. The convex curves indicate chemical and/or electrochemical complications. A detailed analysis of the mechanism for  $Ag_2S$  formation will be presented elsewhere (34).

Normal pulse voltammograms are compared with a steady state voltammogram in Figure 7. Two steps appear in the normal pulse voltammograms at both RDE and stationary disc electrode, of which the second (more positive) is clearly the oxidation of silver to silver sulfide and corresponds to the steady state voltammogram. From the potential at which the first step appeared (ca -1.05V), this step seems not to be due to oxidation of silver but may result from a change in the electrical double layer at the electrode/solution interface with time, although slow formation of a monolayer of  $\text{Ag}_2\text{S}$  cannot be ruled out. However, more detailed studies are required to clarify this first step.

It may be dangerous to extend the frequently employed pulse techniques to an electrochemical system forming a deposit or film at a solid electrode. A variation of the thickness of the deposited film with time may cause a change in double layer capacity and thus capacitive currents may still remain at the current sampling time. There are still differences in opinion with regard to the published work on mercury - sulfide system (35), for example.

#### Passivation

In solutions more than a few  $\text{mmol dm}^{-3}$  sodium sulfide, the anodic current on the voltammogram rises and reaches a limiting current during the anodic potential scan, but then diminishes with a steep slope after a certain time as illustrated in Figure 8. To determine whether passivation results from the potential at the electrode surface being different from the applied potential or if mass transfer within the deposited film is limiting, we performed chronoamperometric experiments at the silver RDE at the potential of the limiting currents (-0.6 V) for several



sodium sulfide concentrations. Chronoamperometric curves in Figure 9, normalized to the appropriate limiting currents, decrease suddenly after a given time ( $\tau_p$ ). Dependence of  $\tau_p$  on the inverse of limiting currents at the rotation rate of 2500 rpm (Figure 10) shows that passivation begins after the quantity of electricity for film formation on the electrode surface exceeds  $7.7 \times 10^{-2} \text{ C cm}^{-2}$  ( $Q_T$ ). This corresponds to about 700 monolayers if a molar volume of crystalline  $\text{Ag}_2\text{S}$  is taken as  $33.9 \text{ cm}^3 \text{ mol}^{-1}$  (36). Assuming the deposited  $\text{Ag}_2\text{S}$  forms a porous film, the number of monomolecular layer must be greater than 700. Chronoamperometric measurements at potentials more anodic than -0.6 V show a similar behavior except that  $\tau_p$  increases slightly. This argues against passivation occurring because a sufficiently anodic potential is not applied to the charge transfer interface due to a high electric field in the anodic film.

Galvanostatic experiments were also carried out at the RDE at various rotation rates. The galvanostat was adjusted to constant anodic currents which were a little less than RDE limiting currents. When the constant current was applied, the observed potential was initially quite constant (Figure 11) corresponding to slightly more cathodic potentials than those on the limiting current plateau. After a certain time, the potential shifted rapidly to about +0.2 V at which the next reaction, probably formation of silver oxide or hydroxide may take place (37). Roughly, the break in the potential time curves occurs after approximately  $8 \times 10^{-2} \text{ C cm}^{-2}$  were passed, in accord with the value of  $Q_T$  obtained above from the decrease in current at the rotating disc. It is also worth noting that the potential of the electrode under these conditions

rises to a value characteristic of silver oxidation in the base supporting electrolyte. These results support the argument that passivation is independent of potential.

The other possibility for occurrence of passivation is that the transport of sulfide ions or silver ion is blocked within the porous thick film on the electrode. We could not conclude which processes or ions controlled the passivation. However, as noted above, the potential of the electrode ultimately reaches +0.2 V, which implies that a subsequent reaction takes place through the  $\text{Ag}_2\text{S}$  film.

#### Cathodic polarization

A cathodic current begins to flow at the equilibrium potential and a sharp reduction peak is obtained. The thickness of silver sulfide to be stripped from the electrode is a macroscopic value in these experiments, e.g. 450 monomolecular layers for the voltammogram in Figure 2 if the intermolecular distance of silver sulfide in porous film is assumed as  $10^{-7}$  cm. Therefore the deposited film may function as a porous electrode, being replaced by porous silver. Thus all silver sulfide on the electrode can be reduced if a sufficiently cathodic potential is applied to the electrode. This suggests that the rate of conversion may be controlled by chemical and/or electrochemical kinetics rather than mass transfer.

A detailed study of the cathodic stripping process for sulfide analysis will be reported elsewhere (38).

ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research.

REFERENCES

1. Healy T. W., "Electrochemistry" The Past Thirty and The Next Thirty Years, chapter 19, Edited by Bloom H. and Gutman F., Plenum Press, New York and London, 1977.
2. Richard A. D., "Ion-Selective Electrodes" National Bureau of Standard Special Publication 314, 1969.
3. Covington A. K., "Ion-Selective Electrode, Methodology", vol. 1, CRC Press, Inc., 1977.
4. Weber N., "Superionic Conductors", Edited by Mahan G. D. and Roth W. L. p. 37, Plenum Press, New York and London, 1976.
5. Peters E., "Trends in Electrochemistry", p. 267, Edited by Bockris J. O'. , Rand D.A.J. and Welch B. J., Plenum Press, New York and London, 1976.
6. Koch D.F.A., "Modern Aspect of Electrochemistry", No. 10, chapter 4, Edited by Bockris J. O'. and Conway B. E., Plenum Press, New York and London, 1975.
7. Tischer R. P. and Ludwig F. A., "Advances in Electrochemistry and Electrochemical Engineering", vol. 10, chapter 5, Edited by Gerischer H. and Tobias C. W., John Wiley & Sons, Inc., 1977.
8. Golding M., J. Chem. Soc., (1959) 1838.
9. Freybergerger W. L. and de Bruyn P. L., J. Phys. Chem., 61 (1957) 586.
10. Wagner C., J. Chem. Phys., 21 (1953) 1819.
11. den Engelsen D., v. Gorp A.A.C.M., and Heyne L., J. Electrochem. Soc., 126 (1979) 242.
12. Sasaki J., Mizusaki J. and Fueki K., Bull. Chem. Soc. Jpn., 51 (1978) 1027.
13. Corish J. and Warde G. J., Ber. Bunsenges. Phys. Chem., 82 (1978) 282.
14. Rickert H., Sattler V., and Wedde Ch., Phys. Chem., N. Y., 98 (1975) 339.
15. Bartkowiez I. and Mrowec S., Bull. Acad. Polo. Sci. Chim., 20 (1972) 145.
16. Ives D.J.G. and Janz G. J., "Reference Electrodes", Academic Press, 1969.
17. Bockris J. O'. M., Devanathan M.A.V. and Reddy A.K.N., Proc. Roy. Soc. A279 (1964) 327.

18. Cornish D. C., Dibbs H. P. Feates F. S., Ives D.J.G. and Pittman R. W. J. Chem. Soc., (1962) 4104.
19. Jaenicke W., Khairy E., and Schafer W., Ber. Bunsenges. Phys. Chem., 70 (1966) 421.
20. Katan T., Szpak S. and Bennion D. N., J. Electrochim. Soc., 120 (1973) 883.
21. Fleischmann M. and Thirsk H. R., Electrochim. Acta, 1 (1959) 146.
22. de Voys D. A. and Pieper J.H.A., J. Electroanal. Chem., 72 (1976) 147.
23. Gruz T. E., "Kinetics of Electrode Process", Chapter 7, Wiley-Interscience, New York (1972).
24. Kolthoff I. M. and Miller C. S., J. Amer. Chem. Soc., 63 (1941) 1405.
25. Armstrong R. D., M. F. Bell, "Electrochemistry", Specialist Periodical Reports, vol. 4, chapter 1, The Chemical Society, 1974.
26. Armstrong R. D., Edmondson K., and West G. D., "Electrochemistry", Specialist Periodical Reports, vol. 4 chapter 2, The Chemical Society, 1974.
27. Belcher R., Nutten A. J., and Macdonald A.M.G., "Quantitative Inorganic Analysis" p. 248, Butterworths and Co. Ltd., 1970.
28. Diehl H., "Quantitative Analysis", p. 245, Oakland Street Science Press, 1970.
29. Bruckenstein S. and Albery W. J., Trans. Faraday Soc., 62 (1966) 1920.
30. Schwarzenbach V. G. and Widmer W., Helv. Chim. Acta.
31. Bjerrm J., Schwrzenbach G. and Sillen L. G., "Stability Constants of Metal - Ion Complexes". Supplement No. 1, p. 129, The Chemical Society, London (1971).
32. Shumilova N. A. and Zhutaveva G. V., "Encyclopedia of Electrochemistry of Elements", vol. 8, p. 5, Edited by Bard A. J., Marcel Dekker, Inc., New York, (1978).
33. Latimer W. M., "The Oxidation state of the elements and their potentials in aqueous solutions", second edition, p. 191, Prentice-Hall, Inc., New York (1952).
34. Aoki K., Shimizu K. and Osteryoung R. A., J. Electroanal. Chem., in press.
35. Canterford D. R., J. Electroanal. Chem., 52 (1974) 144.

36. Weast R. C. (editor), "Handbook of Chemistry and Physics", 59th edition, p. D-303, CRC Press Inc., 1978 - 1979.
37. Hampson A. N., MacDonald K. I. and Lee J. B., J. Electroanal. Chem., 45 (1973) 149.
38. Shimizu K. and Osteryoung R. A., Anal. Chem., 53 (1981) 584.

Table 1. Comparison of quantity of anodic charge ( $Q_a$ ) and cathodic charge ( $Q_c$ ).

$c_0/10^{-4}$ mol dm <sup>-3</sup>	$I_d/10^{-4}$ A	$Q_a/10^{-2}$ C	$Q_c/10^{-2}$ C	$(I_d/c_0)/A$ mol <sup>-1</sup> dm <sup>3</sup>
1.74	3.00	2.19	2.14	1.72
2.61	4.50	3.30	3.20	1.72
3.63	6.25	4.63	4.51	1.72
4.33	7.45	5.51	5.30	1.72
5.08	8.75	6.48	6.50	1.72

The values of  $Q_a$  were calculated from Faraday's law using the limiting currents. Experimental conditions: 0.2 mol dm<sup>-3</sup> of NaOH solution; rotation rate = 2500 rpm; scan rate = 10 mV s<sup>-1</sup>; time of electrolysis = 60 s, potential of electrolysis = -0.6 V.

Table 2. The mean diffusion coefficients for  $S^{2-}$  and  $HS^{-}$  in sodium hydroxide solutions

$c_{NaOH}/\text{mol dm}^{-3}$	$(I_d/^{1/2}c_o)/A \text{ s}^{1/2}\text{mol dm}^3$	$\bar{D}/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$\bar{D}(\eta/\eta_0)/10^{-5} \text{ cm}^2 \text{ s}^{-1}$
0.05	0.1095	2.79	2.81
0.20	0.1050	2.64	2.75
1.00	0.0935	2.29	2.83



FIGURE CAPTIONS

Fig. 1. Cyclic voltammogram in  $0.2 \text{ mol dm}^{-3}$  NaOH solution at the silver RDE  
 $\omega = 2500 \text{ rpm}$ ,  $\underline{v} = 50 \text{ mV s}^{-1}$ ; potential scan from  $-1.10 \text{ V}$  positive.

Fig. 2. Cyclic voltammogram for sulfide ion at the silver RDE  
Solution:  $0.852 \times 10^{-5} \text{ mol dm}^{-3}$   $\text{Na}_2\text{S}$  in  $0.2 \text{ mol dm}^{-3}$  NaOH,  
 $\omega = 2500 \text{ rpm}$ ,  $\underline{v} = 10 \text{ mV s}^{-1}$ , potential scanned from  $-1.20 \text{ V}$   
positive.

Fig. 3. Nernst plot for  $\text{Ag}_2\text{S}$  deposited at a silver disc, potential vs  
concentration of sodium sulfide in  $0.2 \text{ mol dm}^{-3}$  NaOH solution.

Fig. 4. Dependence of the limiting current during anodic polarization  
curves on the concentration of sodium sulfide  
Solutions: (a) 6.85 (b) 5.99 (c) 5.14 (d) 4.28 (e) 3.42 (f) 2.57  
(g)  $1.71 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{Na}_2\text{S}$  in  $0.20 \text{ mol dm}^{-3}$  NaOH,  $\omega = 2500$   
 $\text{rpm}$ ,  $\underline{v} = 10 \text{ mV s}^{-1}$ .

Fig. 5. Plots of  $\underline{I}_d$  vs  $\underline{c}_0 \omega^{1/2}$   
Solutions: ( $\circ$ ) 8.85, ( $\odot$ ) = 7.08, ( $\diamond$ ) = 5.31, ( $\nabla$ ) = 3.54,  
( $\triangle$ ) =  $1.77 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{S}$  in  $0.20 \text{ mol dm}^{-3}$  of NaOH,  
 $\underline{v} = 10 \text{ mV s}^{-1}$ .

Fig. 6. Dependence of anodic current ( $\underline{I} < \underline{I}_d$ ) on  $\omega^{1/2}$  at various potentials.  
Solutions:  $5.31 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{S}$  in  $0.20 \text{ mol dm}^{-3}$  of NaOH,  
potentials: (a)  $-0.550$ , (b)  $-0.675$ , (c)  $-0.700$ , (d)  $-0.725$ ,  
(e)  $-0.750$ , (f)  $-0.775 \text{ V}$ ,  $\underline{v} = 10 \text{ mV s}^{-1}$ .

Fig. 7. Comparison of normal pulse voltammograms and steady state RDE voltammogram

Solution:  $4.75 \times 10^{-4} \text{ mol dm}^{-3} \text{ Na}_2\text{S}$  in  $0.20 \text{ mol dm}^{-3}$

NaOH, (a) normal pulse voltammogram at stationary silver disk electrode, (b) normal pulse voltammogram at silver RDE,

$\omega = 2500 \text{ rpm}$ , repetition time = 0.55, pulse width = 50 mV, pulse delay = 33.3 ms, sampling time = 16.6 ms, (c) linear potential sweep voltammogram at silver RDE,  $\omega = 2500 \text{ rpm}$ ,  $\underline{v} = 10 \text{ mV s}^{-1}$ .

Fig. 8. Anodic polarization curve for high concentration of sodium sulfide at silver RDE

Solution:  $4.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{S}$  in  $0.2 \text{ mol dm}^{-3} \text{ NaOH}$ .

$\omega = 2500 \text{ rpm}$ ,  $\underline{v} = 10 \text{ mV s}^{-1}$ .

Fig. 9. Chronoamperograms in sodium sulfide solution at silver RDE

Solutions: ( $\blacktriangle$ ) 1.77, ( $\blacklozenge$ ) 2.66, ( $\blacklozenge$ ) 3.54, ( $\blacklozenge$ ) 4.43, ( $\bullet$ ) 6.20  $\times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{S}$  in  $0.20 \text{ mol dm}^{-3}$  of NaOH.

Fig. 10. Relationship between transition time for passivation and inverse limiting current (data of Figure 9).

Fig. 11. Galvanostatic transients in sodium sulfide in solution using the silver RDE

Solution:  $4.43 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{S}$  in  $0.20 \text{ mol dm}^{-3} \text{ NaOH}$ ,

(a)  $\omega = 3600 \text{ rpm}$ ,  $6.0 \times 10^{-3} \text{ A}$ , (b)  $\omega = 1600 \text{ rpm}$ ,  $4.0 \times 10^{-3} \text{ A}$ ,

(c)  $\omega = 400 \text{ rpm}$ ,  $2.0 \times 10^{-3} \text{ A}$ .

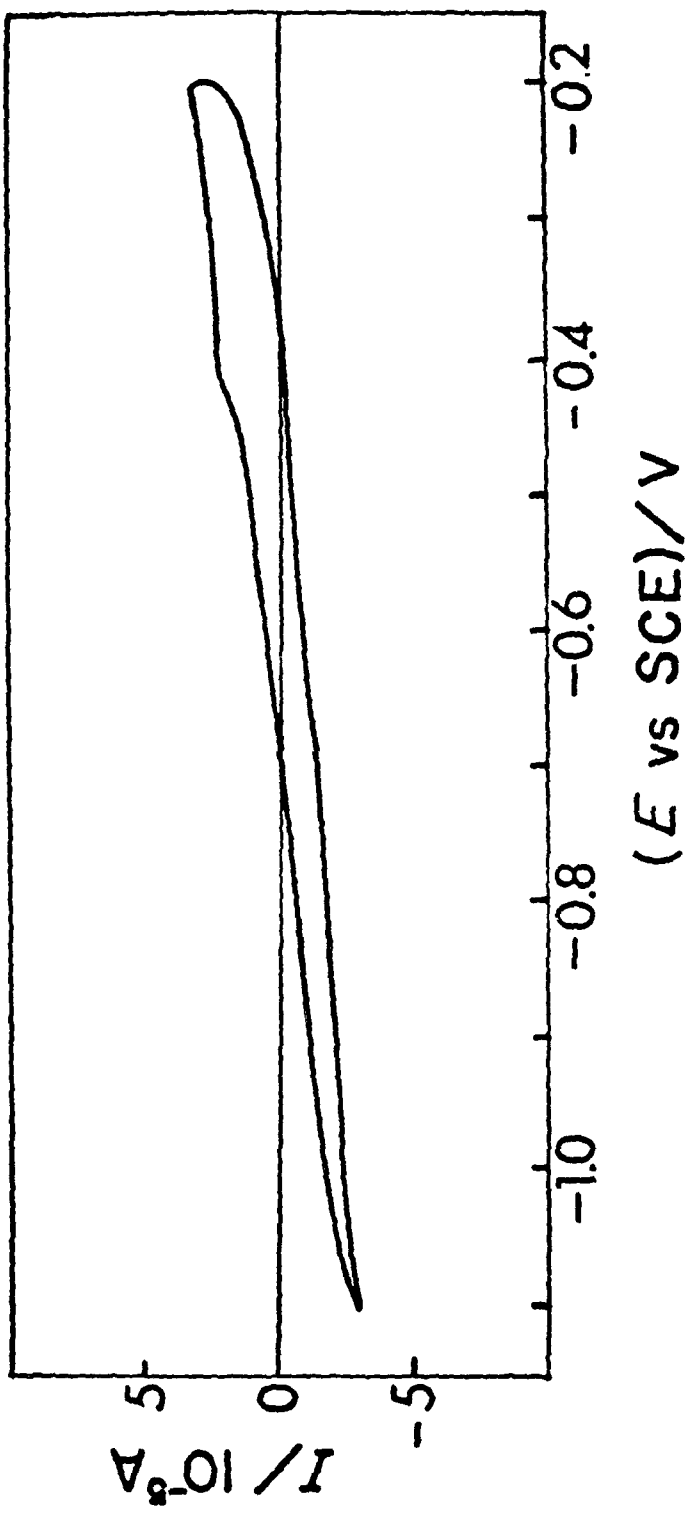


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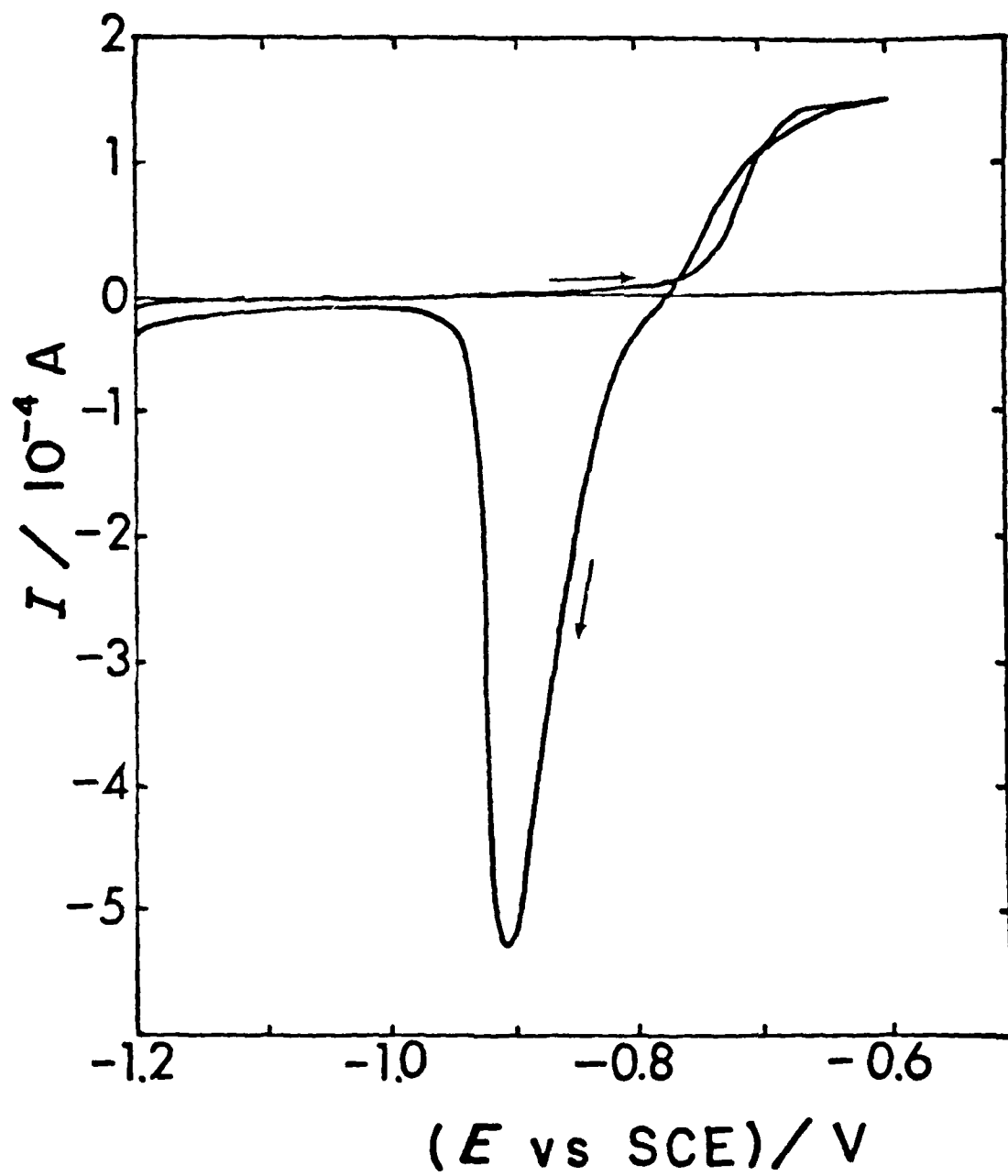


Figure 2

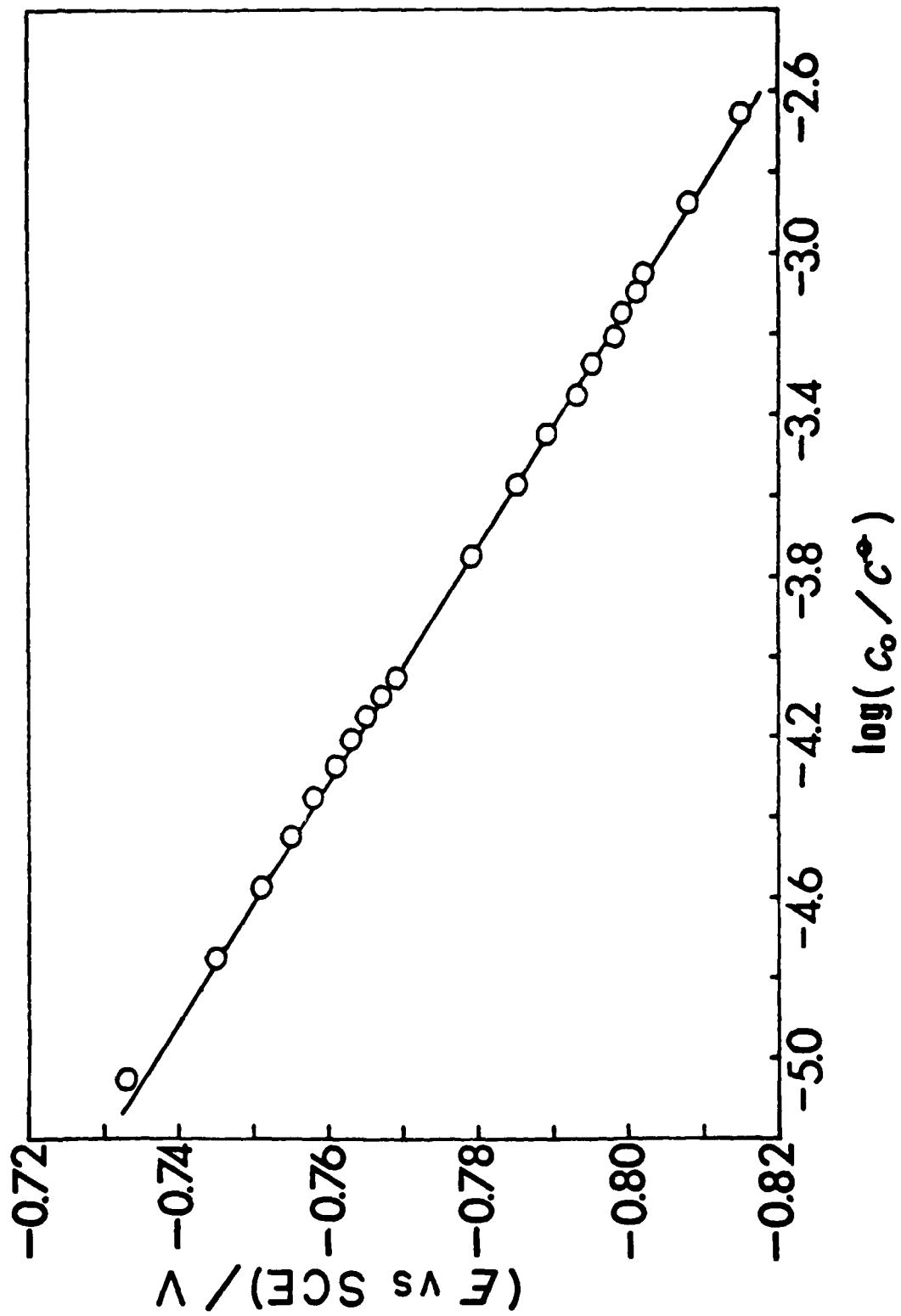


Figure 3

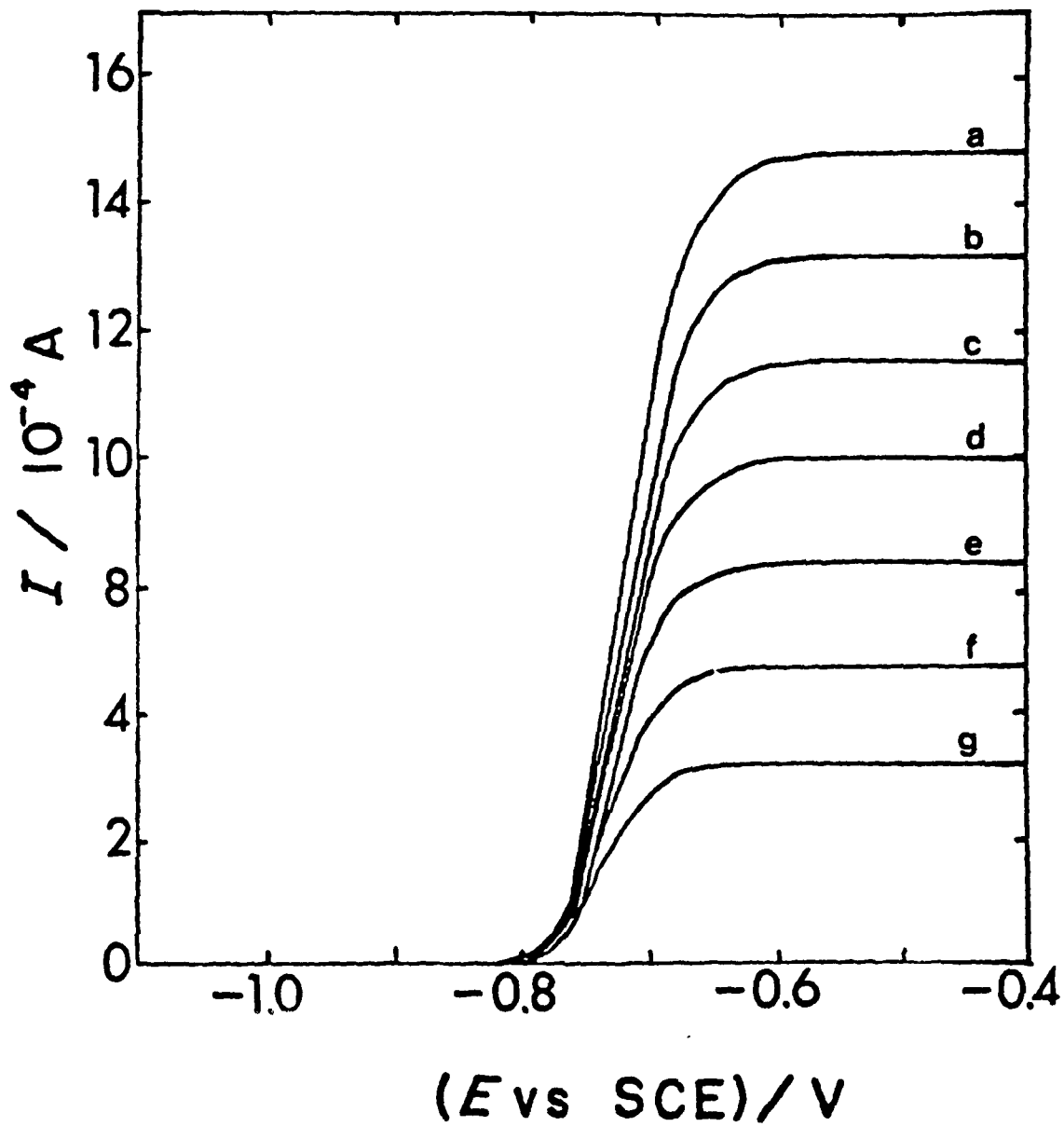


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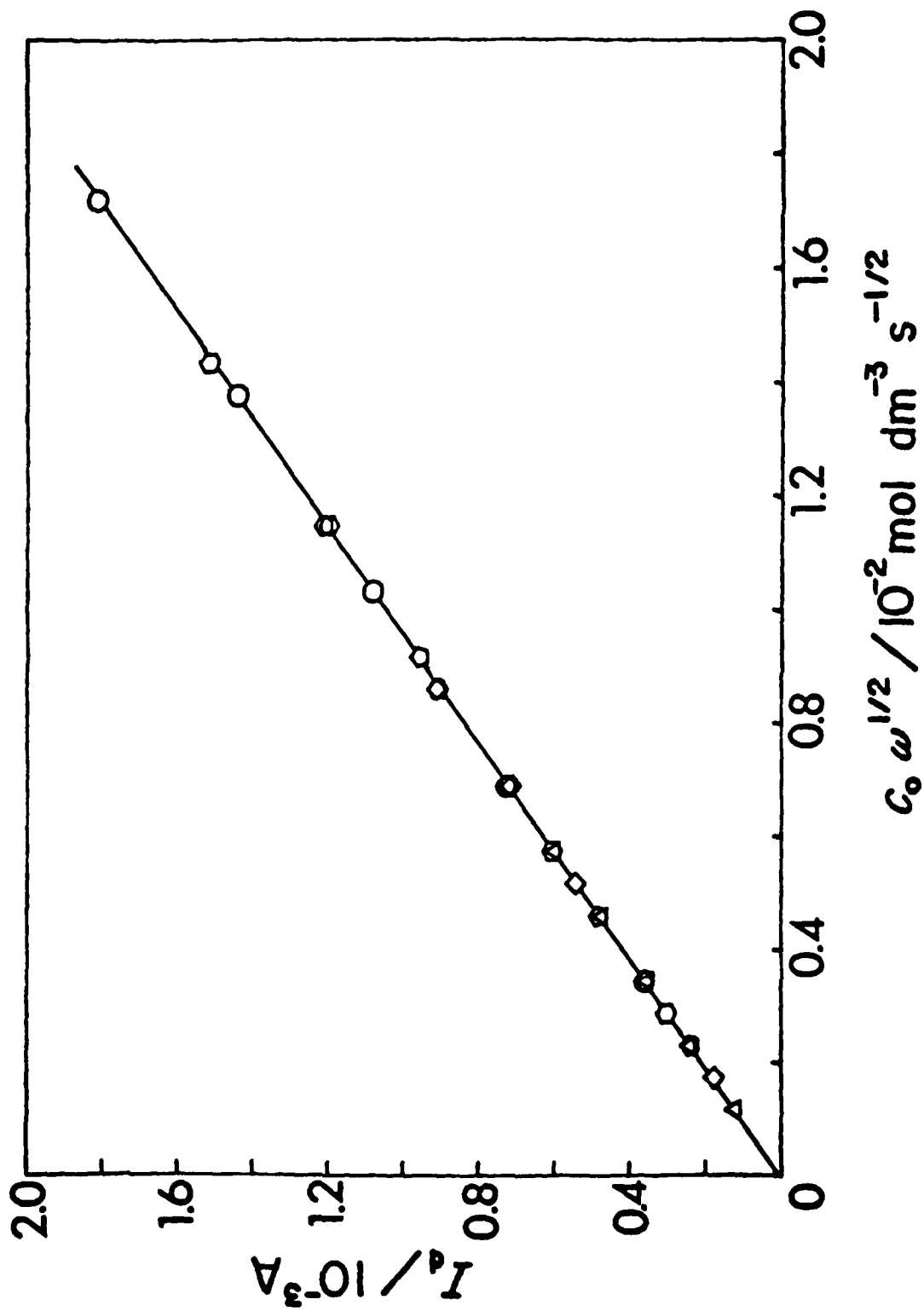


Figure 5

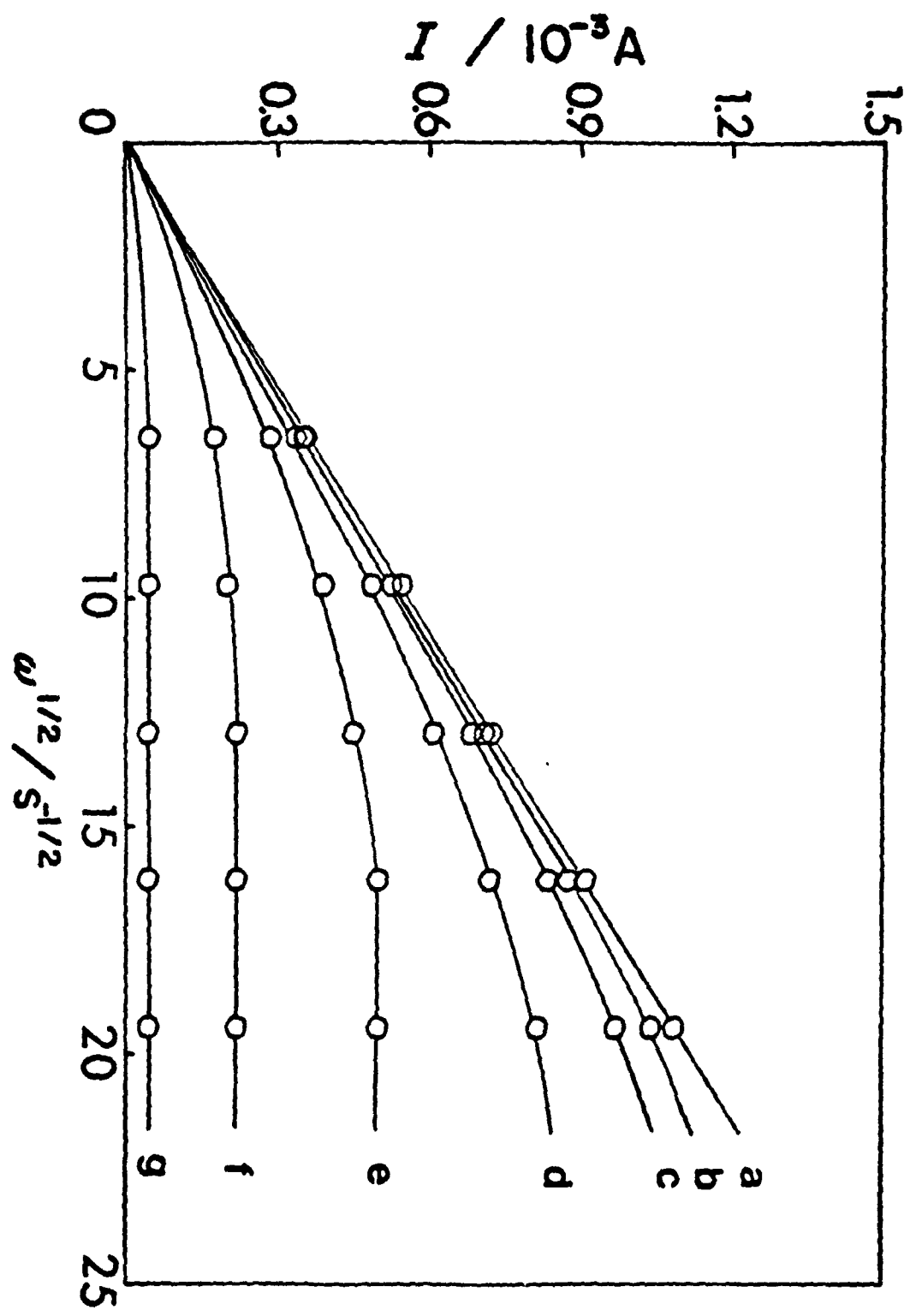


Figure 6



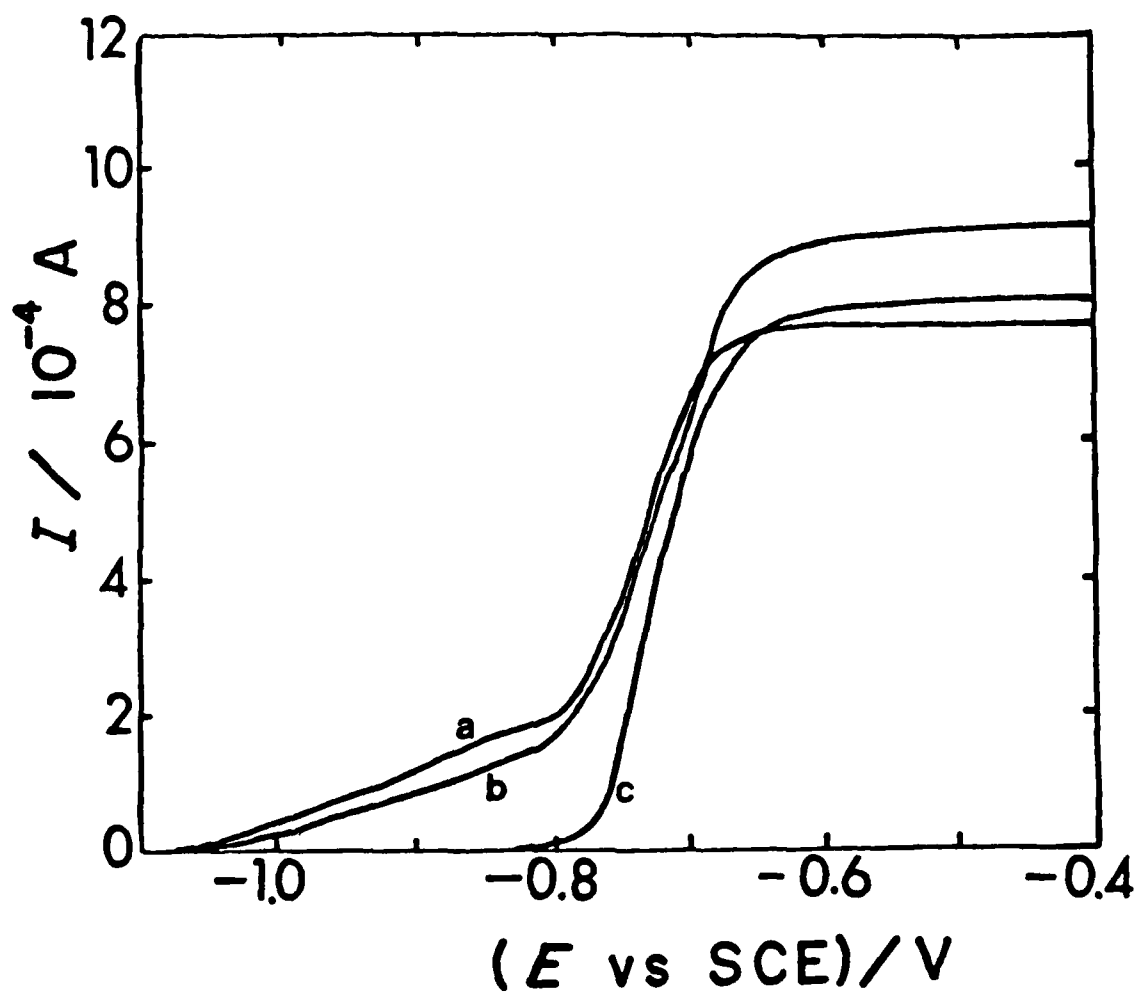


Figure 7

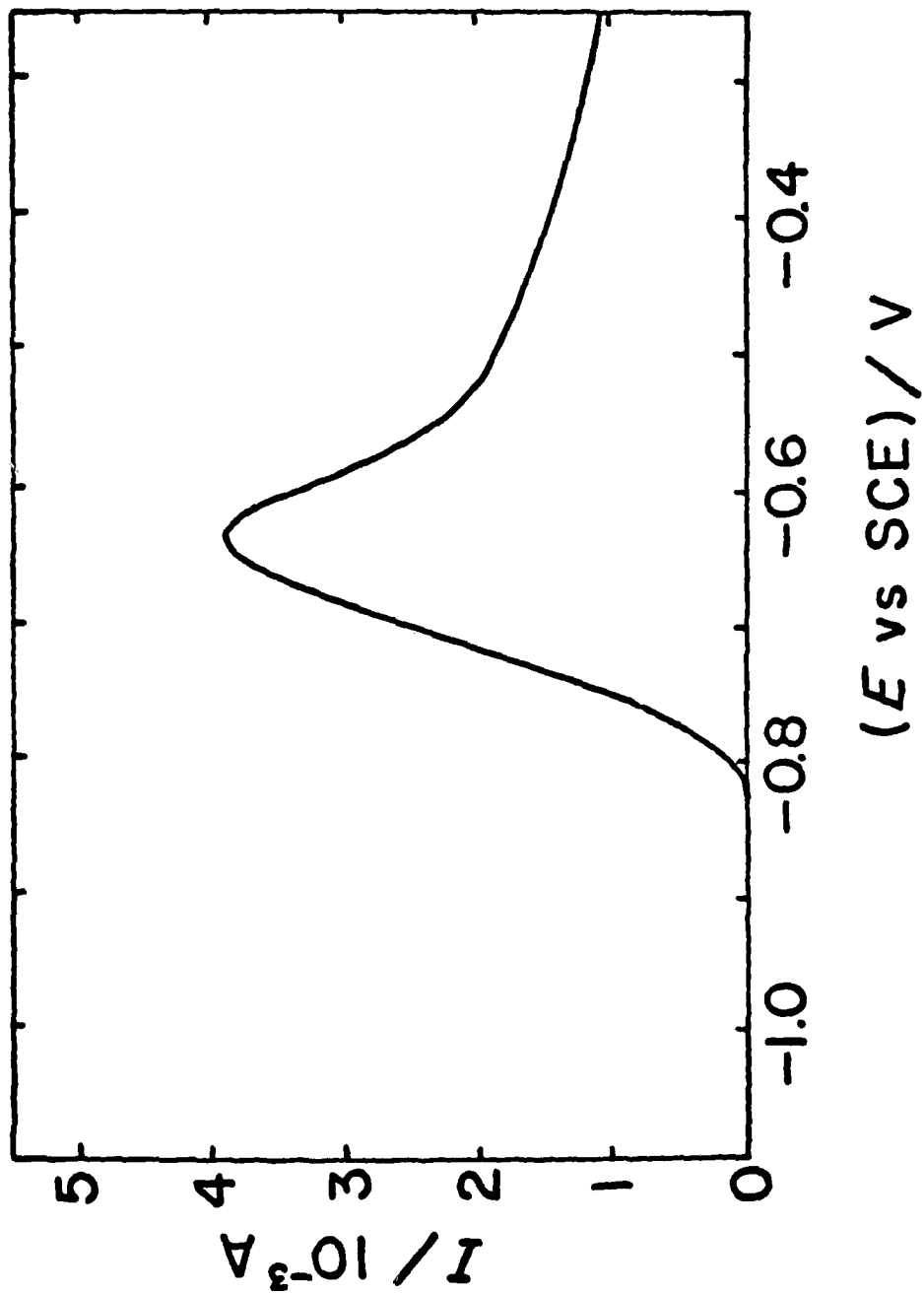


Figure 8

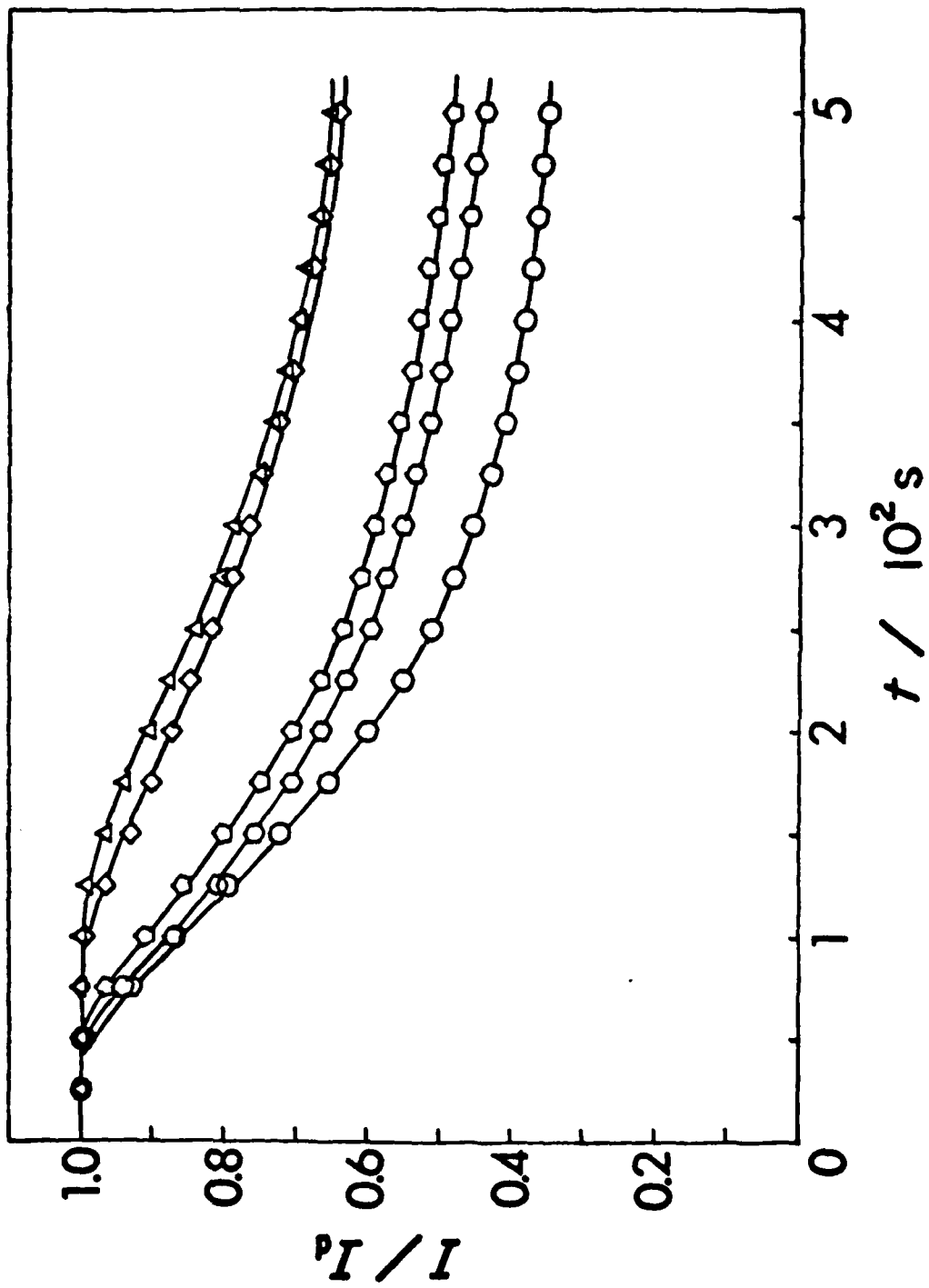


Figure 9

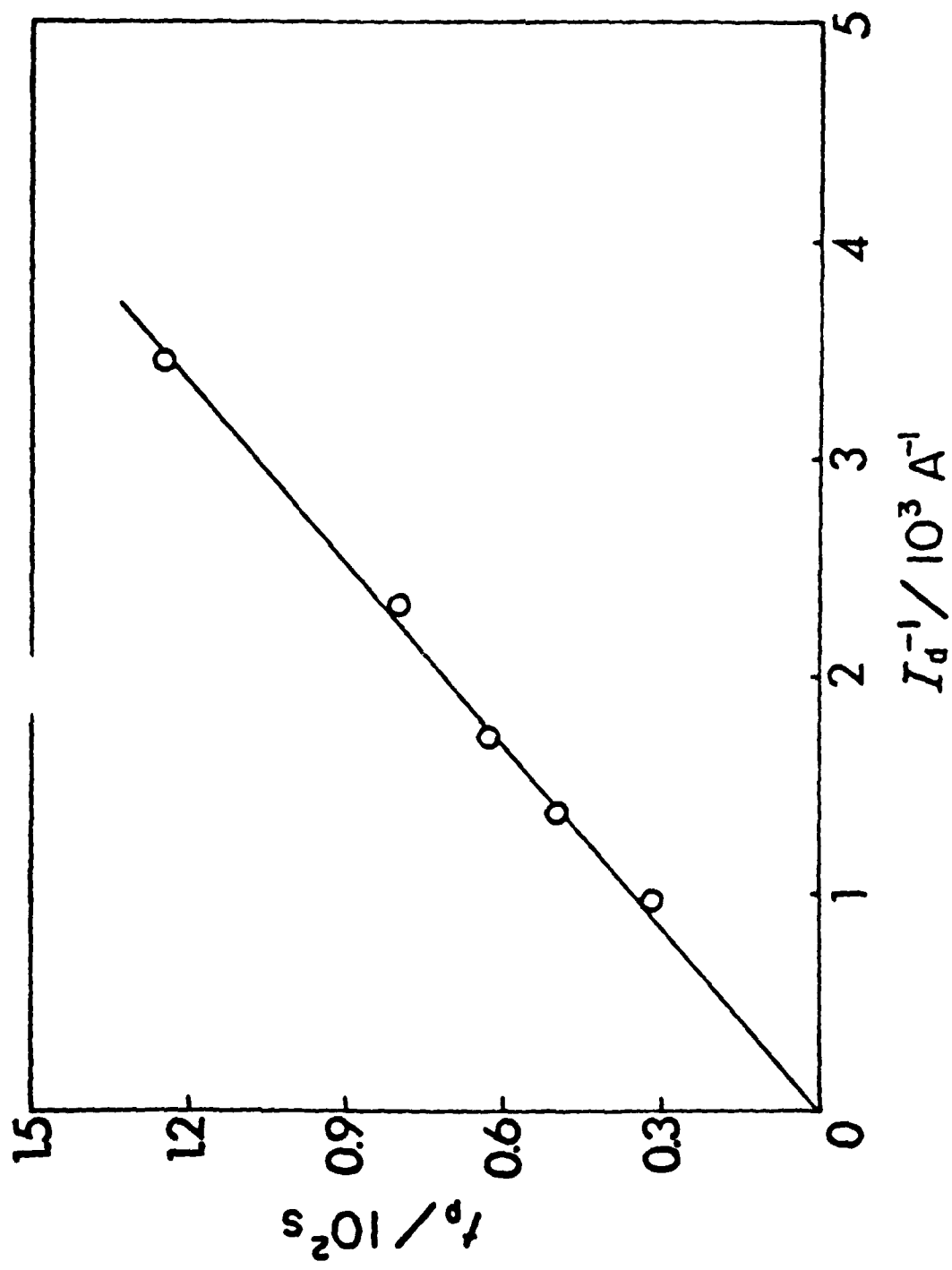


Figure 10

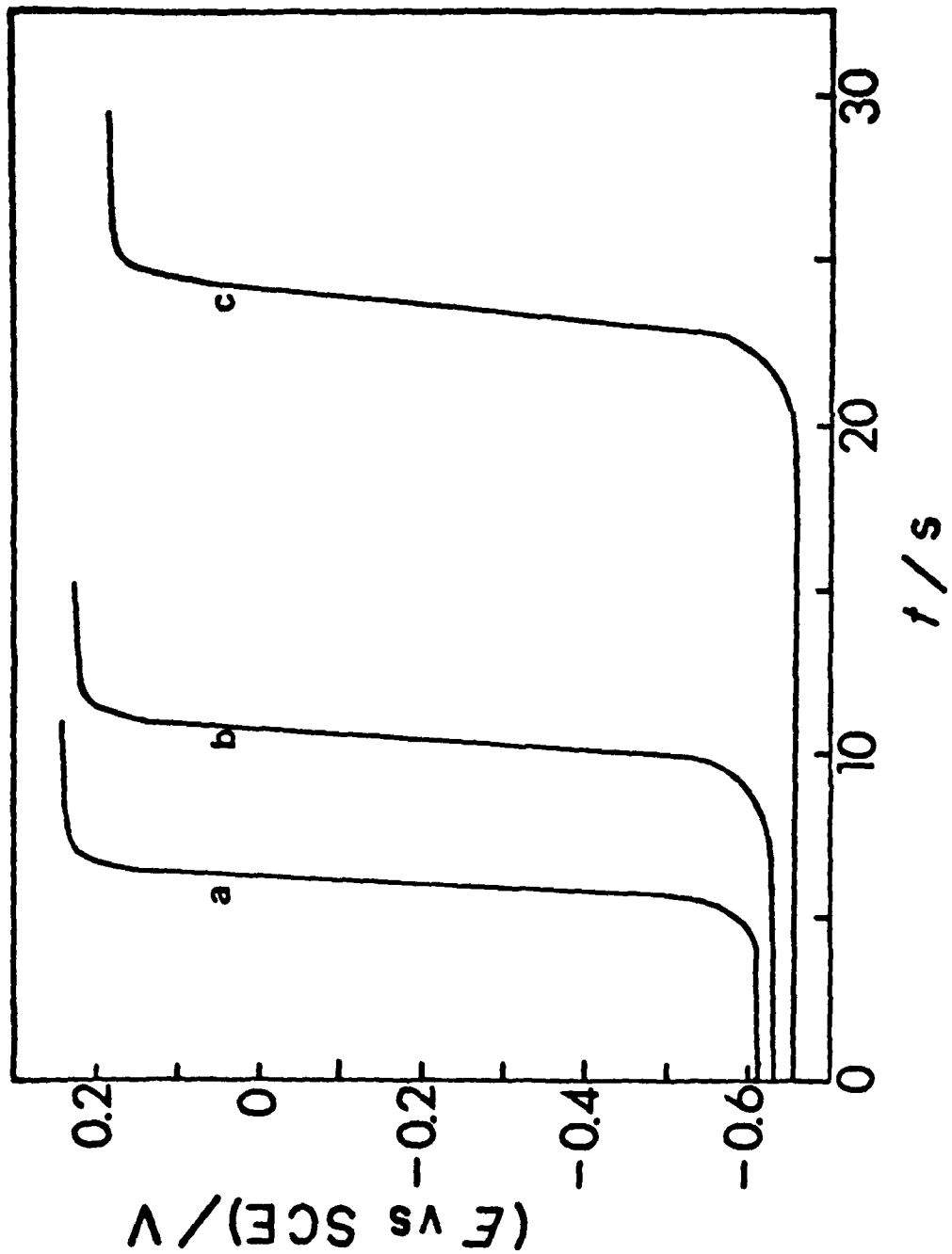


Figure 11

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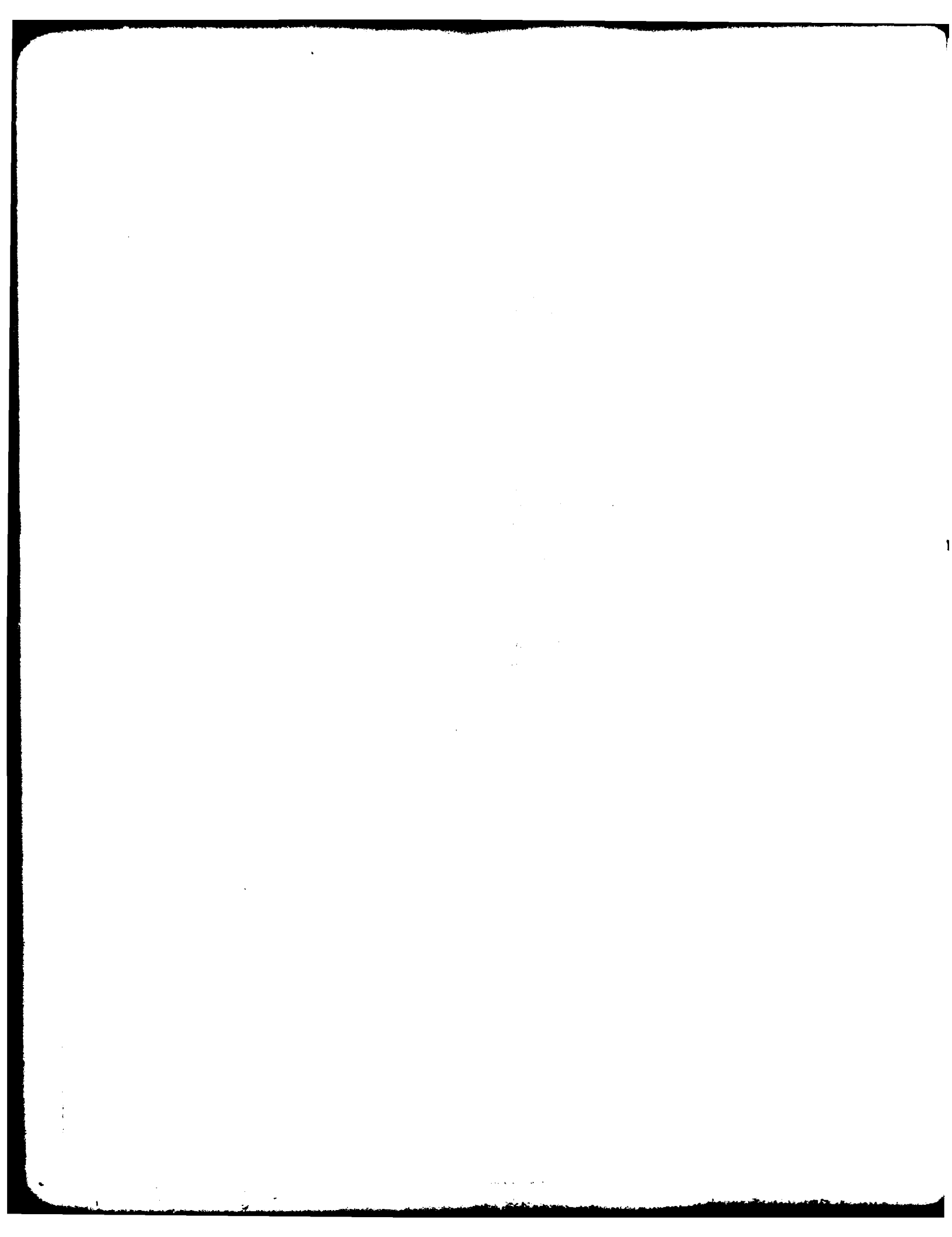
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