

Lawrence Berkeley National Laboratory

Recent Work

Title

Electrochemical Properties of Organic Disulfide/Thiolate Redox Couples

Permalink

<https://escholarship.org/uc/item/7cw0834v>

Journal

Journal of the Electrochemical Society, 136(9)

Authors

Liu, M.

Visco, S.J.

Jonghe, L.C. De

Publication Date

2017-12-11



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Journal of the Electrochemical Society

Electrochemical Properties of Organic Disulfide/Thiolate Redox Couples

M. Liu, S.J. Visco, and L.C. De Jonghe

July 1988

RECEIVED
LAWRENCE
BERKELEY LABORATORY
OCT 2 1988
LIBRARY AND
DOCUMENTS SECTION

For Reference

Not to be taken from this room



LBL-25638
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**ELECTROCHEMICAL PROPERTIES OF
ORGANIC DISULFIDE/THIOLATE REDOX COUPLES**

Meilin Liu, Steven J. Visco, and Lutgard C. De Jonghe

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory

and

Department of Materials Science and Mineral Engineering

University of California

Berkeley, CA 94720

Abstract

The redox behavior, kinetic reversibility, chemical reversibility and stability, and the specific adsorption or chemisorption at electrode surfaces of a diverse group of organosulfur compounds have been studied by potential-sweep and potential-step methods. The number of electrons involved in the redox reaction and the diffusion coefficients of the organodisulfide species in electrolyte solutions were determined with a rotating disk electrode in conjunction with chronocoulometry/chronoamperometry. Results indicate that the redox reaction is



where R represents an organic moiety. These reactions are chemically reversible; yet, the charge transfer kinetics at room temperature are sluggish. In addition, the specific adsorption or chemisorption of the organic disulfides at platinum electrode is negligible.

Introduction

A group of organic disulfides have been recently introduced as positive electrodes for high energy-density battery applications^[1]. The attractive features of these compounds include low operating temperatures (ambient to 150°C), high energy densities, low cost, passive behavior to many materials, and low toxicity. Furthermore, properties of the organodisulfides can be modified by appropriate choice of the organic groups. To date, however, the fundamental physical, chemical, and electrochemical properties of these materials have not been established. The purpose of this study has been to investigate the redox behavior, chemical stability/reversibility, kinetic reversibility, and adsorption phenomena of organodisulfides at electrode surfaces.

Experimental

Several organic disulfides, sodium thiolate salts, and precursors used in the experiments were obtained from Aldrich*. Tetramethylthiuram disulfide (TMTD), tetraethylthiuram disulfide (TETD), and phenyl disulfide (PDS) were recrystallized several times from the appropriate alcohols (n-butanol, ethanol, etc.). Sodium diethyl dithiocarbamate (NaDEDC) and sodium dimethyl dithiocarbamate (NaDMDC) were purified by dissolving the salts in a minimum amount of absolute ethanol and precipitated by addition of absolute ether. The purified solid organosulfur compounds were stored under vacuum in a dessicator. Hydroxyethyl disulfide (HEDS) was distilled under vacuum over

* Aldrich Chemical Company, Inc., 940 West Saint Paul Avenue, Milwaukee, Wisconsin 53233.

molecular sieves. Di-fluorophenyl disulfide (FPDS) was synthesized from the stoichiometric oxidation of 4-fluorothiophenol by iodine, and subsequently distilled under vacuum. Supporting electrolyte tetraethylammonium perchlorate (TEAP) and reference electrode filling electrolyte tetramethylammonium chloride (TMAC) were obtained from Southwestern Analytical Chemicals^{**}, ground to fine powders, dried in a vacuum furnace at 80° C, and kept under vacuum in a dessicator. Anhydrous dimethylsulfoxide (DMSO) was obtained from Aldrich^{*} and stored over molecular sieves in an argon atmosphere dry box. Unless otherwise stated, all electrolyte solutions consisted of 0.1 M TEAP in DMSO at 293 K. The electrolyte solutions were purged with dry argon for 10 minutes before each experiment.

Three-electrode electroanalytical cells with platinum counter electrodes and Ag/AgCl reference electrodes (0.1 M Me₄NCl) were used throughout the experiments. Platinum metal, graphite, or glassy carbon electrodes were used as working electrodes. All working electrodes were polished to a mirror finish with diamond paste (1μm) and rinsed with acetone before each experiment.

In *potential sweep experiments*^[2-5], a linear or triangular potential function, generated using a PAR 173 Potentiostat/Galvanostat^{***} in conjunction with a PAR 175 Universal Programmer^{***}, was applied to a stationary electrode immersed in a quiet solution. The corresponding currents were measured as a function of potential or time and recorded with a 4120T Bascom-Turner digital recorder[†]. The sweep rates ranged from 1 mV/sec to 1000 mV/sec.

** Southwestern Analytical Chemicals, Inc., P.O. Box 485, Austin, Texas 78767

*** Princeton Applied Research, 26102 Eden Landing Road, Suite 3, Hayward, California 94545

† Bascom-Turner, Inc., 111 Downey Street, Norwood, MA 02062

In *potential-step experiments*^[2,3,6-8], excitation signals of one or more potential steps (pulse width of 10-500 msec), were generated under computer control. Experiment control/data acquisition was accomplished by interfacing an IBM-PC/AT with a DT2801 data acquisition board^{††} to a PAR 173 potentiostat/Galvanostat by means of a program written in ASYST^{†††} language. Computer controlled output signals were applied to a stationary electrode immersed in a quiet solution and the corresponding current or charge responses were measured as a function of time. The potential of a working electrode (w.r.t. a reference electrode) was stepped from a initial value, E_i , at which the system was at equilibrium (no apparent faradaic process), to a potential value at which the surface concentration of the electroactive species was effectively zero, ensuring diffusion control at all times. In the double-potential-step methods, a square wave voltage function was used to step the interfacial potential from a initial value E_i to a potential, E_f , at which the forward reaction was completely controlled by diffusion, and then to a potential, E_r , at which the reverse reaction was completely controlled by diffusion. The potentials E_f and E_r were determined from chronoamperometric waves^[2].

In *rotating disk electrode (RDE) experiments*^[2,3,15,16], an ASR Electrode Rotator and Speed Controller[‡] were used to modulate the rotation speeds of platinum or carbon working electrodes. Solution viscosities were measured using an Ostwald Viscometer. The convective-diffusion controlled currents were measured as a function of rotation speed.

†† Data Translation, Inc., 100 Locke Drive, Marlborough, Massachusetts 01752-1192

††† Macmillan Software Company

‡ Pine Instrument Co., 101 Industrial Drive, Grove City, PA 16127.

Electrochemical Methods

Linear sweep voltammetry (LSV) and *cyclic voltammetry* (CV) have been used to characterize the redox behavior and the kinetic reversibility of the organodisulfide compounds^[2-5]. The determination of kinetic reversibility from experimental observations is important since it influences further interpretation of the experimental data. In electrochemical systems, a chemically stable redox couple is considered kinetically reversible if electron transfer is sufficiently rapid that the Nernst equation is always applicable, and voltammetric peak potentials (E_{pa} or E_{pc}) are independent of scan rate. For a kinetically irreversible process, however, the peak potentials depend on sweep rate and can be expressed as^[2]

$$E_{pc} = E^{o'} - \frac{RT}{\alpha_c F} \left[0.780 + \ln \frac{D_0^{1/2}}{k^o} + \frac{1}{2} \ln \frac{\alpha_c F v}{RT} \right] \quad [1]$$

and the corresponding peak currents are

$$i_{pc} = 0.227 (nFA) C_0^* k^o \exp \left[- \frac{\alpha_c F}{RT} (E_p - E^{o'}) \right] \quad [2]$$

The dependence of peak potentials on sweep rate, v , the relationship between the peak currents and the peak potentials, E_p , and the separation of peak potentials in CV have been determined and used to characterize the redox behavior and to classify the systems studied in terms of kinetic reversibility.

Chronoamperometry and *chronocoulometry*^[2,3,6-8] have been used to study the

chemical stability/reversibility of the redox couples and the adsorption of organodisulfide species at electrode surfaces^[9-14]. Under the assumption that a uniform Nernst diffusion layer is established near the electrode surface, the diffusion-controlled chronoamperometric responses for the forward and reverse reactions can be expressed as

$$i_f(t \leq \tau) = \frac{(nFA)D_i^{1/2}C_i^*}{\pi^{1/2}} \frac{1}{t^{1/2}} \quad [3]$$

and

$$-i_r(t > \tau) = \frac{(nFA)D_i^{1/2}C_i^*}{\pi^{1/2}} \left[\frac{1}{(t - \tau)^{1/2}} - \frac{1}{t^{1/2}} \right] \quad [4]$$

and the corresponding chronocoulometric responses can be expressed as

$$Q_f(t \leq \tau) = Q_{dl} + Q_d(t \leq \tau) + Q_{ads} \quad [5]$$

and

$$Q_r(t > \tau) = Q_{dl} + Q_d(t > \tau) \quad [6]$$

where Q_{dl} is the charge due to double-layer charging and $Q_d(t < \tau)$ and $Q_d(t > \tau)$ are the charge due to electrolysis of the electroactive species at diffusion controlled rate. These parameters can be expressed as

$$Q_d(t \leq \tau) = \frac{2(nFA)D_i^{1/2}C_i^*}{\pi^{1/2}} t^{1/2} \quad [7]$$

and

$$Q_d(t > \tau) = \frac{2(nFA)D_i^{1/2}C_i^*}{\pi^{1/2}} \left[\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2} \right]. \quad [8]$$

Q_{ads} is the charge due to electrolysis of the electroactive species adsorbed.

at electrode surface and is given by

$$Q_{\text{ads}} = nFA \Gamma_i \quad [9]$$

In conjunction with single-step chronoamperometry and chronocoulometry, *rotating disk electrode* techniques were used to determine n , the number of electrons participating in the overall electrochemical reaction, as well as the diffusion coefficient of the organodisulfide species in electrolyte solutions^[2,3,15,16]. Under mass transfer controlled conditions, the convective-diffusion limited current at a rotating disk electrode is given by

$$i_d(\omega) = 0.62 (nFA) C_i^* D_i^{2/3} \nu^{-1/6} \omega^{1/2} \quad [10]$$

where ν is the kinematic viscosity [cm^2/sec] of the electrolyte solution and ω is the electrode rotation speed [Hz].

Results and Discussions

Redox behavior and kinetic reversibility

Cyclic voltammograms of a group of organic disulfides on platinum electrodes in DMSO containing 0.1 M TEAP are shown in Fig.1. These voltammograms allow direct insight into the kinetic (thermodynamic) reversibility of the redox couples. The most striking observation was the separation of the anodic and the cathodic peak potentials, which ranged from 1250 mV for TMTD at sweep rate of 20 mV/sec, to 1630 mV for PDS at sweep rate of 100 mV/sec. The large peak separations imply slow electron transfer rates; the redox couples are kinetically irreversible at the sweep rates

studied. Further, comparison of the separation of the peak potentials for different disulfides indicates the relative reversibility of the redox couples. At a given sweep rate, the smaller the peak separation the faster the electrode kinetics. Thus, for example, the redox couple TMTD/DMDC⁻ is more reversible than the redox couple TETD/DEDC⁻, and FPDS/FPT⁻ is more reversible than PDS/PT⁻.

Cyclic voltammograms of TETD on different electrode materials are shown in Fig.2. Since the cathodic peak potential for TETD/DEDC⁻ on platinum is more negative than that on graphite, the reduction of the disulfide is easier on graphite electrodes than on platinum electrodes. The anodic peak potential, however, is more positive on graphite than that on platinum and hence the oxidation of the corresponding thiolate anions is easier on platinum than on graphite. Nevertheless, the separation of anodic and cathodic peak potentials on a graphite electrode is smaller than that on a platinum electrode. Therefore, the overall reaction rate is expected to be faster on graphite than on platinum.

The amplitude of the peak currents and the position of the peak potentials at different sweep rate were determined precisely from linear sweep voltammograms and from the corresponding differential voltammograms, as shown in Fig.3 and 4 for reduction of TMTD to DMDC⁻ and oxidation of DMDC⁻ to TMTD, respectively. The dependence of the peak currents on potential sweep rate is shown in Fig.5. As predicted by Eqn.1 and Eqn.2, the peak current, i_p , is linearly related to the square root of the sweep rates, $v^{1/2}$. The relations between the peak currents and peak potentials (Eqn.2) are shown in Fig.6 and the dependence of the peak potentials on sweep rates (Eqn.1) are shown in Fig.7. The plot of $\ln i_p$ vs the peak potentials, E_p , at different sweep rates, gives

slope of $-\alpha_c F/RT$ for cathodic processes and $\alpha_a F/RT$ for anodic processes. Similarly, the plot of peak potentials, E_p , vs $\ln v$ gives slopes of $-RT/2\alpha_c F$ and $RT/2\alpha_a F$ for cathodic and anodic processes, respectively, and consequently the transfer coefficients for the redox reaction can be estimated from these slopes. The linear relationship between $\ln i_p$ and E_p , and between E_p and $\ln v$ further confirm that the redox couples are kinetically sluggish and the introduction of appropriate electrocatalysts to aid electron transfer would be beneficial in an energy conversion device based on these organodisulfides.

Adsorption on electrode surface

The charge response, Q , acquired by the computer in double-step chronocoulometry is shown in Fig.8. Curve (x) represents the charge contribution from the blank electrolyte solution (0.1 M TEAP in DMSO), and is mainly due to the charging of the double layer at electrode surface. The featureless appearance of this curve indicates that the solvent (DMSO) and the supporting electrolyte (TEAP) are sufficiently stable at the potentials applied. The other curves represent the total charge response of various organic disulfide species in the electrolyte solution. The total charge response is actually the sum of the charges due to (i) the electrolysis of the electroactive species at diffusion-controlled rate, Q_d , (ii) the double layer charging, Q_{dl} , and (iii) the electrolysis of the adsorbed electroactive species at the electrode surface, Q_{ads} .

The linear plots of $Q_f(t < \tau)$ vs. $t^{1/2}$ and $Q_r(t > \tau)$ vs. $[r^{1/2} + (t - \tau)^{1/2} - t^{1/2}]$ are shown in Fig.9. The intercept in the forward direction is the sum of Q_{dl} and Q_{ads} , and in the reverse direction is Q_{dl} . The

difference between the two intercepts gives directly the charges due to adsorption of electroactive species at electrode surface, $Q_{ads} = nFA\Gamma_i$. The intercepts in both directions, and the charges due to adsorption are tabulated in Table I for different disulfides. Results indicate that the adsorption of these species on platinum electrode is negligible. Further, as it is evident from Eqn.7 and 8, the slopes [$\mu C sec^{-1/2}$] of the linear plots in both directions can be expressed as

$$S_1 = \frac{2(nFA_1)D_i^{1/2}C_{i,1}^*}{\pi^{1/2}} \quad [11]$$

where A_1 is the effective surface area [cm^2] of the micro-working electrode, $C_{i,1}^*$ is the bulk concentration [$\mu mol cm^{-3}$] of the electroactive species i in the chronocoulometric experiment, and the other notations have the standard meanings. These slopes will be used to estimate the number of electrons involved in the overall reaction and the diffusion coefficients of the organodisulfide species in the next section.

Chemical stability and reversibility

The plots of the normalized diffusion-controlled currents and the normalized diffusion-controlled charge against the normalized time (t/τ) are shown in Fig.10 and 11.

From Eqn.3 and 4, it is evident that the ratio of the diffusion-controlled currents from chronoamperometric response for a stable system should be

$$\frac{-i_r(t>\tau)}{i_f(\tau)} = \frac{1 - [1 - (\tau/t)]^{1/2}}{[(t/\tau) - 1]^{1/2}} \quad [12]$$

Similarly, from Eqn.7 and 8, the ratio of diffusion-controlled charges from chronocoulometric response for a chemically reversible system should be

$$\frac{Q_d(t>\tau)}{Q_d(\tau)} = (t/\tau)^{1/2} - [(t/\tau) - 1]^{1/2} \quad [13]$$

Therefore, ratios of $-i_r(2\tau)/i_f(\tau) = 0.2929$ and $Q_d(2\tau)/Q_d(\tau) = 0.4142$ are characteristic of a chemically stable and reversible system; deviations from these ratios indicate chemical complications. The ratios calculated from observed data for different disulfides are listed in Fig.10 and 11. The experimental values closely match the theoretical values indicating that the system is chemically stable and reversible under the present experimental conditions. In other words, both the oxidized and reduced forms are chemically stable and reversible, so that the reaction can be carried out in either direction. This microscopic reversibility is a fundamental criterion for a secondary system for energy conversion/battery applications.

*Number of electrons involved in the overall reactions
and diffusion coefficients*

The convective-diffusion limited current at an RDE (Eqn.10), $i_d(\omega)$, vs. $\omega^{1/2}$, i.e., the Levich plot, is shown in Fig.12 for the reduction of a group of organic disulfides on graphite electrode in DMSO containing 0.1 M TEAP. The viscosities of various electrolyte solutions used in the RDE studies were

determined using an Ostwald viscometer and are listed in Table II. The slopes $[\mu A \text{ sec}^{1/2}]$ of the Levich plots can be expressed as

$$S_2 = 0.62 (nFA_2)C_{i,2}^* D_i^{2/3} \nu^{-1/6} \quad [14]$$

where A_2 is the effective surface area $[cm^2]$ of the rotating disk electrode and $C_{i,2}^*$ is the bulk concentration $[\mu mol \text{ cm}^{-3}]$ of the electroactive species i in the RDE experiment.

The linear plots of chronoamperometric responses for reduction of different disulfides at platinum electrode in DMSO are shown in Fig.13.

The slopes $[\mu A \text{ sec}^{1/2}]$ of these plots can be expressed as

$$S_3 = S_1/2 \quad [15]$$

From these slopes, the number of electrons involved in the reaction can be calculated as

$$n = 0.1470 \frac{1}{F\nu^{1/2}} \frac{S_1^4}{S_2^3} \frac{(A_2 C_{i,2}^*)^3}{(A_1 C_{i,1}^*)^4} \quad [16]$$

and the diffusion coefficient can be estimated as

$$D_i = 36.3396 \nu \left[\frac{S_2}{S_1} \frac{A_1 C_{i,1}^*}{A_2 C_{i,2}^*} \right]^6 \quad [17]$$

The slopes of these plots, S_1 , S_3 and S_2 , the diffusion coefficients, D_i , and the number of electrons participating the overall reaction, n , for various organosulfur compounds are tabulated in Table II.

Since the calculated number of electrons involved in the reduction of these organic disulfides are reasonably close to 2.0 (with some experimental error), the overall reaction is expected to take the form of



where R represents a organic moiety.

Conclusions

The disulfide/thiolate redox couples, RSSR/RS^- , are chemically reversible, yet, kinetically slow. The overall electrochemical redox reaction for this couple is $\text{RSSR} + 2 e^- = 2 (\text{RS}^-)$. The microscopic reversibility of these compounds makes it possible to construct rechargeable batteries based on the organic disulfides. The sluggish kinetics indicate that the introduction of suitable electrocatalysts to assist charge transfer will probably prove useful in this system. Since the adsorption of organic disulfides on platinum electrodes is negligible, the electrode kinetics can be described using simple electrodic equations and studied without consideration of surface coverage.

Acknowledgement

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 with the Lawrence Berkeley Laboratory.

Abbreviations

CV	cyclic voltammetry
DEDC ⁻	diethyl dithiocarbamate anion, $[(C_2H_5)_2NCSS]^-$
DMDC ⁻	dimethyl dithiocarbamate anion, $[(CH_3)_2NCSS]^-$
DMSO	dimethylsulfoxide
HEDS	hydroxyethyl disulfide, $(HO-CH_2-CH_2-S-)_2$
FPDS	di-fluorophenyl disulfide, $(F-C_6H_4-S-)_2$
FPT ⁻	fluorophenyl thiolate anion, $[F-C_6H_4-S]^-$
LSV	linear sweep voltammetry
NaDEDC	sodium diethyl dithiocarbamate
NaDMDC	sodium dimethyl dithiocarbamate
PDS	phenyl disulfide, $(C_6H_5-S-)_2$
PT ⁻	phenyl thiolate anion, $[C_6H_5-S]^-$
RDE	rotating disk electrode
RS ⁻	a group of thiolate anions, R represents an organic moiety
RSSR	a group of organic disulfides, R represents an organic moiety
TEAP	tetraethylammonium perchlorate
TETD	tetraethylthiuram disulfide, $((C_2H_5)_2NCSS-)_2$
TMAC	tetramethylammonium chloride
TMTD	tetramethylthiuram disulfide, $((CH_3)_2NCSS-)_2$

Notation

A	surface area of an electrode, [cm^2]
A_1	surface area of the micro-platinum electrode, $A_1 = 4.1 \times 10^{-3} \text{ cm}^2$.
A_2	surface area of the rotating disk electrode, $A_2 = 0.50 \text{ cm}^2$.
C_i^*	bulk concentration of species i , [$\mu\text{mol cm}^{-3}$]
$C_{i,1}^*$	bulk concentration of species i in potential-step experiment, [$\mu\text{mol cm}^{-3}$]
$C_{i,2}^*$	bulk concentration of species i in RDE experiment, [$\mu\text{mol cm}^{-3}$]
D_i	diffusion coefficient of species i , [$\text{cm}^2 \text{ sec}^{-1}$]
E°	standard potential of an electrode, [V]
$E^{\circ'}$	formal potential of an electrode, [V]
E_i	initial potential, [V]
E_f	potential of working electrode during forward step, [V]
E_p	peak potential in voltammetry, [V]
E_{pa}	anodic peak potential in voltammetry, [V]
E_{pc}	cathodic peak potential in voltammetry, [V]
E_r	potential of working electrode during reverse step, [V]
F	Faraday's constant, [C mol^{-1}]
i_d	diffusion-limited current or convective-diffusion limited current, [μA]
i_f	current during forward step, [μA]
i_p	peak current in voltammetry, [μA]
i_{pa}	anodic peak current in voltammetry, [μA]
i_{pc}	cathodic peak current in voltammetry, [μA]
i_r	current during reverse step, [μA]
k°	standard (intrinsic) heterogeneous rate constant
n	number of electrons transferred in the electrode reaction

Q	<i>total charge, [μC]</i>
Q_{ads}	<i>charge due to electrolysis of adsorbed species, [μC]</i>
Q_{d}	<i>charge due to diffusion-controlled electrolysis, [μC]</i>
Q_{dl}	<i>charge due to double layer charging, [μC]</i>
R	<i>universal gas constant, $R = 8.3143 [\text{J mol}^{-1} \text{K}^{-1}]$</i>
S_1	<i>slope of linear chronocoulometric plot, [$\mu\text{C sec}^{-1/2}$]</i>
S_2	<i>slope of Levich plot, [$\mu\text{A sec}^{1/2}$]</i>
S_3	<i>slope of linear chronoamperometric plot, [$\mu\text{A sec}^{1/2}$]</i>
t	<i>time, [sec]</i>
T	<i>absolute temperature, [K]</i>
v	<i>potential sweep rate, [mV sec^{-1}]</i>
α_{a}	<i>anodic transfer coefficient</i>
α_{c}	<i>cathodic transfer coefficient</i>
Γ_{i}	<i>surface concentration of adsorbed species, [$\mu\text{mol cm}^{-2}$]</i>
ν	<i>kinematic viscosity of an electrolyte solution, [$\text{cm}^2 \text{sec}^{-1}$].</i>
τ	<i>characteristic pulse width, [sec]</i>
ω	<i>rotation speed of disk working electrode, [Hz]</i>

subscript

a	<i>anodic</i>
c	<i>cathodic</i>
f	<i>forward direction</i>
O	<i>oxidized species</i>
p	<i>peak</i>
r	<i>reverse direction</i>
R	<i>reduced species</i>

References

- [1] S. J. Visco, C. C. Mailhe, L. C. De Jonghe, and M. B. Armand, LBL-23598, June 1987, accepted for publication in *J. Electrochem. Soc.*
- [2] A. J. Bard, and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications", Wiley, New York, 1980.
- [3] W. R. Heineman and P. T. Kissinger, in "Laboratory Techniques in Electroanalytical Chemistry", Marcell Dekker, New York, 52 (1984).
- [4] J. Heinze, *Angew. Chem. Int. Ed. Engl.*, **23**, 831 (1984).
- [5] V. D. Parker, in "Electroanalytical Chemistry," Vol. 14, Marcel Dekker, New York, 1-111 (1986).
- [6] H. J. Christie, R. A. Osteryoung, and F. C. Anson, *J. Electroanal. Chem.*, **13**, 236 (1967).
- [7]. M. K. Hanafey, R. L. Scott, T. H. Ridgway, and C. N. Reilly, *Anal. Chem.*, **50**, 116(1978).
- [8] F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).
- [9] J. H. Christie, *J. Electroanal., Chem.* **13**, 79 (1967).
- [10] T. H. Ridgway, R. P. Van Duyne, and C. N. Reilley, *J. Electroanal. Chem.*, **34**, 267 (1972).
- [11] K. Holub and J. Weber, *J. Electroanal. Chem.*, **73**, 129 (1976).
- [12] F. C. Anson, and R. A. Osteryoung, *J. Chem. Educ.*, **60**, 293 (1983).
- [13] B. Case and F. C. Anson, *J. Phys. Chem.*, **71**, 402 (1967).
- [14] G. W. O'Dom and R. D. Murray, *Anal. Chem.*, **39**, 51(1967).
- [15] V. Y. Filinovsky, and Y. V. Pleskov, in "Comprehensive Treatise of Electrochemistry," Volume 9, Prenum, New York, 293 (1981).
- [16] J. S. Newman, "Electrochemical Systems", Prentice-Hall, Englewood Cliffs, N.J., 1972.
- [17] R. W. Zurilla, R. K. Sen, and E. Yeager, *J. Electrochem. Soc.*, **125**, 1103 (1978).

Figure Captions

Fig.1 Cyclic voltammograms of a group of organosulfur compounds in DMSO containing 0.1 M TEAP at 293 K. (a) blank electrolyte solution, (b) 4.5 mM hydroxyethyl disulfide, $(\text{HO}-\text{CH}_2-\text{CH}_2-\text{S}-)_2$, (c) 4.4 mM tetramethylthiuram disulfide, $((\text{CH}_3)_2\text{NCSS}-)_2$, (d) 4.2 mM tetraethylthiuram disulfide, $((\text{C}_2\text{H}_5)_2\text{NCSS}-)_2$, (e) 4.1 mM di-fluorophenyl disulfide, $(\text{F}-\text{C}_6\text{H}_4-\text{S}-)_2$, and (f) 3.6 mM phenyl disulfide, $(\text{C}_6\text{H}_5-\text{S}-)_2$. A micro-platinum electrode (surface area = $4.1 \times 10^{-3} \text{ cm}^2$) was used as working electrode and referenced to a Ag/AgCl electrode with a Luggin capillary salt bridge.

Fig.2 Cyclic voltammograms of TETD on platinum and graphite electrodes in DMSO containing 0.1 M TEAP at 293 K.

Fig.3 Linear sweep voltammogram and the corresponding differential voltammogram for the reduction of TMTD to the thiolate anions DMDC^- on a micro-platinum electrode (surface area = $4.1 \times 10^{-3} \text{ cm}^2$) at 293 K. Electrolyte solution: 4.4 mM TMTD in DMSO containing 0.1 M TEAP.

Fig.4 Linear sweep voltammograms and the corresponding differential voltammograms for the oxidation of the thiolate anions DMDC^- to the disulfide TMTD at a micro-platinum electrode (surface area = $4.1 \times 10^{-3} \text{ cm}^2$) at 293 K. Electrolyte solution: 8.1 mM NaDMDC in DMSO containing 0.1 M TEAP.

Fig.5 Dependence of the peak currents (i_p , μA) on the potential sweep rate (v , mV/sec) based on the results shown in Fig.3 and 4.

Fig.6 Plot of $\ln i_p$ vs peak potentials (E_p) at different sweep rates for the redox couple TMTD/DMDC⁻ at a micro-platinum electrode. The data is based on the results shown in Fig.3 and 4. The slopes are $-\alpha_c F/RT$ and $\alpha_a F/RT$ for the cathodic and anodic processes, respectively.

Fig.7 Plot of peak potentials (E_p) vs $\ln v$ for the redox couple TMTD/DMDC⁻ at a micro-platinum electrode. The data is based on the results shown in Fig.3 and 4. The slopes are $-RT/2\alpha_c F$ and $RT/2\alpha_a F$ for the cathodic and anodic processes, respectively.

Fig.8 Chronocoulometric response of a group of organic disulfides in DMSO containing 0.1 M TEAP. (x) blank electrolyte solution, (+) 4.4 mM tetramethylthiuram disulfide, (■) 4.1 mM tetraethylthiuram disulfide, (Δ) 4.1 mM di-fluorophenyl disulfide, and (◇) 3.7 mM phenyl disulfide. The surface area of the micro-platinum working electrode is $4.1 \times 10^{-3} \text{ cm}^2$. Potentials (w.r.t. Ag/AgCl) were stepped from the rest potential (- 0.25 V) to cathodic active potential -2.1 V for reduction, then to anodic active potential + 0.4 V for oxidation, and finally back to the rest potential. The duration of the potential steps was 50 ms.

Fig.9 Linear plot of the chronocoulometric response data shown in Fig.8. The plot of the total charge in the forward direction (Eqn.5), $Q_f(t < \tau)$, vs. $t^{1/2}$ gives intercepts of $[Q_{dl} + Q_{ads}]$. The plot of the total charge in the reverse direction (Eqn.6), $Q_r(t > \tau)$, vs. $[\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}]$ gives the intercepts of Q_{dl} . The difference between the two intercepts gives the charges due to adsorption of electroactive species at electrode surface, $Q_{ads} = nFA\Gamma_i$. The slope in either direction is S_1 , as defined by Eqn.11.

Fig.10 Normalized diffusion-controlled current response from double-step

chronoamperometry. The experimental conditions are identical to those for chronocoulometry described in Fig.8.

Fig.11 Normalized diffusion-controlled charge, $Q_d(t)/Q_d(\tau)$, from double-step chronocoulometry. The experimental conditions are identical to those described in Fig.8.

Fig.12 Levich plots for the reduction of a group of organic disulfides in DMSO containing 0.1 M TEAP. (+) 1.1 mM tetramethylthiuram disulfide, (■) 2.1 mM tetraethylthiuram disulfide, (Δ) 2.5 mM di-fluorophenyl disulfide, and (\diamond) 2.2 mM phenyl disulfide, Potential (w.r.t. Ag/AgCl) sweep rate was 10 mV/sec. Rotation speed ranged from 500 - 3000 RPM. Surface area of the working electrode is 0.50 cm^2 .

Fig.13 Linear chronoamperometric plots in single-step chronoamperometry. (+) 4.4 mM tetramethylthiuram disulfide, (■) 4.1 mM tetraethylthiuram disulfide, (Δ) 4.1 mM di-fluorophenyl disulfide, and (\diamond) 3.7 mM phenyl disulfide. Micro-platinum electrode surface area is $4.1 \times 10^{-3} \text{ cm}^2$. Potentials (w.r.t. Ag/AgCl) were stepped from the rest potential (-0.25 V) to active potential (-2.1 V) for reduction, and then back to the rest potential. The duration of the potential steps was 50 ms.

Table

Table I

Adsorption of organodisulfide species at platinum electrode at 293K (determined from chronocoulometry)					
organic disulfide	$C_{i,1}^*$ [mM]	$Q_{dl}+Q_{ads}$ [μC]	Q_{dl} [μC]	Q_{ads} [μC]	$nF\Gamma_i$ [$\frac{\mu C}{cm^2}$]
TMTD	4.4	0.0323	0.0256	0.0067	1.63
FPDS	4.1	0.0342	0.0277	0.0065	1.59
TETD	4.1	0.0361	0.0314	0.0047	1.15
PDS	3.7	0.0302	0.0272	0.0030	0.732

Table II

The number of electrons transferred in the electrode reaction and the diffusion coefficient of the organodisulfide species in DMSO containing 0.1 M TEAP at 293K (determined from RDE in conjunction with chronocoulometry/chronoamperometry)										
organic disulfide	$C_{i,1}^*$ [mM]	S_1 [$\frac{\mu C}{sec^{1/2}}$]	S_3 [$\frac{\mu A}{sec^{-1/2}}$]	$C_{i,2}^*$ [mM]	ν [$\frac{cm^2}{sec}$]	S_2 [$\frac{\mu A}{Hz^{1/2}}$]	RDE + chronocoul.		RDE + chronoamp.	
							n	$D_i \times 10^6$ [$\frac{cm^2}{sec}$]	n	$D_i \times 10^6$ [$\frac{cm^2}{sec}$]
TMTD	4.4	7.54	3.76	1.1	0.021855	29.5	2.0475	3.51	2.0259	3.57
FPDS	4.1	6.95	3.47	2.5	0.021101	65.9	2.0914	3.29	2.0794	3.32
PDS	3.7	5.75	2.86	2.2	0.022143	51.8	2.0237	2.96	1.9818	3.04
TETD	4.1	5.86	2.94	2.1	0.021799	44.7	1.9751	2.82	2.0022	2.57

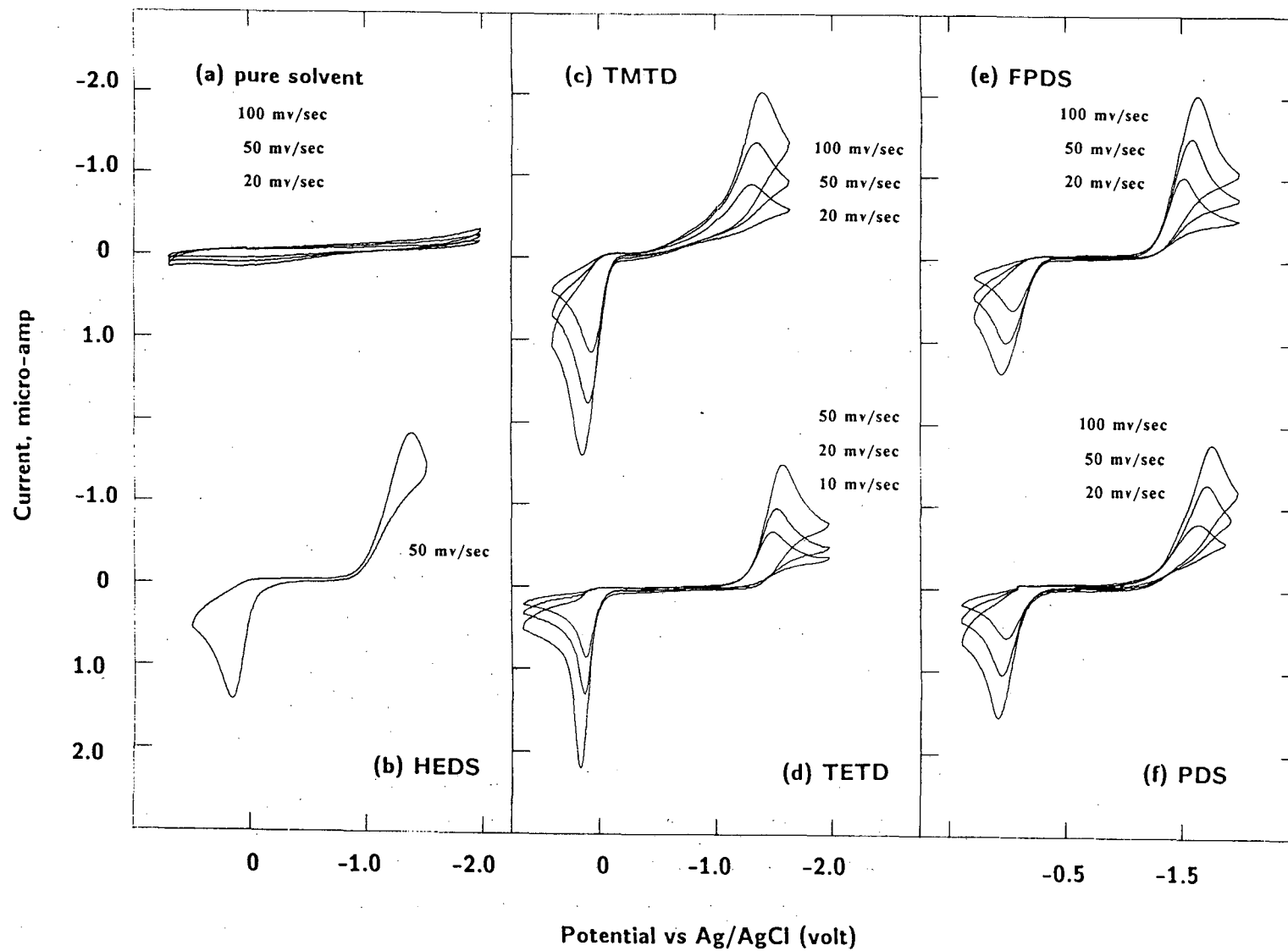


Figure 1

XBL 887-2382

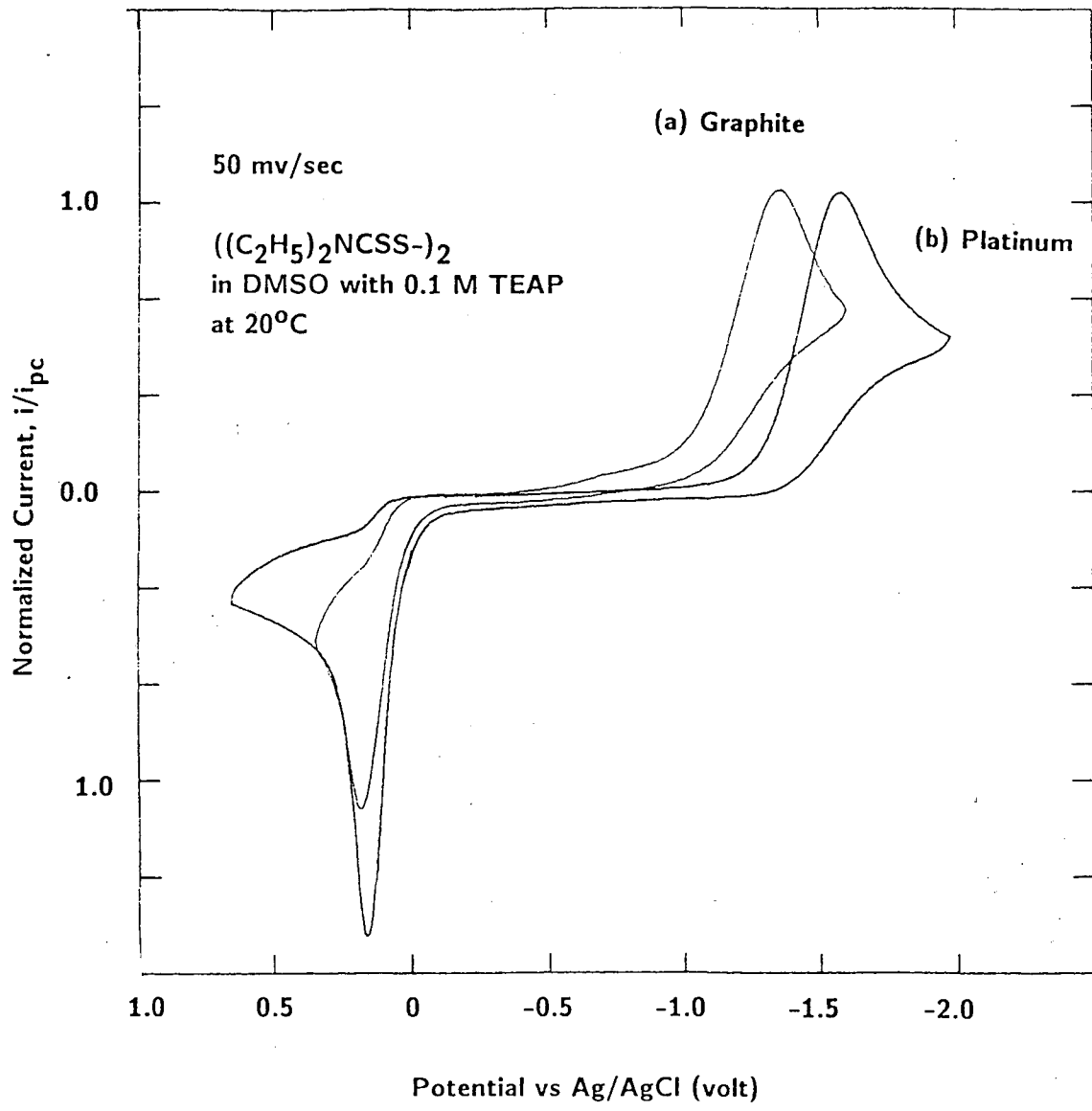


Figure 2

XBL 887-2477

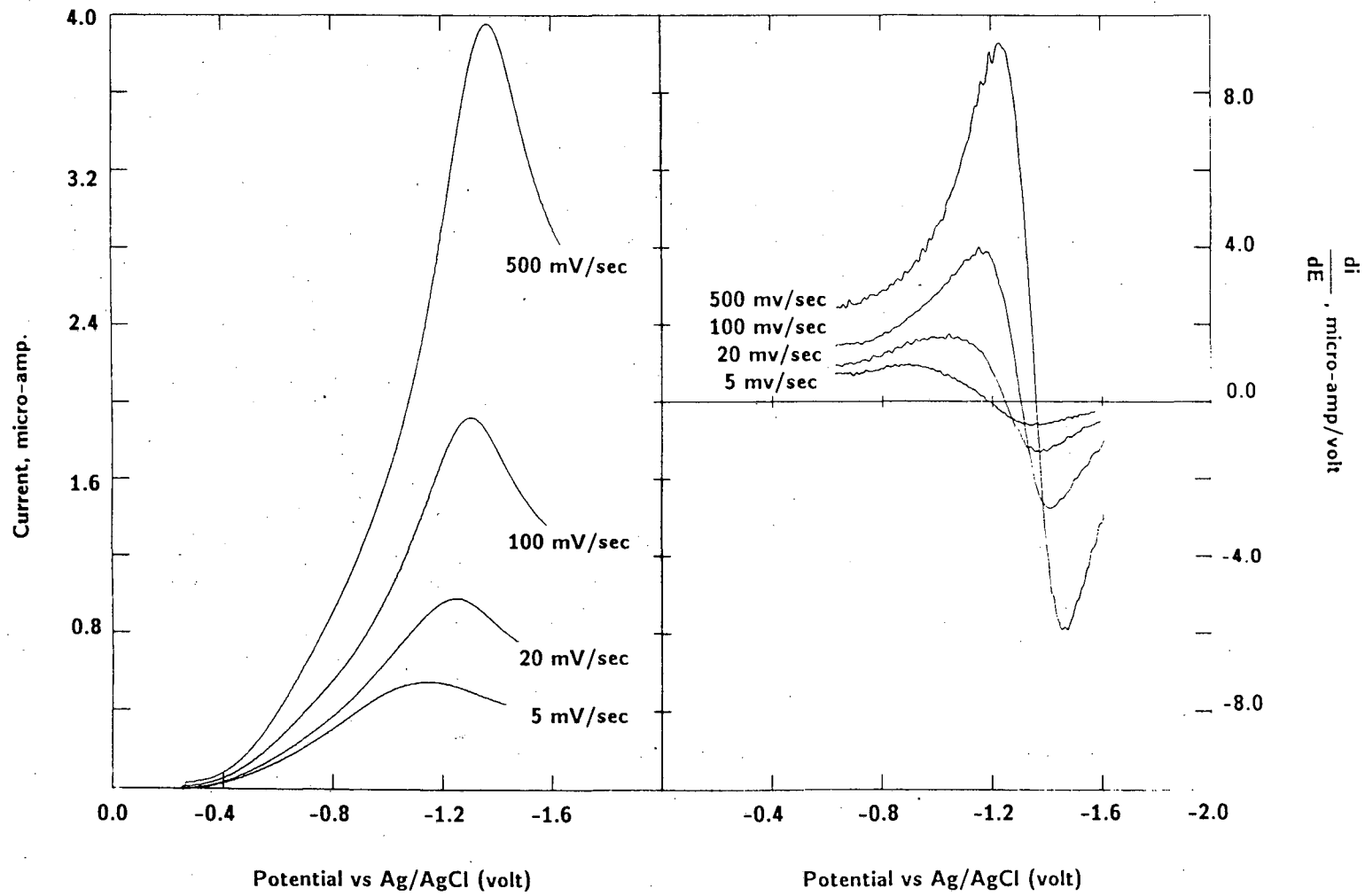
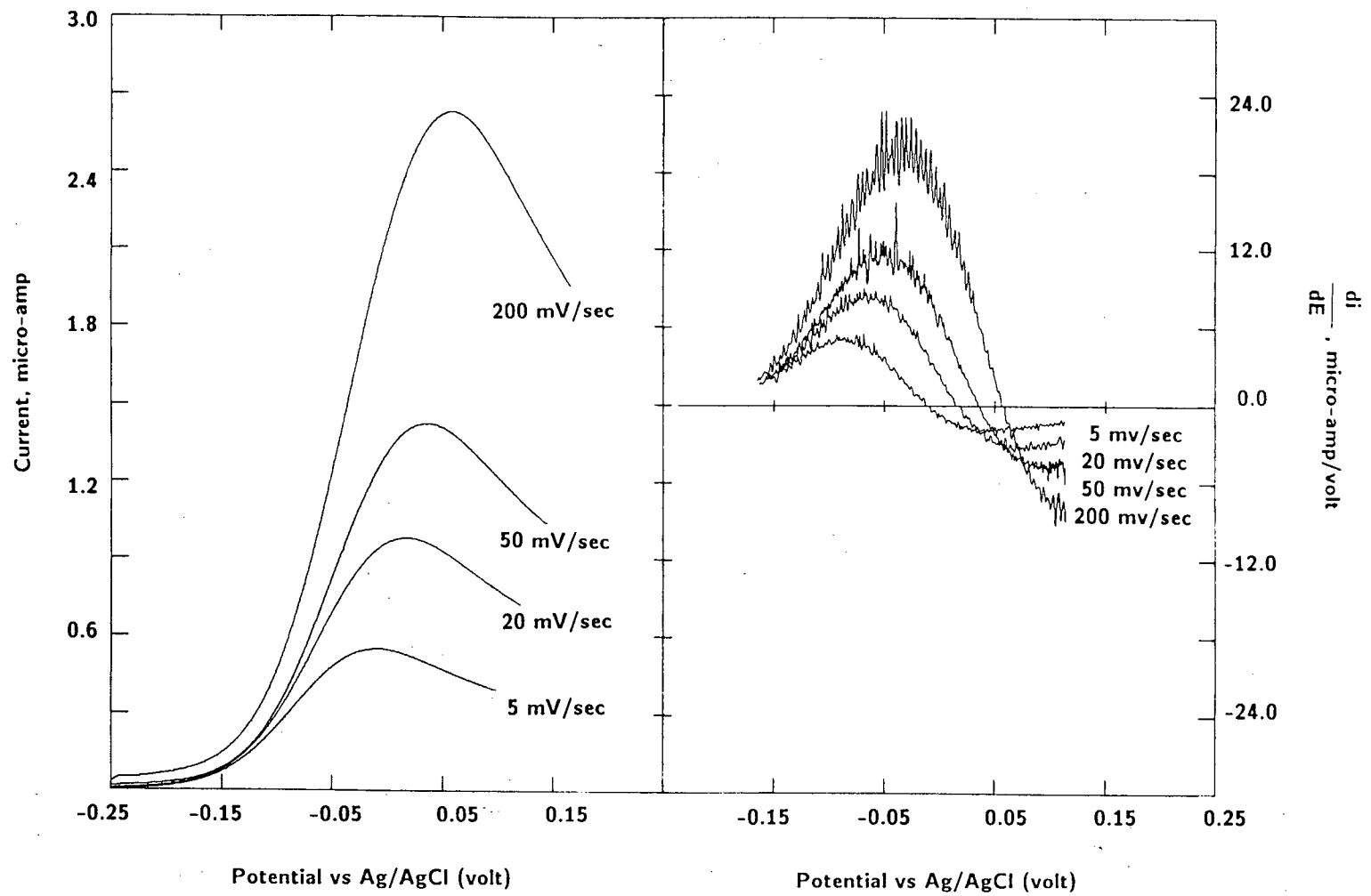


Figure 3

XBL 887-2488



XBL 887-2487

Figure 4

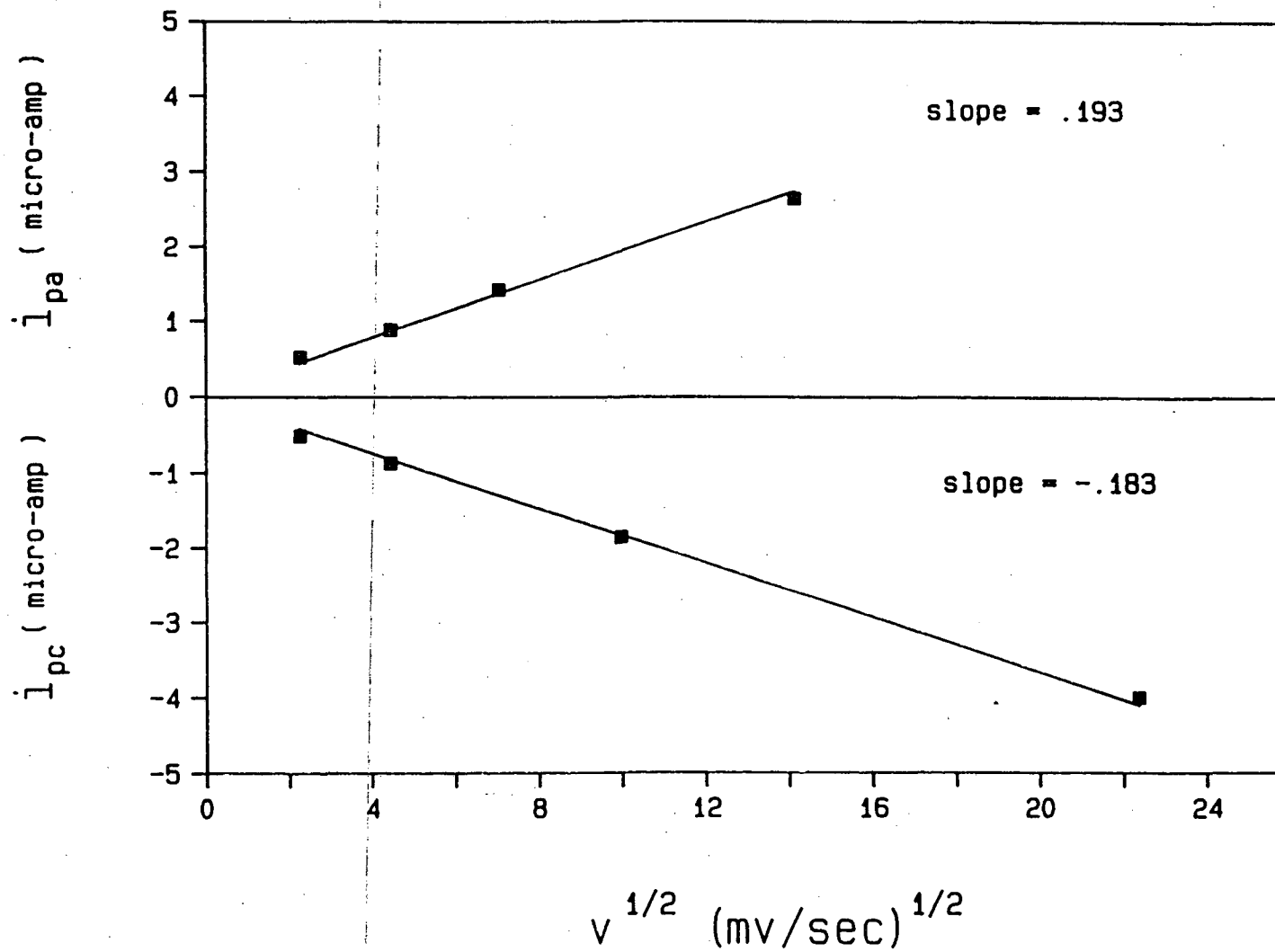
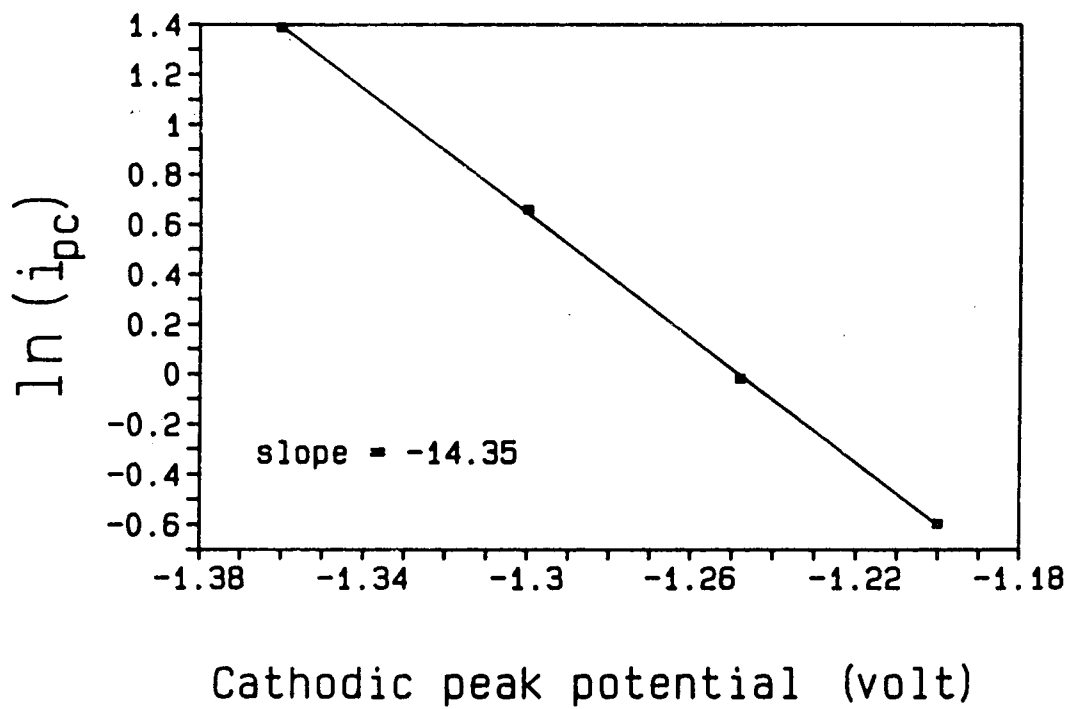
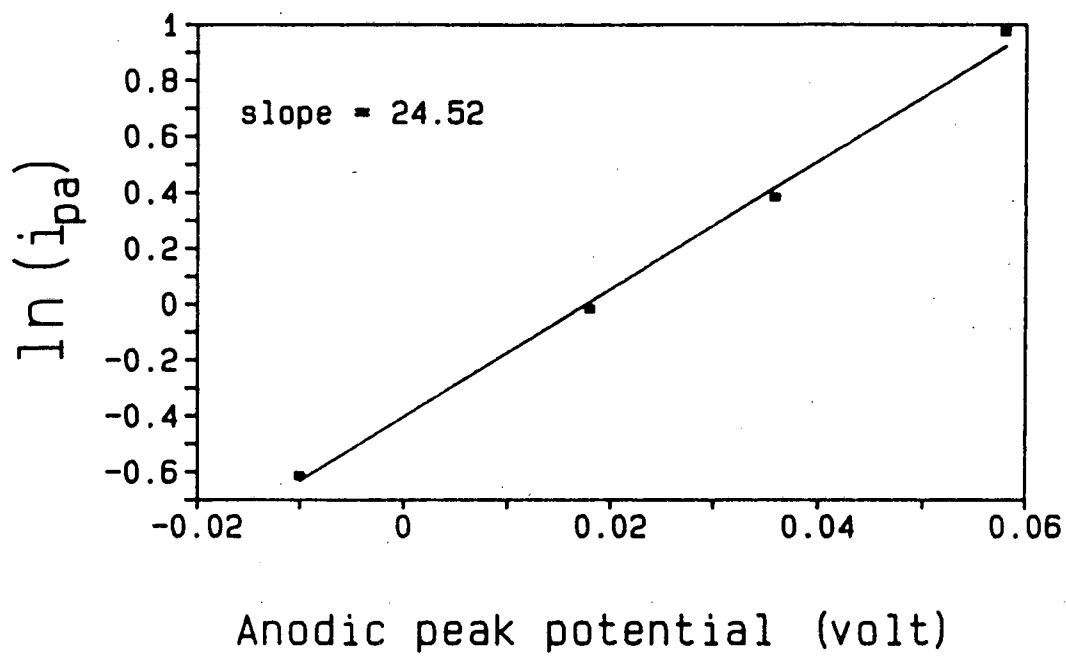


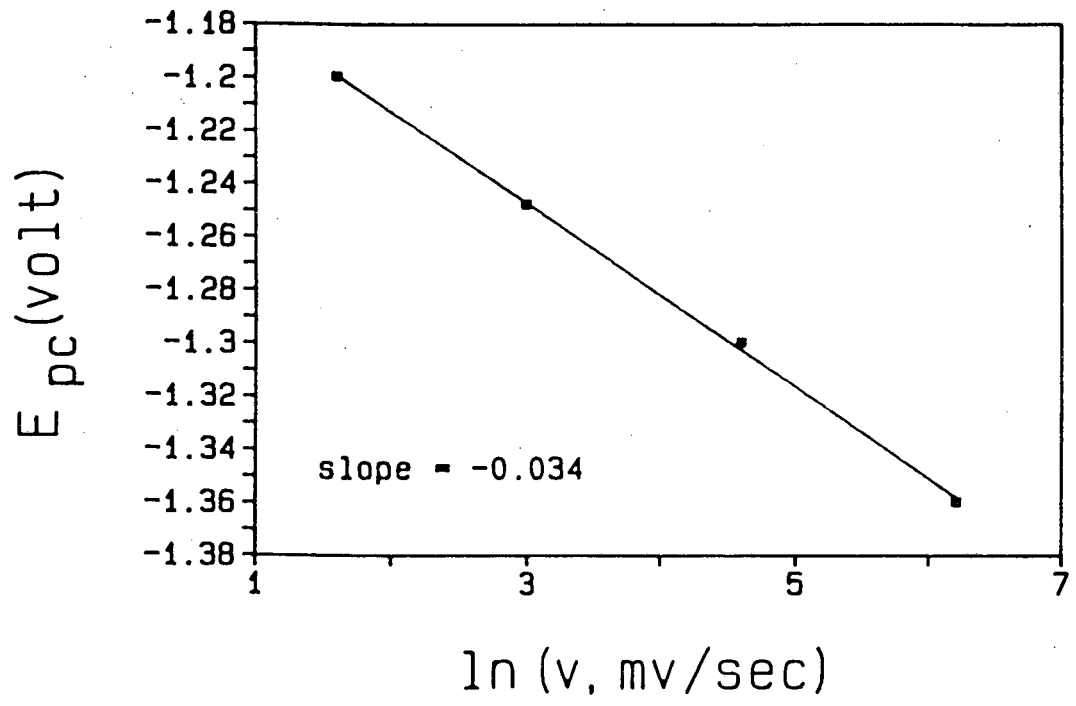
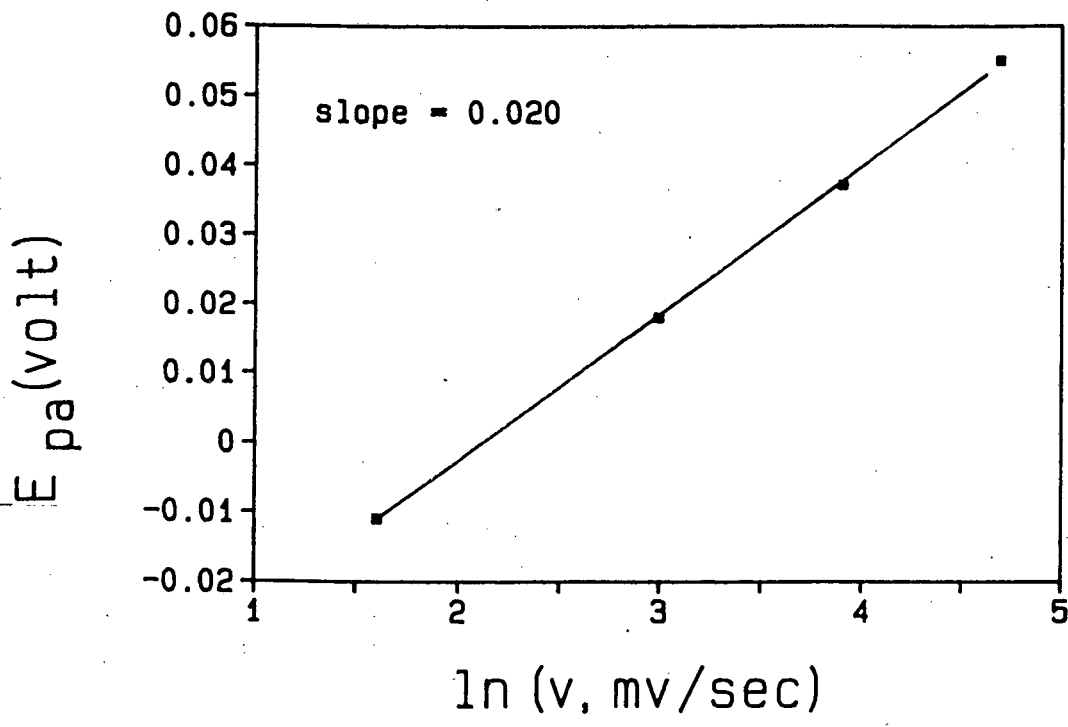
Figure 5

XBL 887-2478



XBL 887-2479

Figure 6



XBL 887-2480

Figure 7

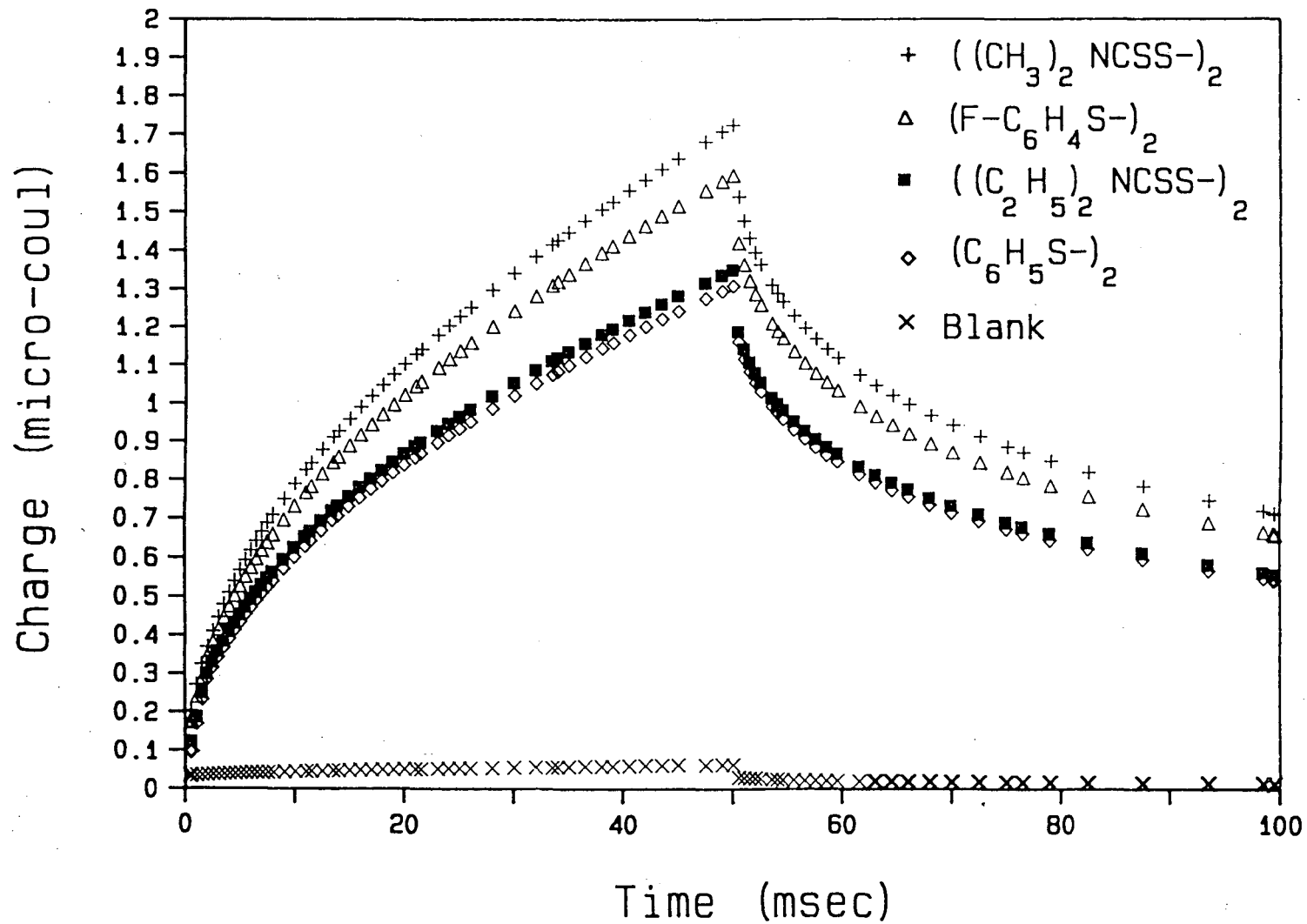


Figure 3

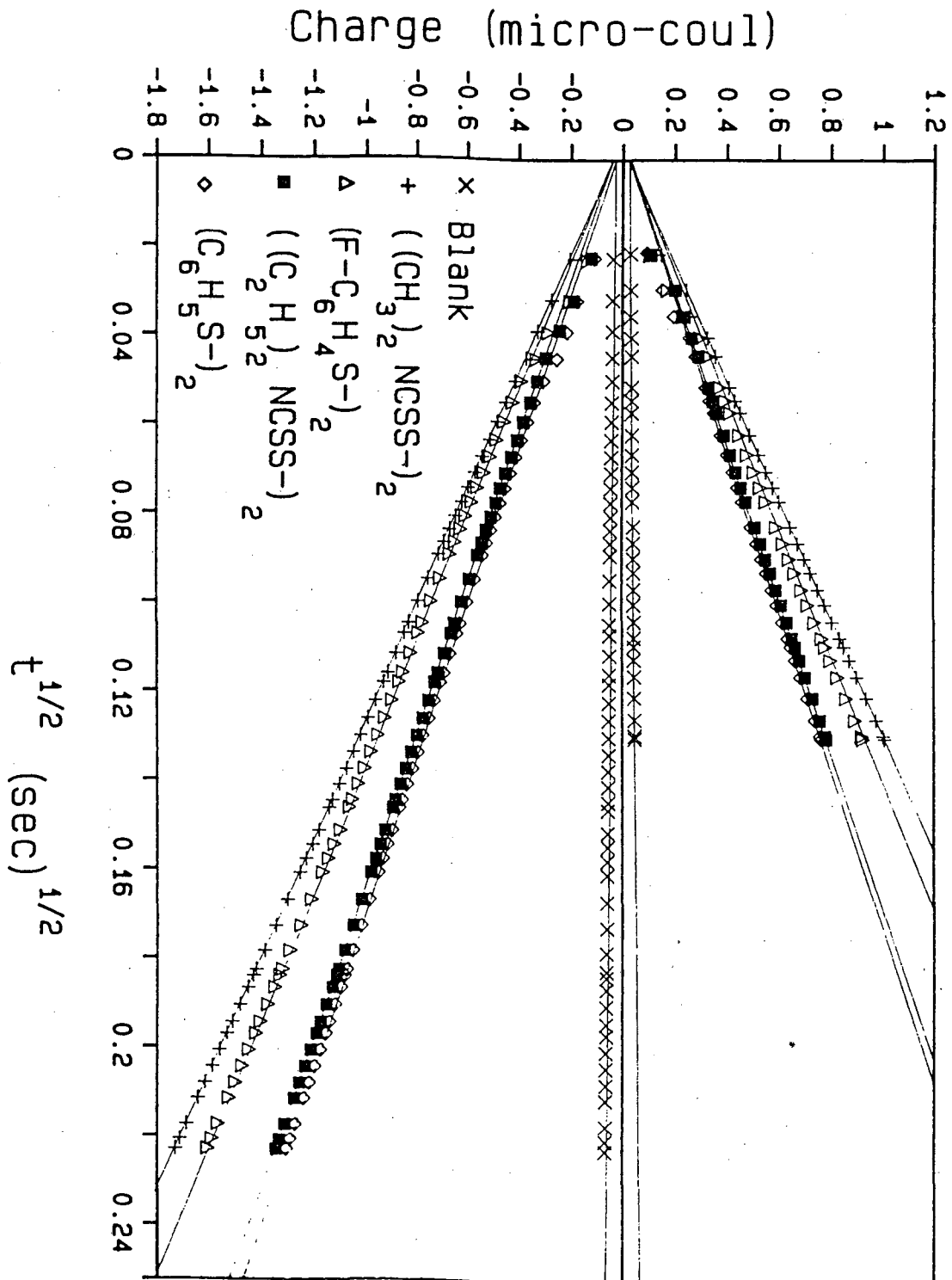


Figure 9

XBL 887-2482

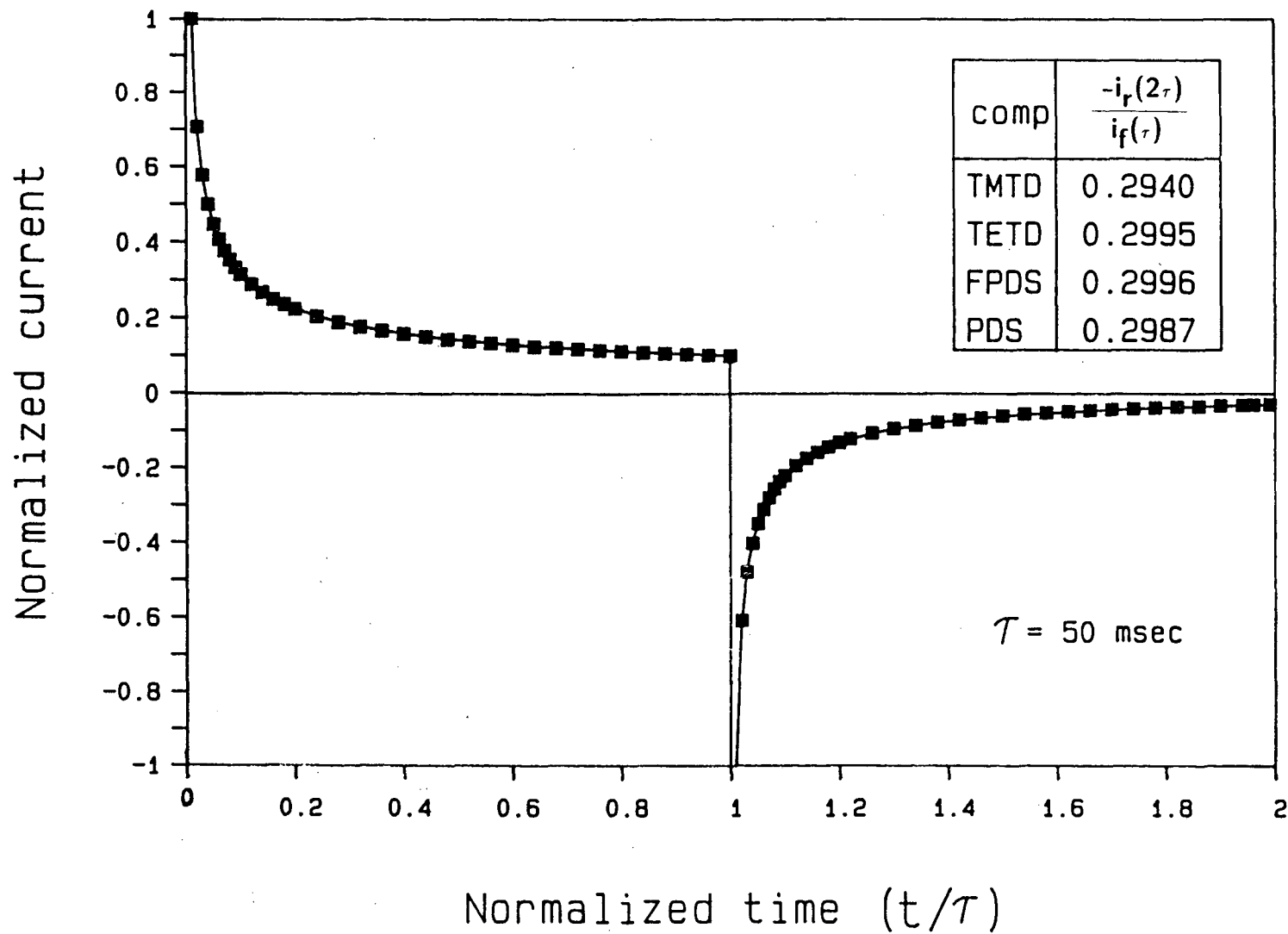


Figure 10

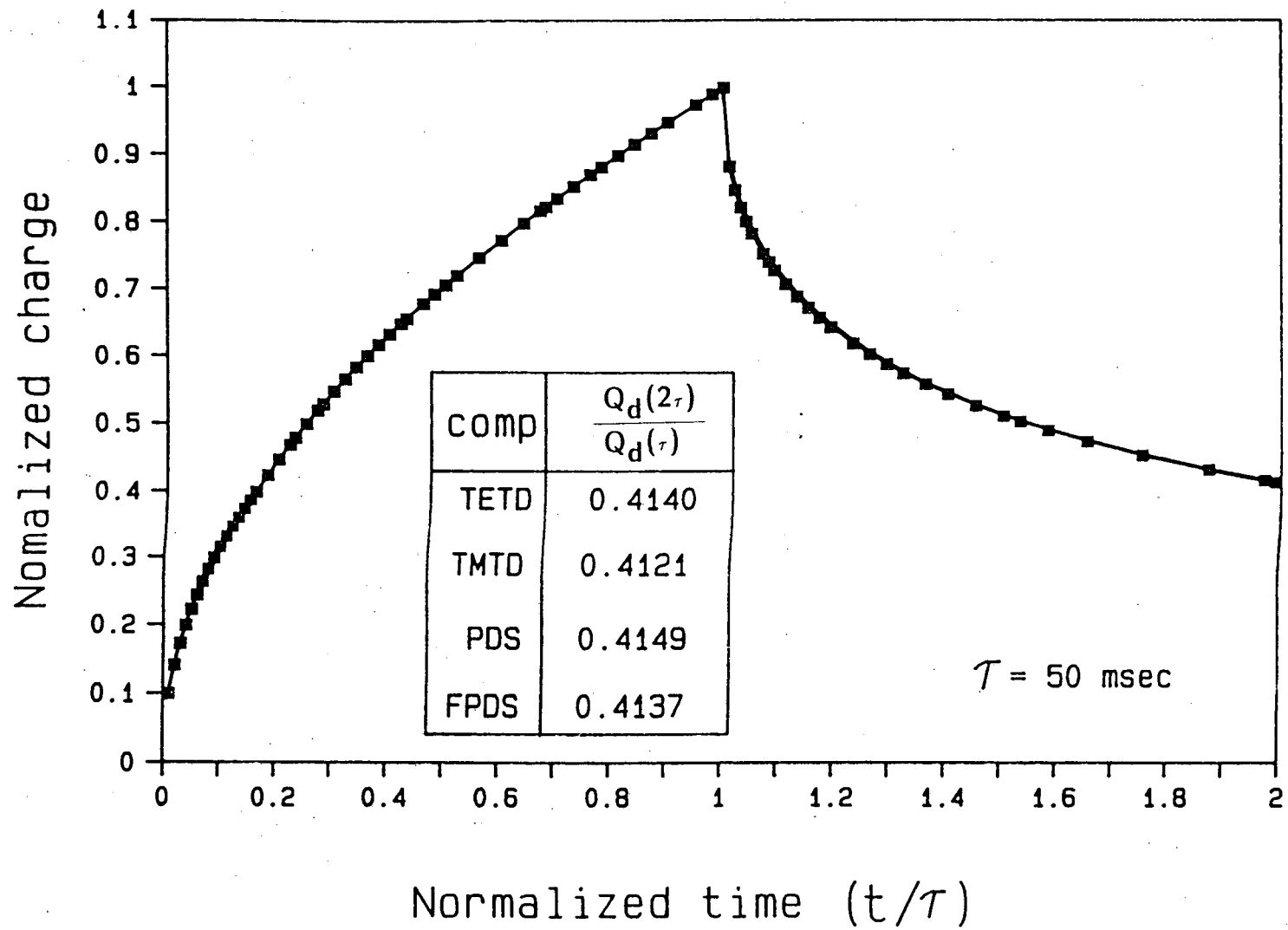
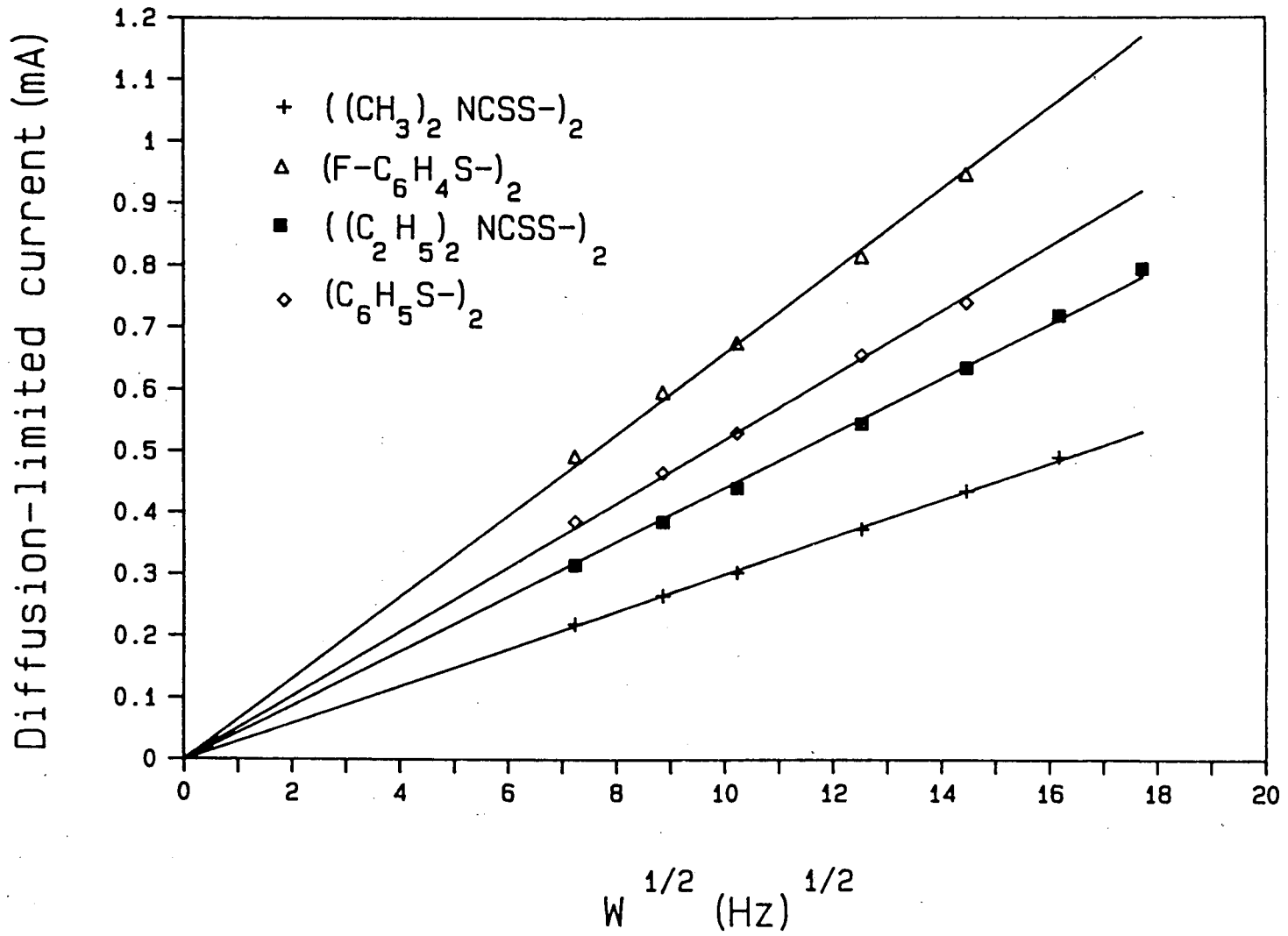
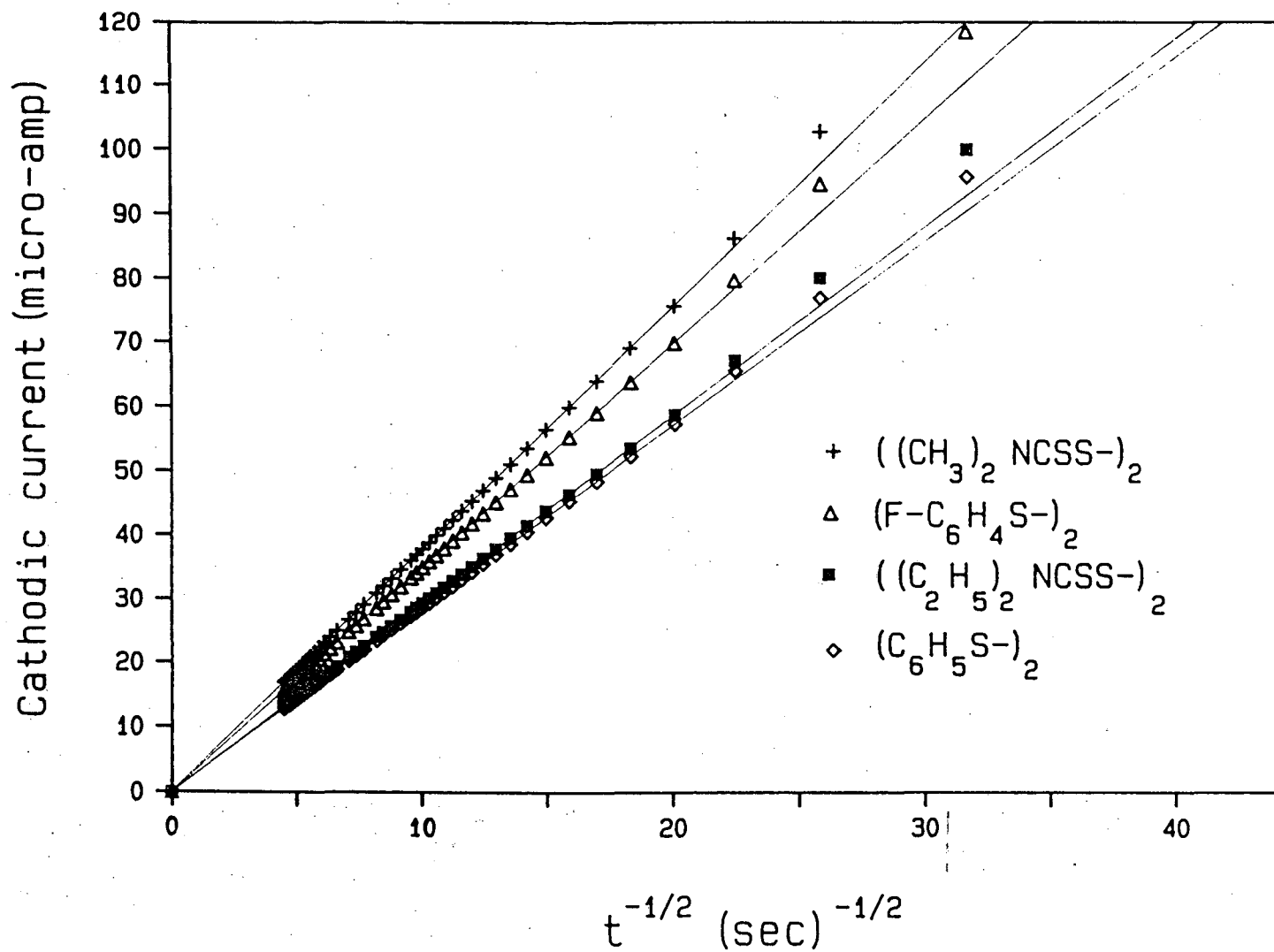


Figure 11



XBL 887-2485

Figure 12



XBL 887-2486

Figure 13

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*