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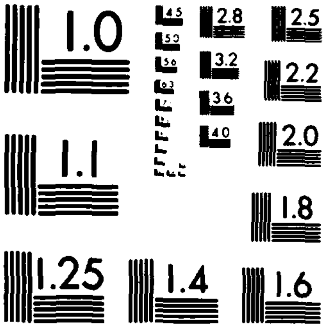

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ELECTROCHEMISTRY OF FERROCENE IN 1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE/ALUMINUM CHLORIDE ROOM TEMPERATURE MELTS

B. J. PIERSMA

J. S. WILKES

August 1986

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

FJSRL-TR-86-0005

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This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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Chief Scientist

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Ferrocene has been studied in 1-Me-3-EtImCl-AlCl$_3$ melts over a range of Lewis acidities by varying the melt composition from 0.4 to 0.6 (mole fraction of AlCl$_3$). The redox potential for ferrocene is not influenced by chloride concentration in the melts and is 0.40 ± 0.005 V (vs Al in 0.6 melt). Ferrocene is stable in basic and neutral melts but reacts chemically in acidic melts. Kinetic studies show the chemical reaction to be second order with a rate constant of about 9 x 10^{-5} 1/M sec, at 27C. The reversible redox processes were studied using cyclic voltammetric, steady-state potentiostatic and rotating disk electrode voltammetry at glassy carbon electrodes. Kinetic parameters indicate the electrode processes to be kinetically controlled and the rate limiting step is a chemical process following the electron transfer for both oxidation and reduction.

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By

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J. S. Wilkes

August 1986

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Directorate of Chemical Sciences
The Frank J. Seiler Research Laboratory
Air Force Systems Command

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SUMMARY

Ferrocene has been studied in 1-Me-3-EtImCl-$AlCl_3$ melts over a range of Lewis acidities by varying the melt composition from 0.4 to 0.6 (mole fraction of $AlCl_3$). The redox potential for ferrocene is not influenced by chloride concentration in the melts and is 0.40 ± 0.005 V (vs Al in 0.6 melt). Ferrocene is stable in basic and neutral melts but reacts chemically in acidic melts. Kinetic studies show the chemical reaction to be second order with a rate constant of about 9×10^{-5} 1/M sec, at 27C. The reversible redox processes were studied using cyclic voltammetric, steady-state potentiostatic and rotating disk electrode voltammetric techniques at glassy carbon electrodes. Kinetic parameters indicate the electrode processes to be kinetically controlled and the rate limiting step is a chemical process following the electron transfer for both oxidation and reduction.

PREFACE

The work described in this report was initiated in the Electrochemistry Task at the Frank J. Seiler Research Laboratory when B. J. Piersma was a visiting professor from Houghton College, Houghton, NY in 1981-1982 under the University Resident Research Program of the Air Force Office of Scientific Research. This report was completed when B. J. P. participated in the Summer Faculty Research Program sponsored by the Air Force Office of Scientific Research/AFSC, United States Air Force, under contract F49620-85-C-0013.

LIST OF TABLES

INTRODUCTION

Electrochemical studies of transition metal cations in a new room temperature molten salt system have shown that ion complexation and hence transport and kinetic behavior are strongly dependent on the Lewis acidity of the melt.(1) The melt acidity is widely variable by changing the mole ratio of aluminum chloride to 1-methyl-3-ethylimidazolium chloride from 0 to 2. Here we express the melt composition as apparent mole fraction $AlCl_3$ (N). Ferrocene (bis(cyclopentadienly)iron) was chosen for this study because it should not be dependent on the melt acidity, i.e., should not be influenced by the chloride ion concentration of the melt.

In a brief communication, Osteryoung, et al. indicated that ferrocene undergoes a reversible one-electron redox process in N=0.67 aluminum chloride - ethylpyridinium bromide melt.(2) The $E_{p/2}$ was found to be 0.25V with reference to Al wire in acidic melt. In a more detailed study of ferrocene and ferricenium ion in butylpyridinium melt, Osteryoung, et al. showed that ferrocene is stable in basic and neutral melts and ferricenium ion is stable in neutral and acidic melts.(3) In that work it was suggested that ferrocene is oxidized by traces of oxygen in the melt.

This report presents our study of ferrocene in $MeEtImCl/AlCl_3$ melts at approximately 25C, with emphasis on reaction kinetics. Cyclic voltammetric and steady-state potentiostatic techniques were used to determine kinetic parameters for the redox processes of ferrocene at a glassy carbon electrode. Rotating disk electrode voltammetry was used to follow the chemical reaction of ferrocene in acidic melt.

EXPERIMENTAL

The experimental details have been previously reported.(4) Measurements were made with a polished Pine Instruments Co. glassy carbon electrode. A large tungsten foil was used a counter electrode and the reference was an Al wire immersed in N=0.6 melt. Other details are as previously discussed.(4)

RESULTS AND DISCUSSION

The electrochemical window in neutral N=(0.50) melt from +2.30V to -1.6V is presented in Fig. 1. Also shown in Fig. 1 is the reversible redox couple for Ferrocene in neutral melt. The redox couples and melt limits are given in Fig. 2 for Ferrocene in basic, neutral, and acidic melts. The average value of $E_{p/2}$ for melts from N=0.4 to 0.6 is +0.403 ± 0.005V vs Al wire in 0.6 melt. Thus the Ferrocene redox couple appears to be unaffected by the chloride concentration of the melt.

Chemical Reaction of Ferrocene

Yellow solutions of Ferrocene in neutral and basic melts were stable for at least two weeks (the length of time observations were made). This was demonstrated by obtaining identical limiting currents at a rotating glassy carbon electrode over this period of time. Greenish-yellow solutions of Ferrocene obtained initially in acidic melts turned dark blue after standing 6-8 hours. Assuming that the limiting current for Ferrocene oxidation is proportional to the Ferrocene concentration in the melt, the reaction of

Ferrocene with acidic melt was followed by measuring limiting currents as a function of time. The linear variations of 1/C vs time for Ferrocene, given in Fig. 3, indicates that the variation is 2nd order in Ferrocene. The rate constant is approximately 9 x 10^{-5} ℓ/M sec. This may be compared with the rate constants determined for the reaction of Fe^{3+} with acidic melt of 5.9 x 10^{-5} ℓ/M sec obtained for a range of concentrations of $FeCl_3$ from 0.03 to 0.155 M, and for the reaction of Cu^{2+} with acidic melt of 5.1 x 10^{-4} ℓ/M sec. The reaction of Ferrocene with acidic melt may be a completely different process than that for Fe^{3+} amd Cu^{2+} since the Fe^{2+} in Ferrocene would be oxidized if it is the reacting species, while Fe^{3+} and Cu^{2+} must be reduced. Osteryoung has suggested that Ferrocene is oxidized to Ferricenium ion in acidic melt by traces of oxygen. (3) This remains an interesting question and could be the subject of another study.

RDE Studies

The anodic oxidation of Ferrocene is kinetically controlled, as demonstrated by plots of 1/i vs $\omega^{-1/2}$ (Fig. 4), but approaches diffusion limitations at higher overpotentials. The slopes of these plots were used to determine heterogeneous rate constants according to the expression

$$\frac{1}{i} = \frac{1}{nFK_f C_R} + \frac{1.61\ \nu^{1/6}}{nFD_R{}^{3/2}\ C_R\ \omega^{1/2}} \qquad (1)$$

Standard heterogeneous rate constants were obtained by plotting k_f vs E with extrapolations to E = Ep/2, using the relationship

$$k_f = k_s \ e^{-\alpha\eta Fe/RT} \tag{2}$$

The results for k_s and $\alpha\eta$ are summarized in Table I.

The Levich equation

$$i_{d,a} = 0.620 \text{ nFA } D_R^{2/3}\omega^{1/2}\nu^{-1/6}C_R \tag{3}$$

was used to calculate diffusion coefficients along with slopes from i vs $\omega^{1/2}$ plots (Fig. 5) for high overpotentials where diffusion control is obtained. The values of the diffusion coefficients reported here (Table I) for Ferrocene in MeEtImCl melts at 25C are about 50% lower than those reported in Butylpyridinium melts at 40C by Osteryoung, et al. (3). The difference we observed in diffusion coefficients for neutral and acidic melts may be the result of a change in concentration from the initial concentration of Ferrocene in acidic melt by reaction of Ferrocene with the melt.

For the reversible Ferrocene redox couple, the number of electrons involved in the oxidation process was calculated from the slope of E vs log $\left(\frac{id - i}{i}\right)$ plots (Fig. 6) according to the equation

$$E = E_{p/2} + \frac{RT}{nF} \ \ln \ \left(\frac{id - i}{i}\right). \tag{4}$$

As expected, one electron is involved in the anodic process irrespective of melt acidity.

Cyclic Voltammetric Studies

Detailed CV studies of the reversible Ferrocene redox couple were carried out in basic (0.4) and acidic (0.6) melts with sweep rate variation from 1 to 500 mV/sec. The parameters are summarized in Table II. The Tafel slope was unchanged by melt composition and is equivalent to b = RT/F for oxidation and b = - RT/F for reduction. This suggests that the redox mechanism for the Ferrocene couple is not dependent on the chloride concentration of the melt.

Steady-state Studies

Steady-state potentiostatic E vs log i curves for the anodic oxidation of Ferrocene are represented in Fig. 7, for basic (0.4) and acidic (0.6) melts. A linear E vs log i plot with a slope equivalent to RT/F was obtained in basic melt over two decades of current. In acidic melt over a slightly smaller current range the Tafel slope was also RT/F. The higher limiting current observed in acidic melt is expected due to the lower viscosity and higher diffusion coefficient of the acidic melt (note that in Fig. 7 the Ferrocene concentration in acidic melt is 1.5 that in basic melt). When the concentration differences of Ferrocene are taken into account, assuming first order kinetics, comparison of steady-state currents at a given potential in the Tafel region shows that the reaction rate for Ferrocene oxidation is essentially independent of melt composition. Tafel slopes of RT/F for anodic oxidation and -RT/F for cathodic reduction obtained from CV measurements are consistent with steady-state results. It appears that although the structure and physical properties of the MeEtImCl melts undergo significant changes with change in melt composition from basic to acidic conditions, the redox processes of Ferrocene are essentially independent of melt composition.

For n=1 and α=0.5, and assuming that adsorption of Ferrocene is not potential dependent, a Tafel slope of RT/F indicates that a step following a reversible electron transfer is the rate limiting step. For the anodic process, desorption of Ferricenium ion is a possible rate limiting step. Thus

$$(C_5H_3)_2\ Fe(melt) \rightleftarrows (C_5H_3)_2\ Fe(ad) \qquad (5)$$

$$(C_5H_3)_2\ Fe(ad) \rightleftarrows (C_5H_3)_2\ Fe^{+}(ad) + e^{-} \qquad (6)$$

$$(C_5H_3)_2\ Fe^{+}(ad) \xrightarrow{rdS} (C_5H_3)_2\ Fe^{+}(melt) \qquad (7)$$

For the cathodic reduction of Ferricenium ion, the reverse of steps 5-7 with desorption of Ferrocene as the slow step is a possible mechanism that satisfies the kinetic requirements.

CONCLUSIONS

1. Ferrocene undergoes a reversible one-electron redox process in MeEtImCl/ $AlCl_3$ melts which is not influenced by the Lewis acidity (i.e., chloride ion concentration) of the melt.

2. Kinetic parameters derived from cyclic voltammetric and steady-state potentiostatic measurements indicate that a step following electron transfer is rate limiting (in the Tafel region) both for the oxidation of Ferrocene and the reduction of Ferricenium ion. Desorption is suggested as a possible rate limiting step for both oxidation and reduction.

3. Comparison of steady-state currents at a given potential in the Tafel region for Ferrocene oxidation in basic and acidic melts indicates that the reaction rate is not influenced by melt composition. The standard heterogeneous rate constants from rotating disk measurements support this conclusion.

4. Ferrocene reacts chemically with acidic melts by a process that appears to be second order in Ferrocene. Ferrocene is stable in basic and neutral melts.

TABLE I

Summary of RDE Experiments

Diffusion Coefficients

Melt	$D \times 10^7$ (cm^2/sec)
0.500	4.3
basic (0.45)	3.5
acidic (0.55)	4.1

Electrons of Anodic Oxidation

Melt	n
0.500	1
basic (0.40)	1
basic (0.45)	1
acidic (0.55)	1

Kinetic Constants

Melt	$k_s \times 10^4$ (cm/sec)	αn
0.50	7.3	0.6
basic (0.45)	~7.3	0.5
acidic	~7.3	0.55

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TABLE II

CV Parameters for Ferrocene

	$E_{p/2}$ (volts)	ΔE_p (mv)	$\frac{i_{p,a}}{i_{p,c}}$	$\frac{i_{p,c}}{\nu 1/2}$	$\frac{i_{p,a}}{\nu 1/2}$	$\frac{d(E_{p/2} - E_{p,c})}{d \log i_c}$	$\frac{d(E_{p,a} - E_{p/2})}{d \log i_a}$	$\frac{dE_{p,c}}{d \log}$	$\frac{d\ E_{p,a}}{d \log \nu}$
0.4 melt	0.400	86	1.08	~const	~const	-60mv	60mv	-14mv	15mv
0.6 melt	0.406	84	1.07	~const	~const	-60mv	60mv	-12mv	13mv

ABBREVIATIONS

α	transfer coefficient
b	Tafel slope
cv	cyclic voltammetry
D	diffusion coefficient
$E_{p,a}$	potential (in volts) of anodic current peak
$E_{p,c}$	potential (in volts) of cathodic current peak
ΔE_p	$(E_{p,a} - E_{p,c})$
$E_{p/2}$	$(E_{p,a} - E_{p,c})/2$
i	total current in μ amps/cm^2
i_d	diffusion limited current density
$i_{p,a}$	current in (μ amps) at the anodic current peak
$i_{p,c}$	current in (μ amps) at the cathodic current peak
k_s	standard heterogenous rate constant
n	number of electrons
RDE	rotating disc electrode
rds	rate determining step
ν	sweep rate (in mv/sec) for CV measurements
ω	rotation rate (in radius/sec) for RDE1

ILLUSTRATIONS

Figure 1: Cyclic Voltammograms in Neutral (0.500) melt

a. N=0.500 melt
ν=100 mv/sec, V=250 mv/cm (horizontal), i=25 μA/cm (vertical), sweep limits are +2.30V (left) to -1.60V (right), initial potential is +0.20V.

b. 2.0 x 10^{-2}M ferrocene in neutral melt. Parameters are the same as (a) except sweep limits are +1.70V to 1.2V and the initial potential is +0.10V.

Figure 2: Cyclic Voltammograms for 2 x 10^{-2}M ferrocene.

a. basic (0.45) melt.
ν=100 mv/sec, V=250 mv/cm, i=25 μA/cm, limits are +1.1V to -1.9V, +0.10V initial potl.

b. neutral (0.50) melt.
ν=100 mv/sec, V=250 mv/cm, i=50 μA/cm, limits are +1.9V to -1.35V, +0.10V initial potl.

c. acidic (0.55) melt.
ν=100 mv/sec, V=250 mv/cm, i=25 μA/cm, limits are +1.95V to -0.35V, +0.20V initial potl.

Figure 3: Chemical Reaction of Ferrocene in Acidic Melt.

2.0×10^{-2}M ferrocene in 0.55 melt.

Figure 4: $1/i$ vs $\omega^{-1/2}$ curves for 2.0×10^{-2}M Ferrocene in 0.55 Melt.

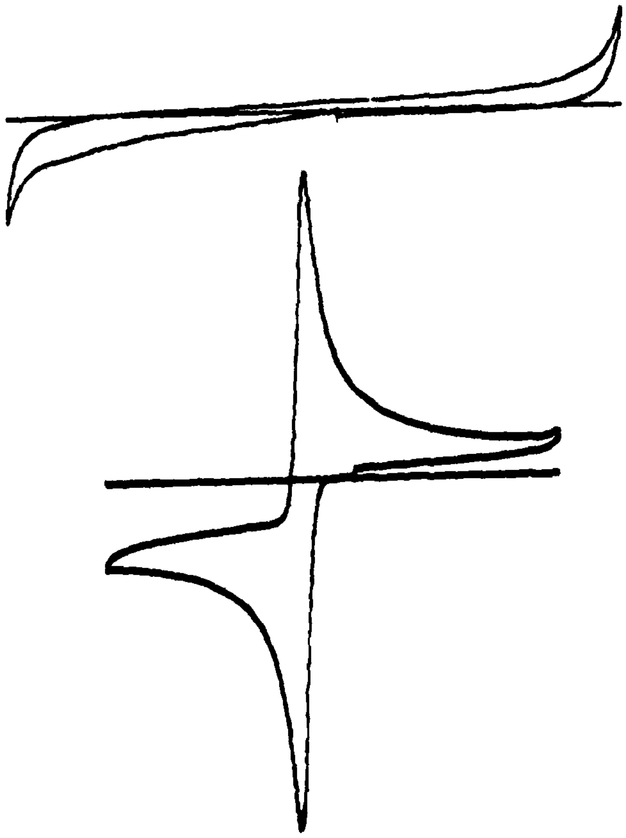
Figure 5: i vs $\omega^{1/2}$ curves at V=+0.70V in basic (0.45), neutral (0.50) and acidic (0.55) melts for 2.0×10^{-2}M Ferrocene.

Figure 6: E vs log $(\frac{id-i}{i})$ curves for 2.0×10^{-2}M Ferrocene in neutral, basic, and acidic melts.

Figure 7: Steady-state E vs log i curves for Ferrocene

(●) 1.5×10^{-2}M Ferrocene in N=0.4 melt
(□) 2.3×10^{-2}M Ferrocene in N=0.6 melt

FIGURE 1



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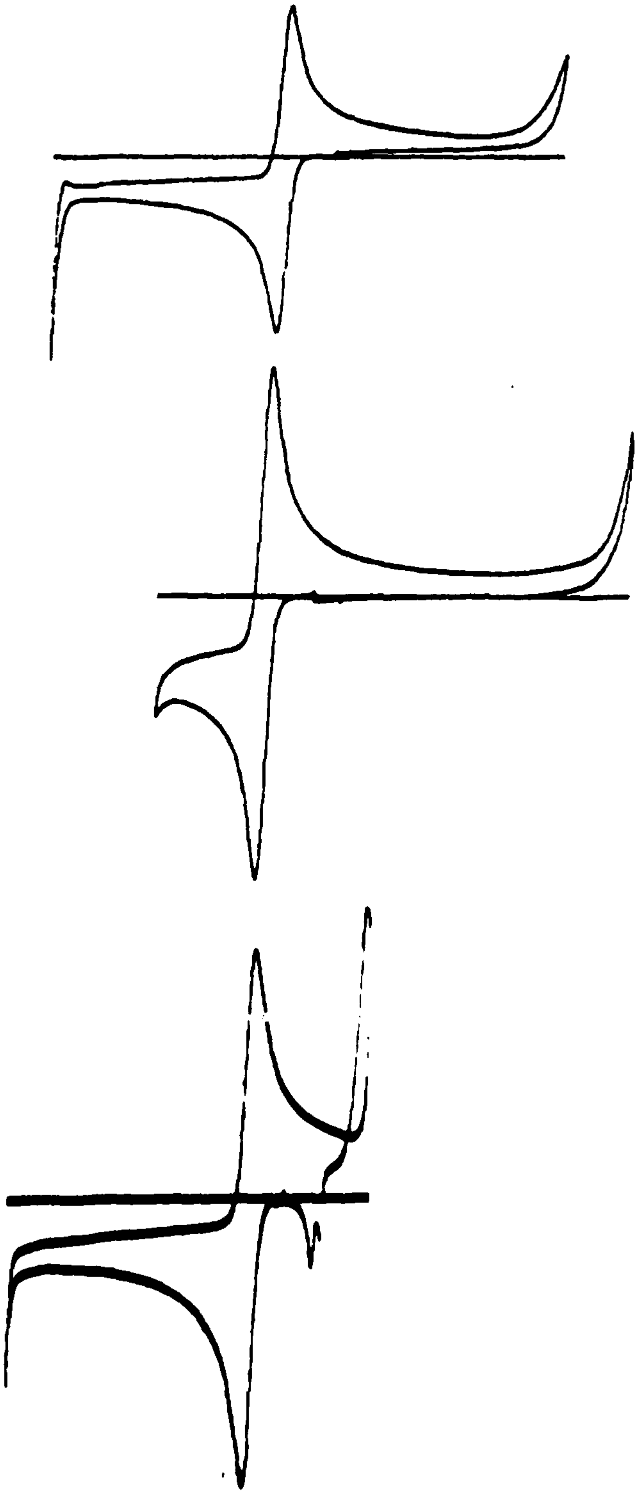

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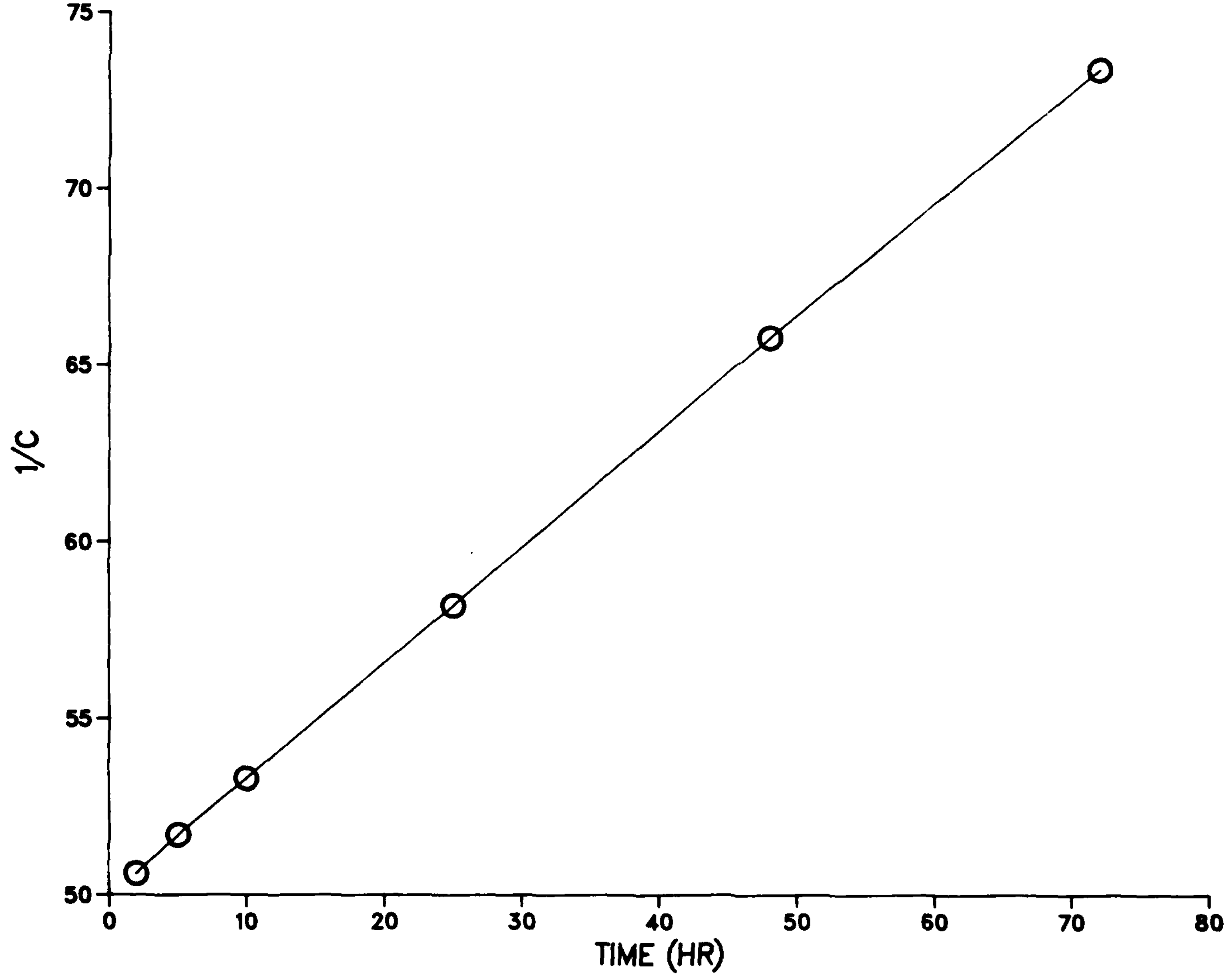

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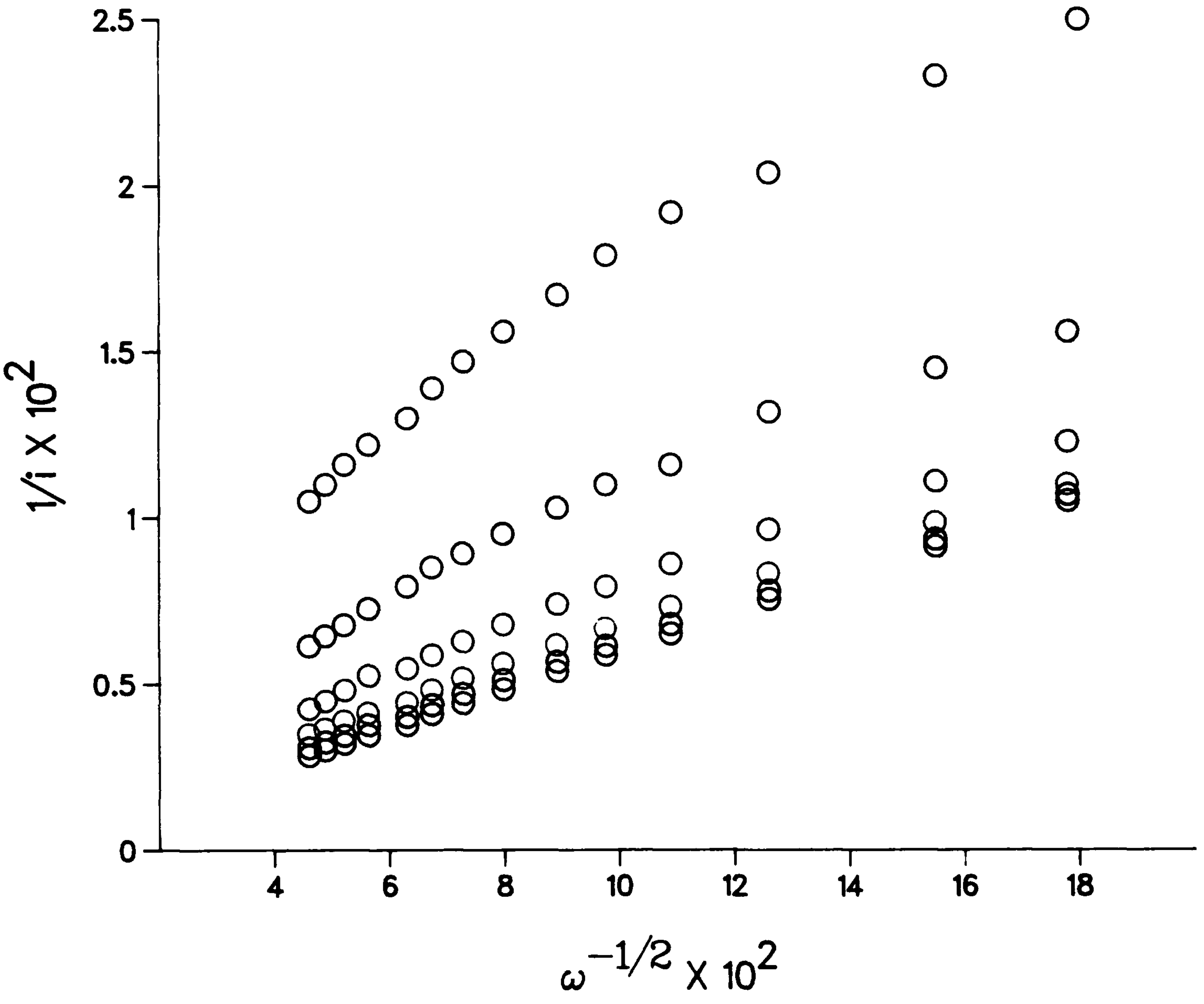

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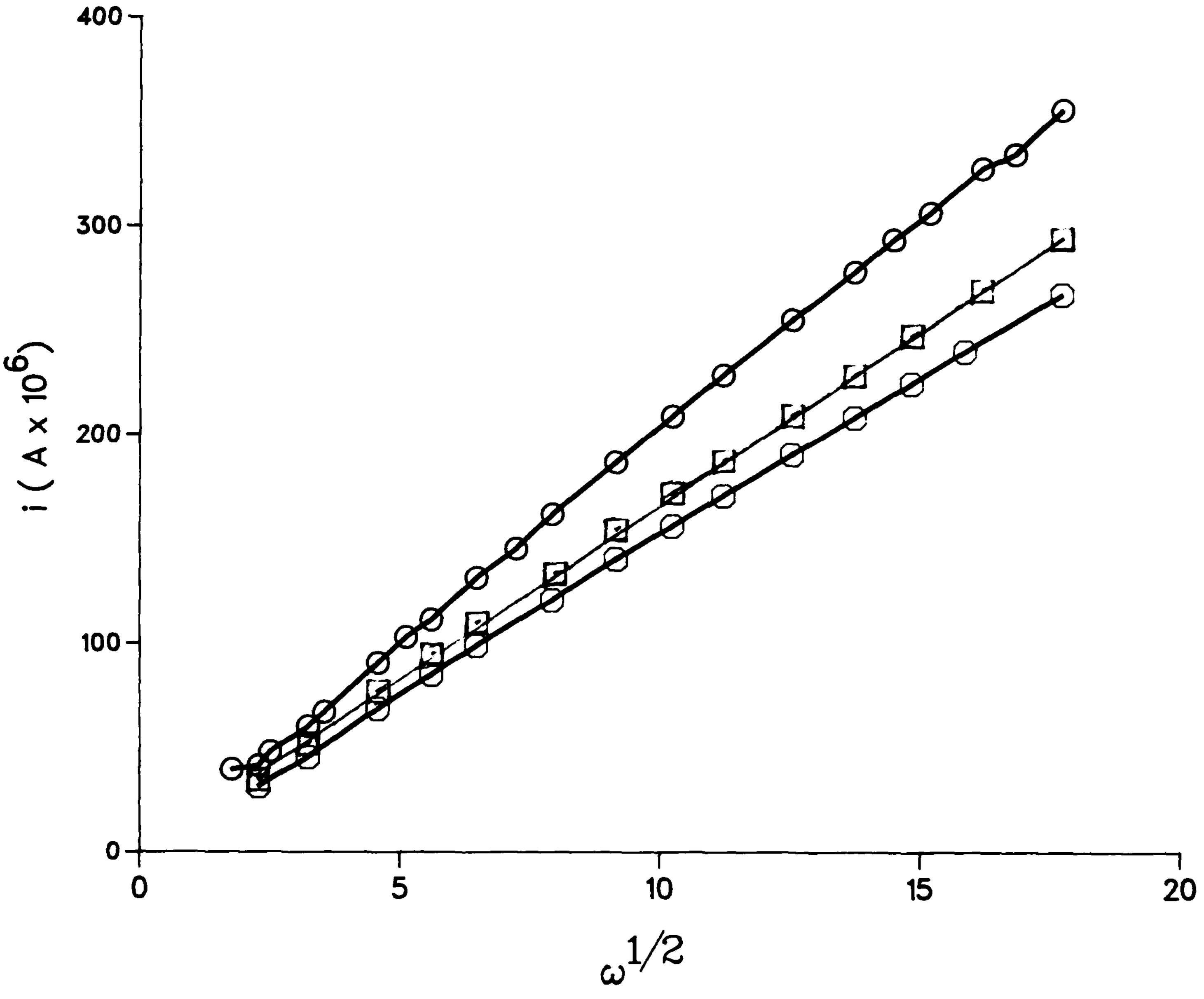

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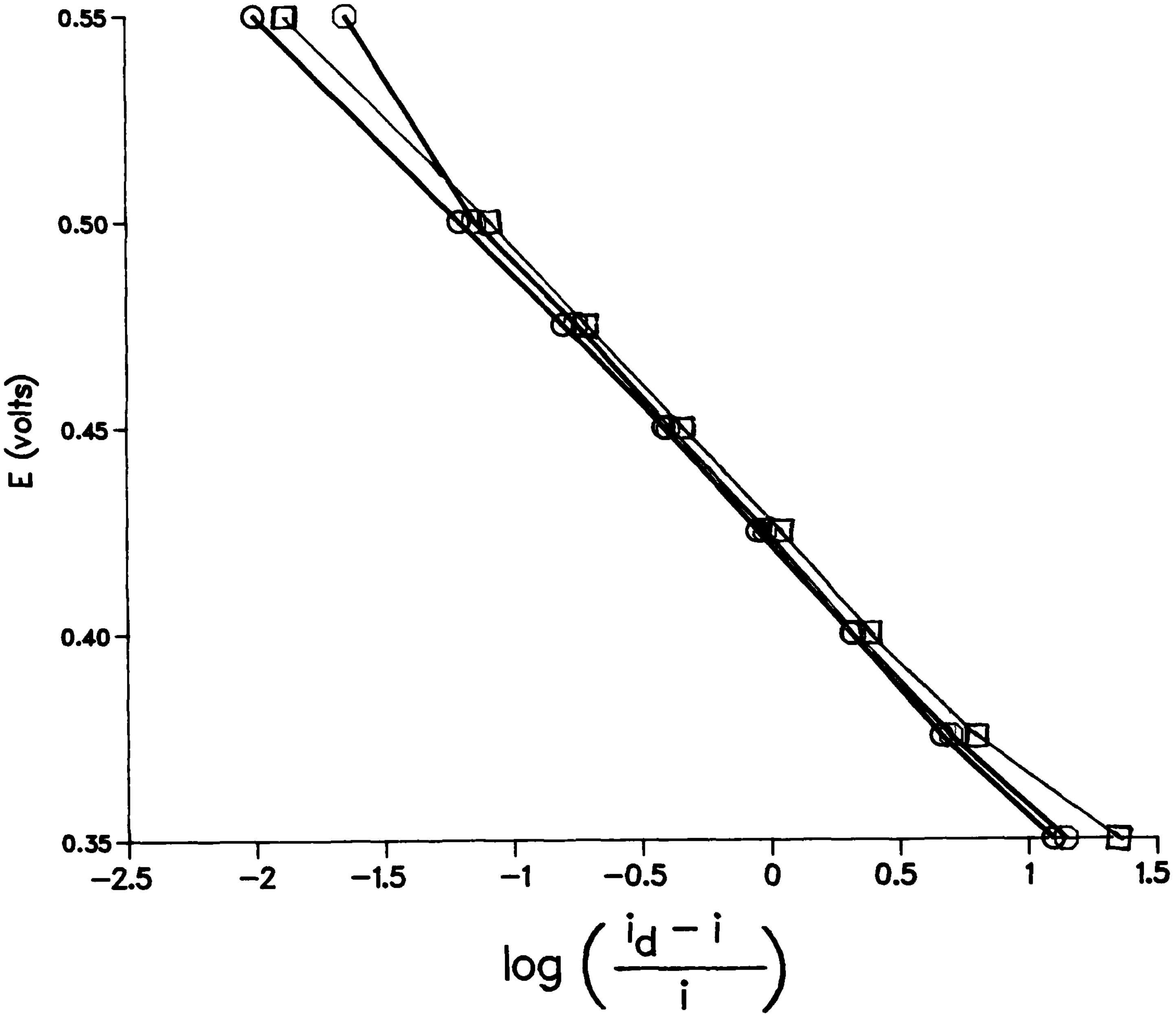
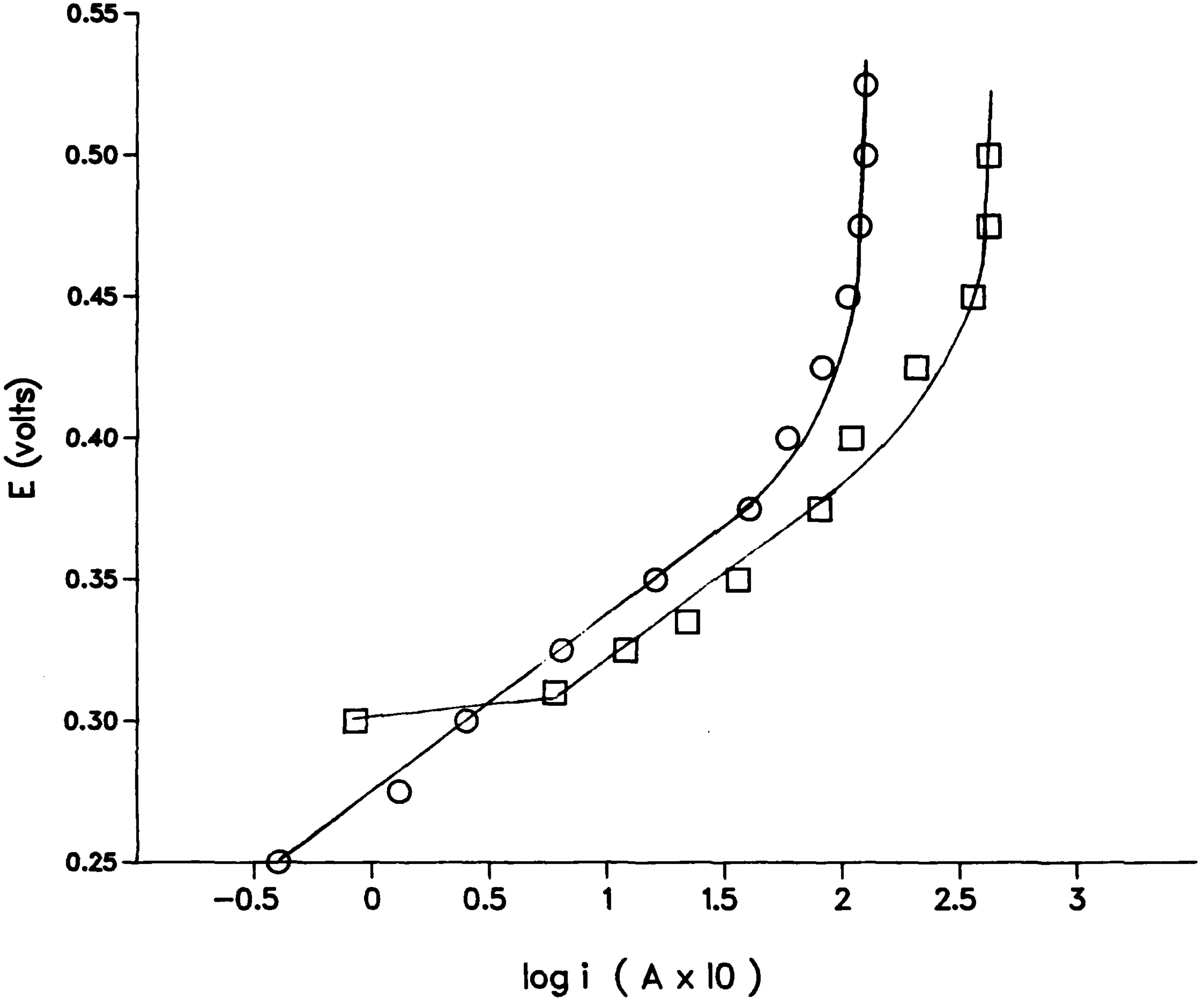

0.55
0.50
0.45
0.40
0.35
E (volts)
−2.5
−2
−1.5
−1
−0.5
0
0.5
1
1.5
$\log\left(\frac{i_d - i}{i}\right)$

FIGURE 7



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