THE POLAROGRAPHIC BEHAVIOR OF DYSPROSIUM (III) AND SAMARIUM (III) IN DIEMETHYL SULFOXIDE

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ABSTRACT

THE POLAROGRAPHIC BEHAVIOR OF DYSPROSIUM(III) AND SAMARIUM(III) IN DIMETHYL SULFOXIDE

by Raymond Thomas O'Donnell

In the investigation of the polarographic behavior of Dy(III) and Sm(III) in DMSO of very low water content containing 0.1 M LiCl, one wave, with $E_{1/2}$ at -2.06 volt vs. SCE, was obtained for Dy(III), whereas two waves, with $E_{1/2}$ values of -2.00 and -2.18 volt vs. SCE, were obtained for Sm(III).

The wave related to Dy(III) in DMSO, which is 4-5 mM in water, is shown to be irreversible by the curvature and dissymmetry observed in the plot of log $i/(i_d - i)$ vs. $E_{d.e.}$, by the slope of 108 mv in this plot, and by the high temperature coefficient of +6 mv per degree for $E_{1/2}$.

Positive chemical tests for dysprosium in the mercury cathode after prolonged electrolysis at -2.22 volt vs. SCE and the decrease in wave height in the polarograms recorded after such electrolysis demonstrate that the ultimate reduction product is dysprosium.

Evidence for a combination of diffusion and adsorption control is obtained from the effect of mercury pressure on wave height, the form of $i - t$ curves, the curvature in the plot of i_d against Dy(III) concentration and the 0.7% temperature coefficient for the wave height. The diffusion coefficient for Dy(III) is 1.56×10^{-6} cm^2 sec^{-1}.

On increasing the water concentration in a 10 mM Dy(III) solution from 4 to 3890 mM, the $E_{1/2}$ was shifted in a

non-linear manner from -2.06 to -1.86 volt vs. SCE, the latter value being only 0.05 volt more negative than $E_{1/2}$ for the Dy(III) aqueous system. As the water content is increased from 4 to 60 mM, i_d decreases. In addition to the effects on interfacial tension, viscosity, junction potential and dielectric constant that water has on the system, it must also alter the species and chemical reactions associated with the electrode process.

The waves related to Sm(III) in DMSO, which is approximately 5 mM in water, are also shown to be irreversible by curvature and dissymmetry observed in the plot of log $i/(i_d - i)$ vs. $E_{d.e.}$ and by the slopes of 109 and 127 mv in this plot for the first and second wave respectively. Although the temperature coefficients for $E_{1/2}$, +1.7 and +2.5 mv per degree for the first and second wave respectively, suggest reversibility, the possibility that the process is irreversible cannot be excluded.

Chemical tests for samarium in the mercury cathode after prolonged electrolysis at -2.36, -2.45 and -2.60 volt vs. SCE indicate that the metal is not the ultimate reduction product. Spectral and vpc evidence suggest that dimethyl sulfide is a reduction product.

From the ratio of the first to the second wave height, one and two-electron reduction steps are assumed. Transfer coefficients of 0.539 and 0.464 are obtained for the first and second step respectively.

That both waves are principally duffusion controlled is concluded from the effect of mercury pressure on each wave height, the temperature coefficients for the wave heights of 1.04% and 0.75% respectively for the first and second wave, and the linearity in the plots of i_d and i_d' against Sm(III) concentration. The form of i - t curves obtained at potentials corresponding to the plateau of the second wave suggests some adsorption influence. The diffusion coefficient for Sm(III) is 2.9×10^{-6} cm^2 sec^{-1}, and the diffusion current constant is 1.038.

As the water concentration is increased from 54. to 1000 m<u>M</u>, $E_{1/2}$ remains constant at -2.00 volt <u>vs</u>. SCE for the first wave but becomes more positive at a rate of 0.06 mv/m<u>M</u> for the second wave which indicates that water influences only the electrode process associated with the second step. The wave heights increased approximately 5 and 10 percent for the first and second waves respectively as the water content was varied from 5.4 to 550 m<u>M</u>, then remained constant as the water concentration was increased to 1.0 <u>M</u>.

It is proposed that the first step is due to the reduction of Sm(III) to Sm(II) and the second step is due to the reduction of DMSO coordinated with Sm(III) to dimethyl sulfide. Since the wave height for the first step of a solution containing Sm(III) is unchanged after prolonged electrolysis, it is concluded that Sm(II) formed in the first step is re-oxidized by DMSO.

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INTRODUCTION

The aqueous polarography of the tripositive lanthanide ions has been characterized by two types of behavior. In one group, which includes europium(III), ytterbium(III), and samarium(III), reduction to the divalent state followed by reduction to the metallic state has been reported. Varied explanations have been presented pertaining to the polarographic behavior of the remaining group, and none has conclusively demonstrated what electrode processes occur. In general, the following processes have been proposed:

(a) reduction of the tripositive state to the dipositive state with subsequent reduction to the metal;

(b) direct reduction of the tripositive state to the metal;

(c) reduction of hydrogen ion to hydride ion which results in the formation of lanthanide hydride;

(d) reduction of a hydrogen ion dissociated from a hydrated lanthanide species.

Since conclusions in the most recent investigations assume the involvement of hydrogen ions in the elctrode process in aqueous media, this investigation was undertaken to examine the polarographic behavior of lanthanide ions in an aprotic solvent. By adding varying amounts of water to an initially anhydrous system, the role of protons from water in the electrode process in the aqueous system could possibly be established.

The following guide-lines were established as criteria in the selection of a suitable solvent:

(a) The solvent must be easily purified to the anhydrous state.

(b) The solvent should have a convenient liquid range.

(c) The solvent should have a reasonable dielectric constant.

(d) The solvent should be non-protonic to avoid hydrogen ion involvement in the electrode process.

(e) The solvent should not be too viscous so that reducible substances have reasonable diffusion coefficients.

(f) The solvent must readily dissolve supporting electrolytes and lanthanide salts.

(g) The solvent should be miscible with water.

Since dimethyl sulfoxide (DMSO) appeared to meet these requirements, it was selected as the solvent for this investigation.

HISTORICAL

The initial report pertaining to the polarographic behavior of the tripositive lanthanide ions was that of Noddack and Bruckl (34), who electrolyzed sulfate solutions of all the available lanthanides without supporting electrolyte. These authors noted the appearance of a double wave for all the tested lanthanide ions, which they attributed to the stepwise reduction of the trivalvent ion to the divalent ion and then to the metal, and reported decomposition potentials for the two-step process. Since the appearance of this report, some workers have obtained supporting results while others have obtained conflicting results.

Those lanthanide ions having a stable dipositive state in aqueous solution would be expected to be reduced under polarographic conditions to the dipositive state, and this has been conclusively demonstrated that europium(III), Eu(III), is reversibly reduced to Eu(II) in 0.1 M ammonium chloride and the half-wave potential has been reported as -0.671 volt vs. saturated calomel electrode (SCE). This reduction also proceeds in acid medium, and since the half-wave potential is considerably less negative than that for any of the other lanthanide ions, europium may be quantitatively determined in the presence of the other lanthanide ions by the polarographic method.

Laitinen and Taebel (19) also demonstrated that ytterbium(III), Yb(III), is reversibly reduced to the

divalent state in 0.1 M ammonium chloride, and the half-wave potential was reported as -1.169 volt vs. SC E. However, this reduction cannot be carried out in an acid medium as the wave due to the discharge of hydrogen ion obscures the Yb(III) ⟶ Yb(II) wave. Quantitative determinations of ytterbium based on this process have been reported (11,19,36).

Laitinen and Taebel reported that no second wave for either europium or ytterbium was observed in 0.1 M ammonium chloride, but other authors have observed a second wave for both of these ions in other media (13,26).

The only other lanthanon exhibiting a dipositive state in aqueous solution is samarium, and samarium(II), Sm(II), is quite unstable in aqueous solution. Timnick and Glockler (56) studied the polarographic reduction of Sm(III) and reported a two step wave in either 0.1 M tetramethylammonium iodide or 0.1 M lithium chloride, with half-wave potential values of -1.80 v. and -1.96 volt vs SC E. The authors noted a discrepancy between the calculated and experimentally determined I_d values which they rationalized by consideration of a cyclic reoxidation of Sm(II) formed in the initial reduction by reaction with water and subsequent precipitation of a portion of the Sm(III) by the hydroxide ion produced in the reoxidation process.

Purushottam and Raghava Rao (38) have suggested the two step reduction process for samarium.

Iwase (12) reported only a single wave for Sm(III) employing either lithium chloride or tetramethylammonium iodide as a supporting electrolyte, and attributed the wave to direct reduction to the metallic state. Yakubson and Kastromina (61) also reported the process as the direct reduction to the metallic state.

As for all the other lanthanons, no evidence for the existence of the dipositive state in aqueous media has been presented, and the reports concerning the polarographic behavior of their tripositive ions have been quite varied.

Purushottam and Raghava Rao (38) studied the polarography of yttrium(III), Y(III), lanthanum(III), La(III), praseodymium(III), Pr(III), neodymium(III), Nd(III), gadolinium(III), Gd(III), and dysprosium(III), Dy(III), and reported a double wave for all of these lanthanide ions in 0.1 M lithium chloride and attributed the waves to the stepwise reduction process. Sarma and Raghava Rao (45) also reported a stepwise process for the reduction of holmium (III), Ho(III), erbium(III), Er(III), terbium(III), Tb(III), thulium(III), Tm(III), and lutecium(III), Lu(III).

Swensen and Glockler (52) reported only a single polarographic wave for Pr(III) in either 0.1 M lithium chloride or 0.1 M tetramethylammonium iodide and attributed the wave to direct reduction to the metal. Similar observations were noted by Estee and Glockler (6) for Nd(III) in 0.1 M lithium chloride or 0.1 M tetramethylammonium chloride.

Iwase (13) reported only a single wave in 0.1 M lithium chloride for Gd(III), Dy(III), Ho(III), Er(III), Tm(III) and attributed the wave to the direct reduction to the metal. Misumi and Iwase (28,29) have reported a single wave for both Pr(III) and Nd(III).

Yakubson and Kastromina (61) reported only a single wave for La(III), Nd(III), and cerium(III) in 0.1 M tetramethylammonium iodide and suggested direct reduction to the metal. These authors also noted that the wave believed to be due to reduction of the simple ion disappears upon addition of citrate or tartrate ion, and no wave for the redution of a complex is observed.

Misumi and Ide (26) obtained for Y(III) in tetramethylammonium iodide and lithium perchlorate a double wave in halide medium and only a single wave in perchlorate medium. These authors suggested that for both media, the first wave was due to reduction of hydrogen ion produced by dissociation of the hydrated Y(III) ion but offered no rational explanation for the origin of the second wave.

Treindl (54) studied the polarographic behavior of La(III), cerium(III), Pr(III), Nd(III), and Sm(III) and reported a single wave in a lithium halide solution which was not observed in solutions containing other alkali metal ions nor in the presence of sulfate or perchlorate ions. Treindl also employed impulse polarography and polarography with a periodically changed rectangular voltage, and with the results from these two methods quoted as

evidence, has proposed that the polarographic reduction of the ions studied involved the formation of lanthanide hydrides.

Considerable interest has been shown in the electrolytic separation of the lanthanons by reduction at mercury or amalgam electrodes (35,41,42,43,50). The conditions employed in gross electrolysis differ greatly from those employed in polarographic work in that large electrode surface areas, very high potentials, and high current densities are employed. However, some of the information gained from this work is of interest, and the basic observations are the following: (1) the reduction from ordinary solutions gives a very poor yield, (2) the addition of citrate or tartrate ions considerably improves the yield, (3) precipitates are sometimes formed at the electrode.

Hamaguchi, Hashimoto, and Hosohara (10) carried out neutron activation analysis on mercury drops collected in a Ho(III) solution at an applied potential corresponding to that at which limiting currents are attained. Much less holmium than would be expected was found in the mercury, and these authors concluded that there was no reduction to the metallic state. However, no precautions were taken in their work to avoid redissolution of any holmium that might have been present as an amalgam.

In a recent study (21) of the polarographic behavior of Dy(III), Large and Timnick observed two-step polarograms in aqueous 0.1 M LiCl, 0.01% gelatin. Their observations lead to the conclusion that two-step polarograms

recorded with solutions containing lanthanide ions which do not yield dipositive ions in aqueous solutions, result from the reduction of hydrogen ions produced by the hydrolysis of the hydrated lanthanide ions in the immediate vicinity of the electrode and the subsequent reduction of additional hydrogen ions from water associated with the adsorbed lanthanide hydrous oxide.

Under gross electrolysis conditions, Moeller and coworkers (30,31,32) found "metallic" deposits on cathodes of platinum and copper from solutions of Nd(III), Gd(III) and La(III) in ethylenediamine, pyridine, N,N'-dimethylformamide, and acetonitrile; however, conclusive evidence for the deposition of the metals was not obtained.

Hall and Flanigan (9) observed single, irrversible waves for La(III) and Pr(III) acetates in anhydrous ethylenediamine using 0.1 M tetrabutylammonium perchlorate supporting electrolyte. Coulometry established three electron reduction steps. That metal amalgams were formed was shown by chemical tests.

Kolthoff and Coetzee (15) studied the polarography of the perchlorates of seven lanthanide ions and yttrium in acetonitrile with tetraethylammonium perchlorate as supporting electrolyte. Neither the solvent nor the perchlorates were anhydrous. Single waves were obtained for La(III), Pr(III), Nd(III), Gd(III), Y(III), and Sm(III) and double waves for Eu(III) and Yb(III). The first step for Eu(III) and Yb(III) as well

as the only step for Sm(III) was attributed to the reduction of the tripositive state to the dipositive state. The second step for Eu(III) and Yb(III) as well as those yielding only a single step was attributed to the discharge of a proton resulting from a solvolysis reaction.

Coetzee and Siao (5) also reported interference from hydrogen ion discharge when hydrated lanthanide perchlorates were studied polarographically in acetone.

Interest in dimethyl sulfoxide (DMSO) as a polarographic solvent has been relatively recent. The initial report by Gutmann and Schober (8) concerned the reduction of ten alkali and alkaline earth ions and six other metals as halides or organo-metallic species with tetraethylammonium nitrate as supporting electrolyte.

Gritzner, Gutmann and Schober (7) reported that La(III), Ce(III), Pr(III), Nd(III), Gd(III), Tb(III), Dy(III), Ho(III), and Er(III) gave one wave and Sm(III), Eu(III), and Yb(III) gave two waves in DMSO and DMF using 0.1 M tetraethylammonium perchlorate as supporting electrolyte. The electrode reactions were all irreversible and diffusion controlled in the 10^{-4} to 10^{-3} M concentration range at 21°C. The influence of water was investigated for La(III), Ce(III), Pr (III), and Nd(III). The addition of water lowered the wave height and greater than 1 percent water caused drop time irregularities. The absence of maxima at less than 3 percent water was also noted. No conclusive proof for the

formation of lanthanon amalgams was given and the effect of water was considered negligible.

In a recent review article by Butler (4), half-wave potentials which have been observed by various authors for various ions in DMSO are listed. These have been generally referred to an aqueous saturated calomel electrode (SCE). The liquid junction between the aqueous KCl and DMSO electrolyte appears to be stable to ± 3 mV and was found to be the same for 0.1 M tetraethylammonium perchlorate and 0.1 M tetraethylammonium nitrate. In general, the order of the half-wave potentials in DMSO is similar to that in aqueous solutions (46,22), and the DMSO-H_2O liquid junction potential has been estimated to be approximately 120 mV by equating the redox potentials of large ions in the two media (46). Many polarographic reductions appear to be irreversible in DMSO according to the shape observed for the waves (22,47).

Kolthoff and Reddy (17) reported on the polarography of several acids, cobalt(II) and nickel(II) using 0.1 M sodium perchlorate as supporting electrolyte in DMSO. Reddy (39) also estimated DMSO to be a weaker acid and a stronger base than water.

THEORETICAL

Introduction

The experimental information obtained by classical polarography is represented by the current-potential curve observed in the electrolysis of the solution under investigation using a polarizable dropping mercury electrode, (DME), combined with a large, nonpolarizable reference electrode such as the saturated calomel electrode, (SCE). The electrode is polarized by an external voltage which is assumed to be constant during the measurement of the current.

Electrode processes occurring at the polarized electrode fall into two extreme classes, reversible and irreversible.

Electrode processes in reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. For such reactions the variations of current with changing potential reflect changes in solution composition at the electrode surface as described by the Nernst equation. The definition (23) of reversibility is therefore a practical one: a reaction is said to be reversible if, within the limits of experimental error, its behavior cannot be distinguished from that of an infinitely fast reaction.

At the other extreme is the class of "totally irreversible" reactions, which are so slow that they proceed only a fraction of the way toward equilibrium during the life of

each drop. For these reactions it is the rate of the electron-transfer process, and the manner in which this is influenced by the electrode potential and/or species at the electrode surface, that govern the relationship between current and potential.

When the electrode is polarized a net transfer of electrons to or from the solution (an electrode process) takes place, tending to change the concentrations of the electroactive species at the electrode surface in accord with the new conditions and disturbing the homogeneous concentration distribution and chemical equilibria in the solution. The rate at which electrons are transferred across the boundary and the direction of this transfer depend on the sign and magnitude of the deviation from equilibrium conditions, and, at the same time, on the dynamic electrode properties of the components of the solution. The system tends to reestablish the disturbed equilibrium in the solution near the electrode by supplying species consumed by the electrode process, either from the bulk of the solution or from the electrode itself. The electrode process thus induces a mass transfer to and from the electrode surface and the net faradaic current flowing through such an electrode is directly proportional to the flux of the electroactive species at the electrode surface. The greater the deviation from equilibrium the greater the flux induced and the greater the current which flows through the electrode. The flux and also the current increase with increasing

deviation from equlibrium to some limiting value, which depends on the nature of the equilibrium which has been disturbed by the electrode process and on the composition of the solution. If only the concentration distribution has been disturbed, the mass transfer is governed by diffusion and the current is limited by the highest rate of diffusion possible for the given concentration of the depolarizer in the solution studied. If chemical equilibria have been disturbed, the mass transfer is governed by the rate of diffusion or by the rate of reestabilishment of chemical equilibrium, depending on the relative velocities of these processes. In the latter case, the current is limited by the highest rate of formation of the species reacting directly with the electrode (reaction-rate-controlled current).

Criteria for Reversibility

Of the various criteria for reversibility the most widely applicable, and most commonly used, is based on a plot of log $i/(i_d - i)$ against $E_{d.e.}$.

For reversible waves, the current-potential curve can be described, at 25^0, by

$$E_{d.e.} = E_{1/2} - \frac{0.059}{n_d} \log \frac{i}{i_d - i} \qquad (1)$$

where $E_{d.e.}$ and $E_{1/2}$ are usually related to the potential of some chosen reference electrode. The "log plot" should be linear and possess a slope of $(59/n_d)$ mv, n_d being the number of electrons involved in the reduction.

For irreversible waves, the current-potential curve can be described, at 25^0, by

$$E_{d.e.} = E_{1/2} - \frac{0.059}{\alpha n_a} \log \frac{i}{i_d - i} \qquad (2)$$

where, again, $E_{d.e.}$ and $E_{1/2}$ are referred to some chosen reference electrode. In this case n_a is the number of electrons involved in the rate-determining electron transfer step and α is the transfer coefficient for the reduction process ($\beta = 1 - \alpha$, for the oxidation process). Although in principle n_a could have any integral value between one and n_d, it has never been found to exceed two and most generally might be expected to be one. Values for α are rarely far from 0.5 and values of αn_a, obtained from the slope of the "log plot", between 0.3 and 0.6 may be considered to correspond to a rate determining electron-transfer step involving one electron (24).

From an analysis of the experimental current-potential curves three main parameters can therefore be obtained: the half-wave potential, $E_{1/2}$, the limiting current, i_d, and the transfer coefficient, α.

Although it may not be clear from equations (1) and (2), the half-wave potential of an irreversible wave is a purely kinetic function of no thermodynamic significance (23,24).

Comparison of Diffusion, Kinetic, Catalytic and Adsorption-controlled Waves.

The most simple mass transfer takes place by diffusion which is induced by the difference in the concentration of the depolarizer in the bulk of the solution and at the electrode surface. In such a case the Ilkovic equation,

$$i_d = 607\, n_d D^{1/2} C m^{2/3} t^{1/6} , \qquad (3)$$

or one of its extensions should apply. An estimate of the value of n_d or i_d for the substance studied and comparison with the limiting current experimentally observed generally gives a first insight into the mechanism of the electrode process.

The general mechanism for a kinetic wave may be written

$$Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$$

$$O + ne \longrightarrow R$$

where k_f and k_b are first or pseudo-first-order rate constants. The height of the kinetic wave depends both on the ratio of the equilibrium concentrations of Y and O in the bulk of the solution and the rate constants for their interconversion. When the concentration of O is negligibly small and when the transformation of Y to O is very slow it can be shown that

$$i_k = 493\, n\, D^{1/2}\, C_Y\, m^{2/3}\, t^{1/6}\, (k_f/k_b^{1/2}). \qquad (4)$$

The general mechanism for a catalytic wave may be written

$$O + ne \longrightarrow R$$

$$R + Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$$

in which a substance Z, which would not be reducible at a certain potential if it were present alone, causes the current obtained from the reduction of an electroactive substance O at that potential to increase by reacting with the product R to regenerate O or to form some other substance that is reducible. Here $k_f C_Z^0$ describes the pseudo-first-order rate constant where k_f is the second or pseudo-second-order rate constant and C_Z^0 is the concentration of Z at the surface of the electrode. If $k_f C_Z^0$ is small, very little R will be reoxidized and the wave height will be practically equal to the diffusion current of O, but as $k_f C_Z^0$ increases the catalytic current becomes more important. The average catalytic current over the life of a drop is given by

$$i_c = 493\ n\ D_O^{1/2}\ C_O\ m^{2/3} t^{1/6} [(k_f + k_b) C_Z^0]^{1/2} \quad (5)$$

If C_Z^0 remains constant the average catalytic current is proportional to C_O^0, or if C_O^0 remains constant, the average catalytic current is proportional to $(C_Z^0)^{1/2}$.

If in the reaction

$$O + ne \longrightarrow R,$$

R is adsorbed, an adsorption wave results. If the activity

of R is lower in the adsorbed state than in solution, the reduction of O is facilitated. At very low concentration the wave would be diffusion controlled, but as the concentration of O is increased, a point is reached at which enough R is formed during the life of the drop to cover its entire surface. More than this amount of R can be formed only if the excess remains in solution. Since it is more difficult to reduce O to dissolved R than to reduce it to adsorbed R, the reduction of excess O can produce a second wave at a more negative potential. The original wave is the adsorption wave, whose height will be constant and independent of any further increase in the concentration of O; the second wave is the normal wave which represents the reduction of O to dissolved R. Only the total height of the double wave corresponds to the reduction of all the O diffusing to the surface of the drop, and is therefore diffusion controlled. The average adsorption current over the life of a drop is given by

$$i_a = 13.66\ n\ m^{2/3}\ t^{1/3}/a \qquad (6)$$

where a is the area (in $\mathring{A}^2$) covered by each adsorbed molecule.

Dependence of Wave Height on Mercury Pressure

In establishing the character of the limiting current, the dependence of the wave height on mercury pressure and on concentration of depolarizer usually furnishes the primary

information. A change in the h_{eff} changes both the drop time, t, and the rate of mercury flow, m, but the product mt remains constant. It is thus possible to demonstate the effect of mercury height on the limiting current for each of the preceding cases and this (62) has been done as shown in Figure 1.

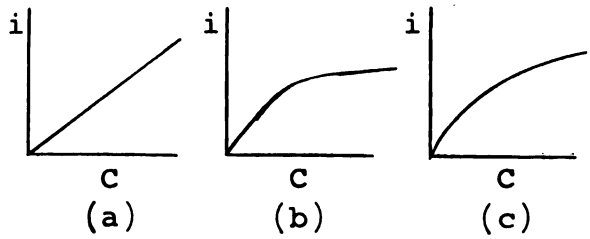
Dependence of Wave Height on Interfacial Tension Between the Solvent and Mercury

The wave height, as shown in a preceding section, depends on the capillary characteristics, m and t. The Poiseuille equation relates m to the interfacial tension between the solvent and mercury and may be written

$$m = \frac{125\pi r_c^4 d_{Hg}}{\ell\eta}\left[h_{hg}d_{hg}g - h_{soln}d_{soln}g - 43.1\,\frac{d_{Hg}^{1/3}\,\sigma}{(mt)^{1/3}}\right] \qquad (7)$$

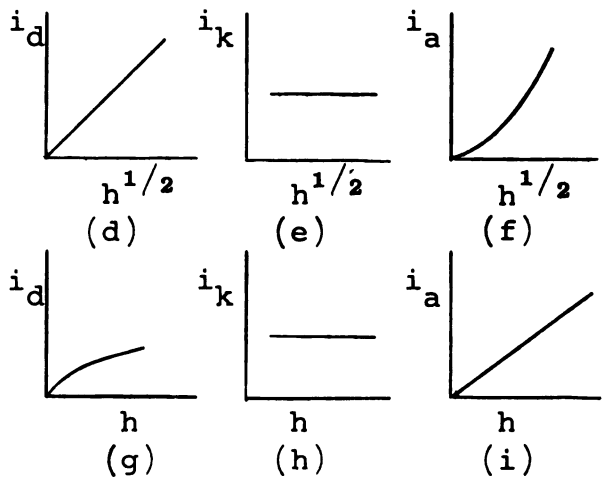
where m is the rate of mercury flow (mg sec^{-1}), r_c and ℓ are the radius and length of the capillary (cm), d_{Hg} and η are the density and viscosity of mercury, h_{Hg} and h_{soln} are the heights (cm) of the mercury column and of the solution, respectively, above the capillary tip, d_{soln} is the density of the solution, σ is the interfacial tension (dynes cm^{-1}) between mercury and the solution, g is the gravitational constant and t is the drop time (sec).

The interfacial tension between mercury and dilute aqueous salt solutions is on the order of 400 dynes cm^{-1} and between mercury and many organic solvents is of the order of 350 dynes $.cm^{-1}$ (5).



Dependence of limiting current on concentration.

(a) Diffusion and most kinetic currents
(b) Adsorption currents
(c) Catalytic and some types of adsorption currents.



Dependence of limiting current on mercury pressure, h.

(d), (g) Diffusion control
(e), (h) Kinetic control
(f), (i) Adsorption control.

Figure 1. Dependence of limiting current on concentration and mercury pressure (ref. 62).

For dilute aqueous solutions it has been shown (23) that the drop time is essentially proportional to the interfacial tension.

Dependence of i_d and $E_{1/2}$ on Temperature

Changes in temperature affect the diffusion coefficient and therefore the wave height. Meites (23) has recommended that temperature coefficients be calculated from the expression $(2.303/\Delta T) \log(i_{d2}/i_{d1})$. Temperature coefficients much larger than 2%/deg are probably at least partially due to kinetic or catalytic behavior since the rates of most chemical reactions increase much more rapidly with temperature than do rates of diffusion.

Generally the temperature coefficient for $E_{1/2}$ is found to be ± 2 mv/deg. For a reversible wave, it may be positive or negative; for an irreversible wave it is usually positive and may exceed several millivolts per degree.

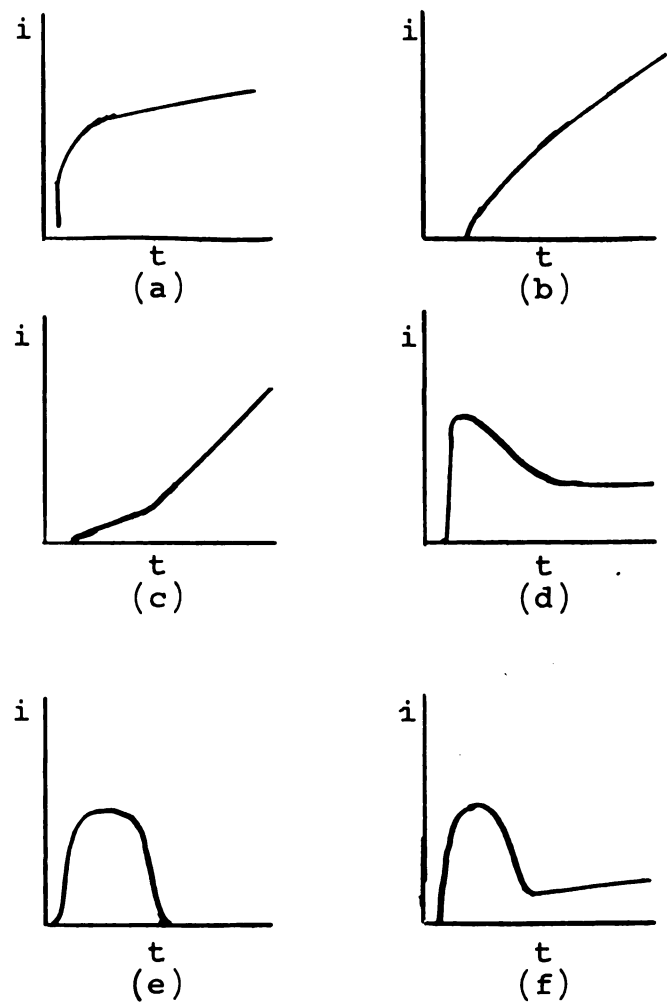
Dependence of Current-time Curves on the Electrode Process

It was previously stated that for a diffusion controlled, reversible process, i_d is proportional to $t^{1/6}$ and thus the rise in current during the drop lifetime should follow a sixth order parabola. Other types of electrode processes cause deviations from this interrelationship. These deviations can be employed to ascertain the nature of the electrode processes.

Vlcek (59) has summarized how various effects, such as diffusion, kinetic, adsorption and catalytic, influence the form of the recorded current-time (i - t) curves. A general expression for the i - t curve is of the form $i = (\text{constant})(t)^{\gamma}$, where γ is a function of i/i_d. Conclusions regarding the nature of the electrode process may be deduced from variations in the γ values as follows:

1. for a reversible electrode process, both forms of the redox system in the solution, $\gamma = 1/6$ for all i/i_1 at $t > 0.5$ sec;
2. for a reversible electrode process, but reduced form in the solid phase (electrode), γ changes from 0.1 to 0.19;
3. for a slightly irreversible process, γ changes from approximately 0.4 through a maximum to 1/6;
4. for an irreversible electrode process γ changes from 2/3 to 1/5 (1/6), γ being not completely constant with t;
5. for decomposition of the product, γ changes from 2/3 to 1/5 (1/6);
6. for catalysis by adsorption of electro-inactive species, γ changes from > 2/3 to 1/6.

Also, i - t curves may be obtained which cannot be described by the general expression over the life of the drop because of the development of a maximum. The types of current-time curves for these complicated cases as well as the normal curves are shown in Figure 2.



(a) diffusion controlled current
(b) reaction rate controlled current
(c) autocatalysis or catalysis by adsorption
(d) adsorption of the electroactive species
(e) hindrance of the electrode process by the adsorption of an electro-inactive species
(f) same as (e), the rate at covered surface different from zero.

Figure 2. Types of current-time curves (ref. 59).

Dependence of i_d and $E_{1/2}$ on Solution Composition

To find out which components of the solution play a role in the electrode process, the dependence of i_d and $E_{1/2}$ on the concentration of all components of the solution must be followed.

Vlcek (59) classifies components as (a) electroactive (b) electro-inactive but taking part in the complexation of an electroactive component or (c) electro-inactive and non-complexing.

In the case of an electroactive component, either i_d will increase to a limiting value or $i_d = (\text{constant})(C)^y$, where C is the concentration of the electroactive component. In the latter case, if $y = 1$, all equilibria or reactions involved in the electrode process are first-order with respect to the depolarizer, the concentration of ligand and all other components are much higher than C. If $y \gtrless 1$, some of the equilibria or reactions could be of higher order with respect to the concentration of the depolarizer or the ligand or some other component could be comparable or lower in concentration than C. If $y < 1$, it is indicative of a preceding dissociation while if $y > 1$, it is indicative of an auto-catalytic process. In the case of adsorption currents or when the electrode process is hindered by the product, i_d increases only to a limiting value.

$E_{1/2}$ is a function of C when the electrode process is complicated by chemical reactions of higher order with respect to the depolarizer or the product of the electrode

process is adsorbed and influences the rate of the electrode process.

The dependence of i_d on the concentration of an electro-inactive complexing component, [X], cannot be simply stated since a knowledge of the various species present along with their stability constants would be required to calculate the concentration of the depolarizer C. Thus [X] effects i_d through its effect on the concentration of C. Prediction of how [X] influences i_d is further complicated by the possibility that the product of the electrode process may react with X to give a species which is active at the same or more positive (negative) potential than the electroactive species itself.

The dependence of $E_{1/2}$ on the concentration of such a component differes for reversible and irreversible processes. For a reversible process, $E_{1/2}$ will be a function of [X] if the oxidized and reduced forms differ in the number of X particles bound in their respective complexes. For an irreversible process, $E_{1/2}$ will be a function of [X] if a preceding chemical reaction is influenced by [X].

EXPERIMENTAL

Instrumentation

The following instruments were employed in this investigation for the purposes described:

A Sargent Model XXI Polarograph to obtain recorded current-potential curves;

A Sargent Number S-30260 Potentiometer to measure the applied potential values;

A Tektronix Type 564 Storage Oscilloscope to obtain current-time curves during the growth of mercury drop;

A Tektronix Type C-12 Oscilloscope Camera Mounting equipped with a Polaroid Camera and type 107 film to record current-time curves;

A Hewlett-Packard Model 412 A Vaccum Tube Volt Meter to measure the potential in the prolonged electrolysis studies.

A Serfass Model RCM 15 Resistance bridge to measure the resistance of the cell;

A Sargent Number S-2770 constant temperature bath to insure temperature control at 25.0 ± 0.1°C when temperature in the laboratory was not controlled;

A Model A-90-P Aerograph Gas Chromatograph utilizing a 15% Ucon Polar column (designated: 50-HB-2000, Support 60-80 mesh chromadsorb W, 8 feet, 1/8 inch stainless steel column) to determine the purity of dimethyl sulfoxide;

A Model IR5-A Beckman Infrared Spectrophotometer to test the purity of dimethyl sulfoxide;

A Model A-60 Varian Associates Nuclear Magnetic Resonance Spectrometer to determine the purity of dimethyl sulfoxide;

A Fischer Scientific Co. "Isolator/lab.," Helium filled dry box to place rare earth trichlorides into weighing bottles;

Two Heathkit Modules, EUW-16 and EUW-19 were used for prolonged electrolysis studies.

Other Equipment

The electrolysis cell employed in this work is shown in Figure 3 and consists of three compartments separated by sintered glass discs. The sample compartment is fitted with a side arm to allow nitrogen to be bubbled through the solution and is separated from the central compartment by a fine porosity sintered glass disc. The central compartment is filled with a solution of supporting electrolyte and is separated from the third compartment by a medium porosity sintered glass disc. The third compartment is also filled with a solution of supporting electroltye into which the side arm of the SCE is placed. This cell design provides adequate electrical connection while minimizing contamination of the sample solution by foreign ions, agar, or water from the side arm of the reference electrode. In practice the cell is rinsed, dried at 110^0C, and cooled in

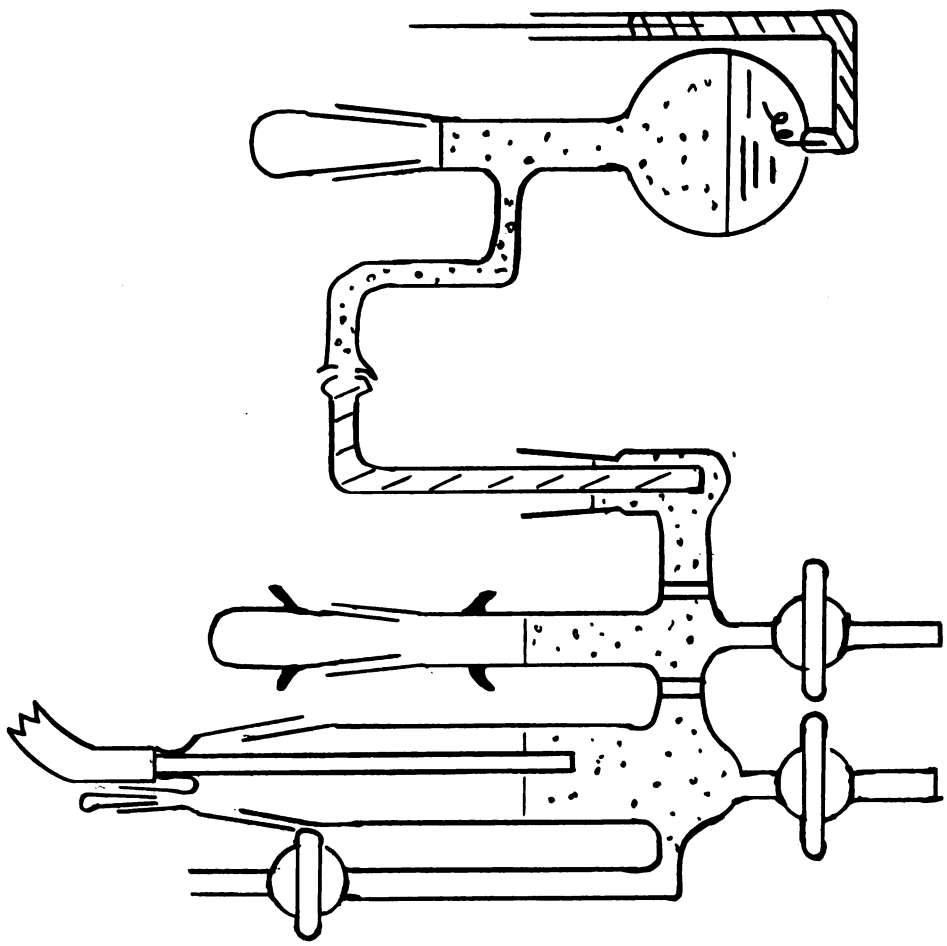


Figure 3. Polarographic cell and reference electrode.

a desiccator prior to each run, although the design permits the sample and central compartments to be filled with new solution prior to each run. Teflon stopcocks were used in all equipment.

A ball-joint is provided on the side arm of the reference electrode so that the agar arm may be replaced when it becomes contaminated without preparing a new reference electrode.

The reference electrode employed was prepared using triple distilled mercury, saturated KCl solution, and mercurous chloride especially prepared for electrode use.

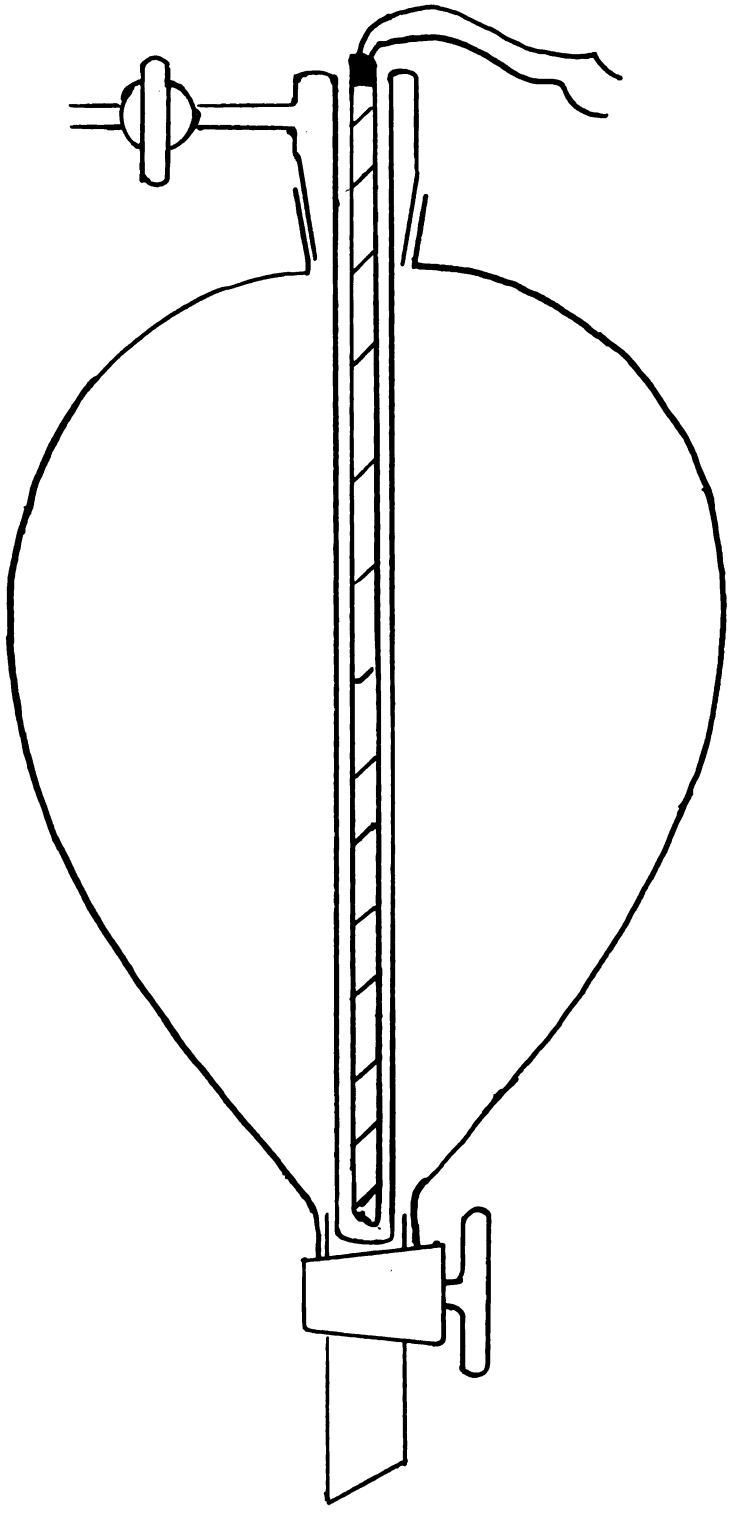
After any residual charge on the mercury is removed, the total resistance between the D.M.E. and the reference electrode when all three compartments contain 0.1 M LiCl in dimethyl sulfoxide is 9000 ohms.

The capillaries were connected to the mercury reservoir with neoprene tubing previously boiled in KOH solution to remove sulfur.

For recording the current-time (i - t) curves a 10K ± 1% resistor was inserted in series with the polarographic cell and the potential drop across this resistor followed with the oscilloscope.

The apparatus constructed for purifying the solvent is shown in Figure 4. A glass probe was inserted almost to the stopcock of a four-liter separatory funnel. Into this probe could be inserted either a heating element or a thermometer. A sidearm, through which nitrogen could be

Figure 4. Apparatus for purification of solvent.



introduced, was sealed to the top of the probe. The entire apparatus was placed in a cold room which was maintained at $1^{0}C$ until the contents were completely frozen. The core of the frozen mass was melted by the heating element and the resulting liquid was withdrawn through the stopcock. These operations were repeated until the water content in the DMSO reached the desired level. This procedure was originally suggested by Sears (49).

After purification, the DMSO was transferred to a storage vessel, shown in Figure 5, which had been previously filled with dry, prepurified nitrogen. Molecular sieve, type 4A, was placed on the bottom of the storage vessel. In the preparation of solutions, a volumetric flask could be attached at a standard taper joint "B" and the introduction of solvent was accomplished by the application of dry, prepurified nitrogen to side arm "A".

Reagents

The chemicals, labeled purities, sources and treatments used in this work were as follows:

Lanthanide Trichlorides were prepared from anhydrous 99.9% lanthanide oxides and supplied by the Lunex Company, Pleasant Valley, Iowa. These were then used with minimum exposure to air. X-ray powder diffraction patterns obtained for these salts yielded no evidence for the presence of oxychloride; however, it is doubtful if less than 10% oxychloride could

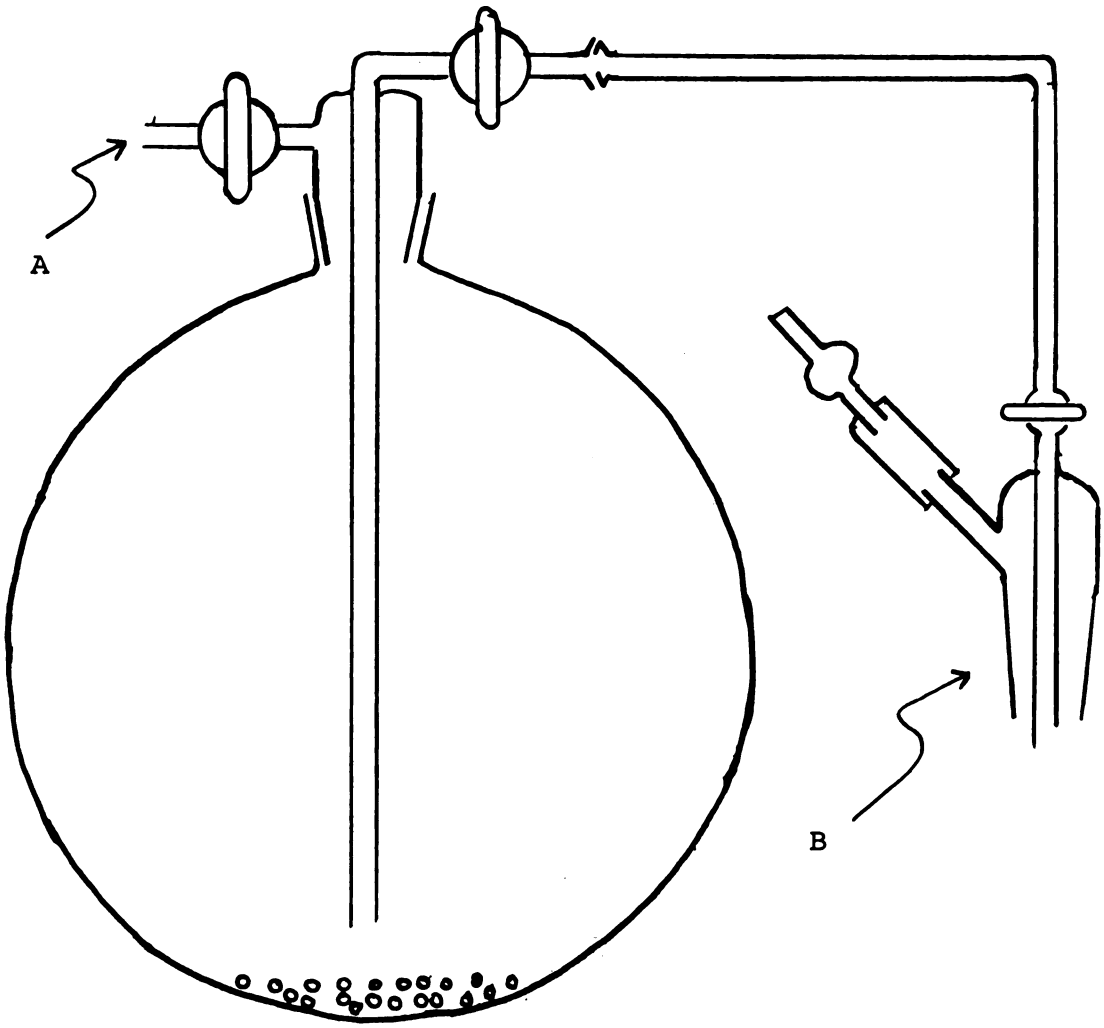


Figure 5. Storage vessel for containing purified solvent.

be detected by this method. Aqueous, acid solutions of the trichlorides were used for analysis. Lanthanide ion content was determined by titration with EDTA (1,2,48), and chloride by precipitation as silver chloride. Water was determined by Karl Fischer titration on the solid as received. The following analytical results were obtained.

	Found			Theoretical	
Compound	%Cl	%Lanthanide	$\%H_2O$	%Cl	%Lanthanide
$DyCl_3$	38.19	57.06	1.48	39.56	60.44
$SmCl_3$	40.58	56.80	none	41.43	58.57

Lithium Chloride, obtained as reagent crystals from Matheson Coleman and Bell, was dried for five hours at 110^0C in a vacuum oven prior to use.

Tetra-n-butylammonium perchlorate, polarographic grade, obtained from Matheson Coleman and Bell was used without further purification.

Prepurified Nitrogen was obtained from Matheson Coleman and Bell.

Dimethyl Sulfoxide was obtained from Matheson Coleman and Bell (m.p. $18-19^0$). Dry, prepurified nitrogen was passed through the solvent, which was maintained at 60^0 for a period from three to six hours. The solvent was then placed in the purification apparatus, Figure 4, and repeatedly frozen and melted six times. The solvent was then stored in the storage

vessel, Figure 5, over Linde molecular sieve, type 4A. After this purification process, the solvent yielded only a single peak when analyzed by vapor phase chromatography.

A single sharp nmr signal was obtained at τ = 7.44 (TMS) from the purified solvent in carbon tetrachloride.

The infrared spectrum for the purified dimethyl sulfoxide was identical to the reference spectrum recorded in the Sadtler Standard Spectra (44). Two small peaks at 2.9 and 6.1 microns were due to traces of water, the presence of which was confirmed by Karl Fischer titration.

Water was determined frequently throughout this work by the Karl Fischer method. It was found that the last traces of water could be removed by molecular sieve, the latter treatment reducing the water content from 0.03% to 0.01% or less.

Dimethyl sulfoxide, spectro-grade, obtained from Crown Zellerbach appeared to be of the highest quality, since it yielded only one nmr peak, one vpc peak, and the water content was so low that it was not detectable by Karl Fischer titration.

In most of the experimental work, this grade solvent was used without further purification.

Experimental Procedures

Preparation of Supporting Electrolyte Stock Solutions

Weighed amounts of the salts were introduced into a volumetric flask which had been previously flushed with dry,

prepurified nitrogen. The flask was then attached to the storage vessel and dimethyl sulfoxide was added.

Preparation of Sample Solutions

Lanthanide trichlorides, transferred to weighing bottles in a dry box, were weighed by difference and introduced into a volumetric flask which had been previously flushed with dry, prepurified nitrogen. They were then dissolved in the stock solution of supporting electrolyte in DMSO. Sample solutions were prepared both directly and by dilution of more concentrated stock solutions. Water was determined by Karl Fischer titration separately on the solvent, solvent plus supporting electrolyte and lanthanide trichlorides. The water concentration was found to increase to the 4 to 5 millimolar level upon the addition of supporting electrolyte; however, insignificant additional water appeared to be added by the lanthanide trichloride.

Water was added directly to the sample solution in determining its effect on the polarographic properties, its concentration being determined by Karl Fischer titration.

Removal of Dissolved Oxygen

Dissolved oxygen was removed from all solutions in the polarographic cell by bubbling a stream of nitrogen, previously bubbled through pure dimethyl sulfoxide, through the solution for a period of 15 minutes.

Recording of Current-Potential Curves

To assure regular mercury flow through the capillary, it was cleaned periodically by immersing it in concentrated nitric acid for a few minutes, while mercury was flowing through it, rinsed thoroughly with distilled water, and immersed in dimethyl sulfoxide for 15 minutes to one-half hour. Just prior to insertion into the cell, the capillary was rinsed with dimethyl sulfoxide and the sides wiped dry with absorbent paper. Care was taken to remove any nitrogen bubles from the tip by a few gentle but quick flicks of a finger against the upper stem of the capillary just before each run.

The majority of the current-potential (i - E) curves were recorded with an initial voltage of -1.00 volts vs. SCE and a span voltage of -2.00 volts vs. SCE. The initial potential was measured at the beginning of each i - E curve. It was found that the span and initial voltage dials on the instrument could be reproducibly set to within ± 1 mv, and that the combination of initial voltage, span voltage, and bridge position could be set within ± 2 mv by advancing the bridge with the driving motor to the desired position. The combination of this uncertainty with that of the measurements from the chart of ± 2 mv results in a total instrumental uncertainty in the reproducibility of the individual potential values of ± 4 mv.

Evaluation of $E_{1/2}$ and i_d

Since the i - E curves obtained in this investigation were not symmetrical, graphical procedures similar to those described by Meites (23) were devised for obtaining practical half-wave potentials ($E_{1/2}$) and diffusion current (i_d) values. The procedure for dysprosium is illustrated in Figure 6. To evaluate $E_{1/2}$, line AB was drawn through the midpoints of the oscillations of the residual current, line CD was drawn through the midpoints of the oscillations on the rising portion of the wave, line EF was drawn through the midpoints of the oscillations on the plateau of the wave. The intersection of lines AB and CD was used as vertices to construct a parallelogram about the rising portion of the wave with the point of intersection of the diagonal GH with line CD taken as the un-corrected half-wave potential. Because of the large resistance incurred in non-aqueous systems, these values were then corrected for the iR drop across the cell. All i_d values were then taken at a convenient, fixed, potential just beyond the rising portion of the curves and were obtained by subtracting the average current value for supporting electrolyte solution alone, run under identical conditions, from the midpoint of the oscillations on the plateau.

The procedure adopted for samarium was slightly different as shown in Figure 7. The first wave was evaluated as just described. However, to evaluate $E_{1/2}$ for the

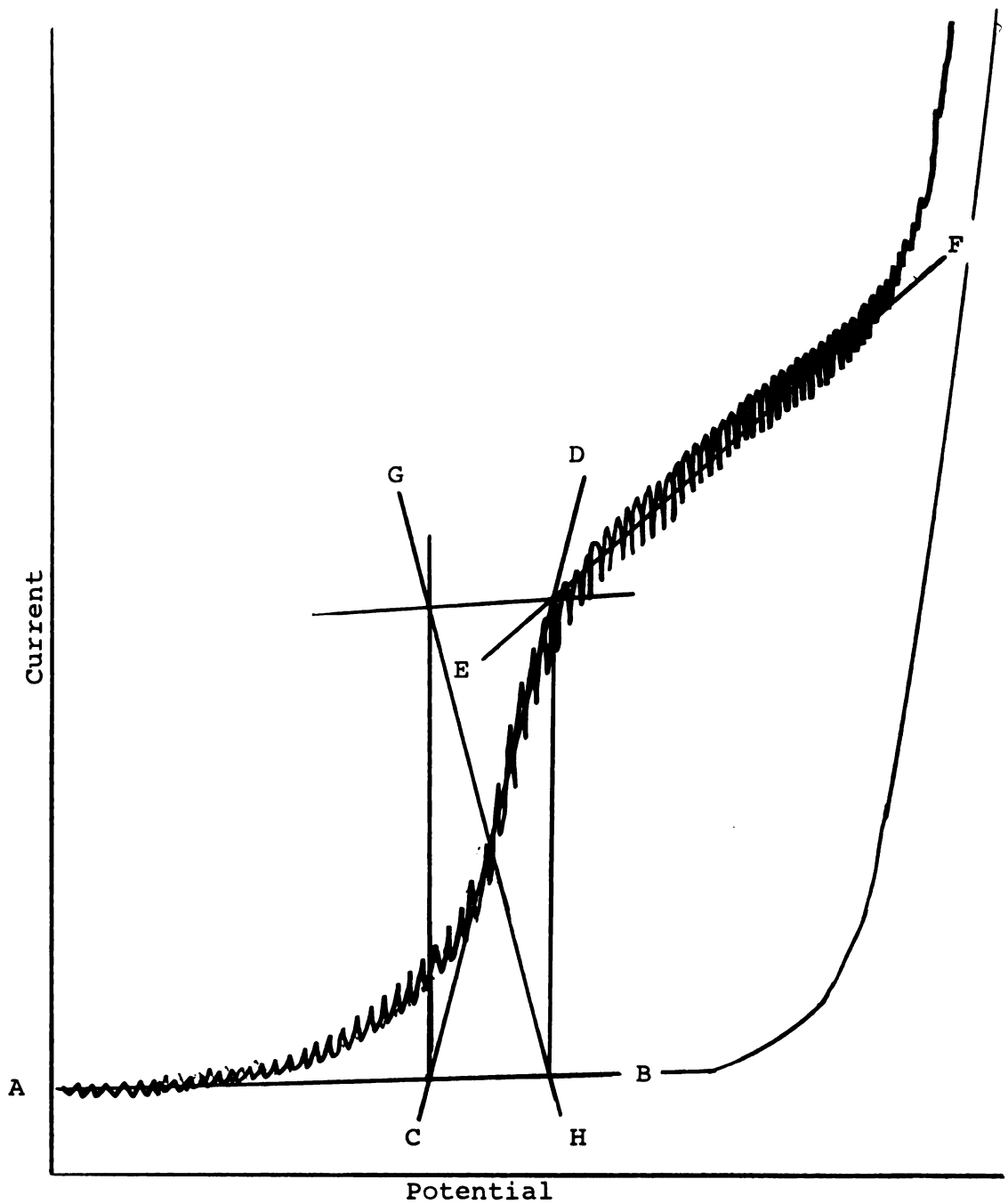
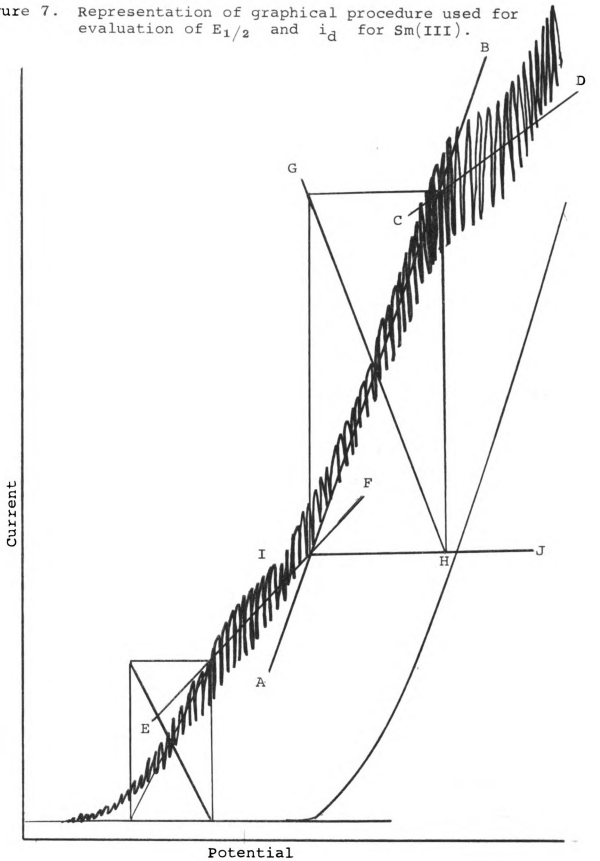


Figure 6. Representation of graphical procedure used for evaluation of $E_{1/2}$ and i_d for Dy(III).

Figure 7. Representation of graphical procedure used for evaluation of $E_{1/2}$ and i_d for Sm(III).



second wave line AB was drawn through the midpoints of the oscillations on the rising portion of the wave, line CD passing through the midpoints of the second plateau. The intersection of lines AB and CD and the intersection of the line AB with the line EF were used to construct a parallelogram. The intersection of the diagonal, GH, with AB was taken as the un-corrected half-wave potential. Because of the proximity to the discharge region the diffusion current measurement (i_d') on this second wave was taken at a fixed potential beyond the rising portion of the curve and was obtained by subtracting the value described by line IJ, drawn parallel to the residual current line previously described, from the midpoint of the oscillations on the plateau.

The total resistance of the polarographic cell system using 0.1 M LiCl was found to be quite reproducible at 9000 ohms. All un-corrected $E_{1/2}$ values were therefore corrected for an iR drop using the current value at the given potential and the above value of R. This rather large correction, in addition to the instrumental error level described previously, prompts the reporting of $E_{1/2}$ values only to ± 10 mV.

Measurement of Capillary Characteristics

The drop time (t, seconds per drop) at various potentials and mercury levels was evaluated by timing the fall of 20 drops with a stop watch and calculating an average.

The variation in drop time with change in potential is shown in Figure 8. The electrocapillary maximum at approximately - 0.4 volt *vs.* SCE is consistent with that found for other supporting electrolytes in DMSO (48). Electrode characteristics at h_{eff} = 30 cm are given in Table I. Measurements of i_d for Dy(III) were taken at E_{appl} = -2.24 volt *vs.* SCE and for Sm(III) at E_{appl} = -2.16 and -2.52 volt *vs.* SCE respectively.

Table I. Electrode characteristics at 25.0° and h_{eff} = 30 cm.

E_{app} (volt *vs.* SCE)	m (mg/sec)	t (sec/drop)	mt (mg/drop)	$m^{2/3}\ t^{1/2}$
open circuit	0.771	9.14	7.06	1.217
-2.24	0.784	3.66	2.87	1 055
-2.16	0.768	4.12	3.16	1 063
-2.52	0.784	3.06	2 39	1.025

Since the composition of the solution also affects the drop rate, the drop time employed for a calculation pertaining to a particular solution was always that measured in a solution of specific composition. The rate of mercury flow (m, mg per second) was evaluated by determining the average drop weight (mt) from the weight of 20 drops delivered under a particular set of conditions, and calculating m previously determined values of t for the same conditions.

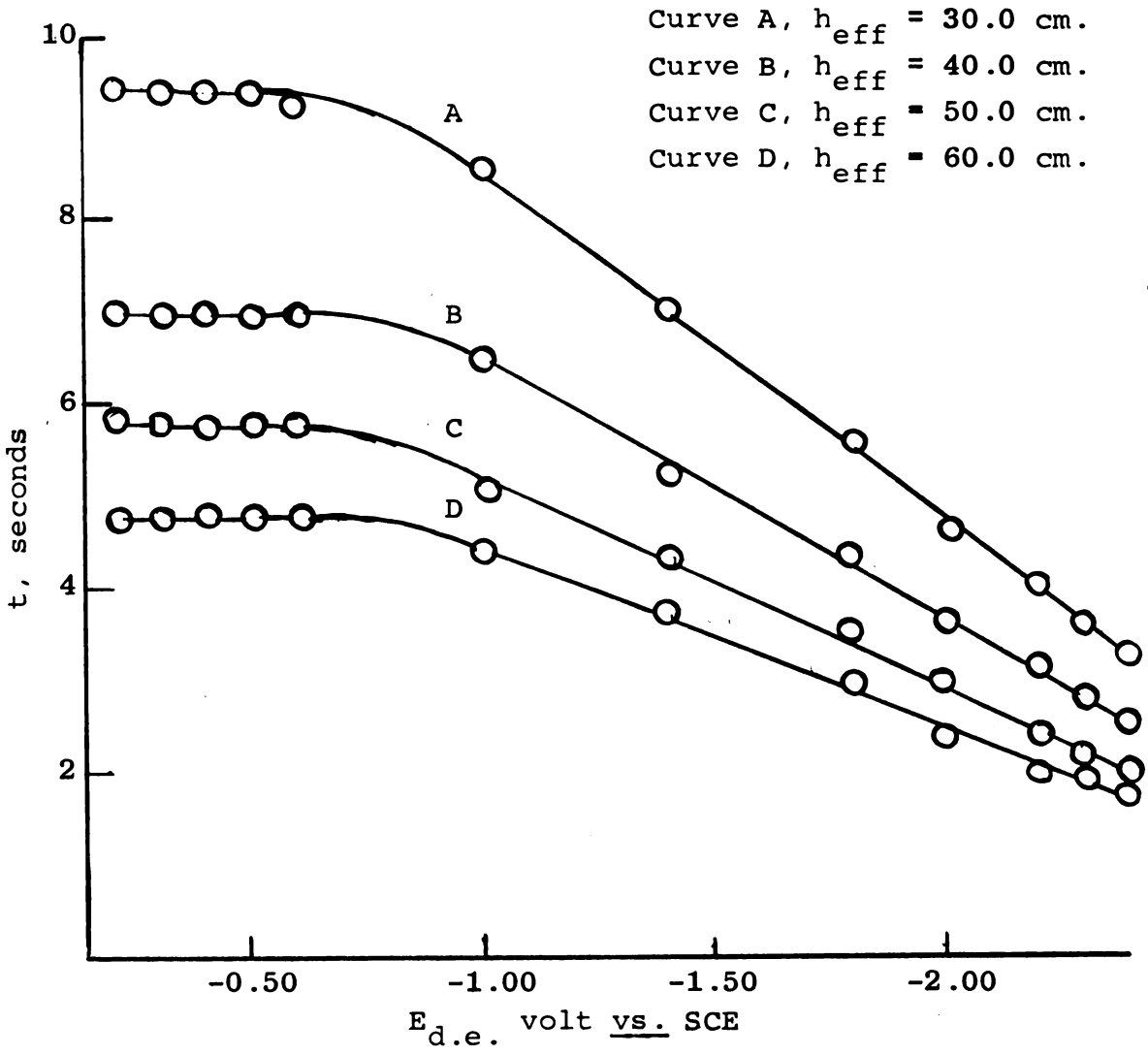


Figure 8. Variation of drop time with potential at selected mercury height values for 0.1 M LiCl solutions in DMSO at 25.0°.

Measurements Related to the Effect of Mercury Pressure on i_d

To measure the height of the mercury head (h, cm), a meter stick was attached to the mercury leveling column and the height from the tip of the capillary to the top of the mercury column was noted. The carriage for the mercury leveling bulb was equipped with a Fisher leveling bulb support with screw adjustment to allow accurate adjustment of the height. Since the position of the DME was fixed due to the cell construction, just enough sample solution was placed in the sample compartment to provide an immerision of the DME of 0.4 cm into the sample solution. All h values were corrected for back pressure in a manner suggested by Coetzee (5) to yield the effective pressure of mercury (h_{eff}, cm).

Recording of Current-Time Curves

To obtain current-time (i - t) curves, a 10K ± 1% ohm resistor was inserted in series with the polarographic cell and the potential drop across this resistor followed with an oscilloscope. The output of the Sargent Model XXI Polarograph was employed as a potential source, with the recording portion of the instrument disconnected. The bridge was advanced by means of the driving motor. Since no precise potential values were necessary in this portion of the work, only the un-corrected applied potentials are listed so as to give the relative position on the rising

portion of the curve. The usual operating conditions for the Tektronix Type 564 Storage Oscilloscope were: sweep time - 1 second per division, calibrated; sensitivity - 5 to 50 mV per division.

For the instantaneous current-time curves the potential was applied just after the fall of a drop and the oscilloscope was simultaneously triggered.

Prolonged Electrolysis Procedure

The cell used for these studies is shown in Figure 9. Sufficient mercury was placed in the cathode compartment, C, approximately 1 1/2 inches in diameter, to cover the platinum wire. The solution to be electrolyzed was then placed in the compartment and nitrogen, was introduced through a fritted glass bubbler, the exit being protected by a drying tube containing Ascarite and magnesium perchlorate. Compartments A and B contained supporting electrolyte solution. A reference electrode, previously described, was inserted into compartment B. The working anode, in compartment A, consisted of platinum wire in the form of a helix. A schematic diagram of the circuit used for prolonged electrolysis is shown in Figure 10. The current flowing at various electrolysis times was calculated after measuring the voltage drop across the 100K resistor placed in the working anode circuit. The cathode potential, vs. SCE, was measured with the VTVM previously described.

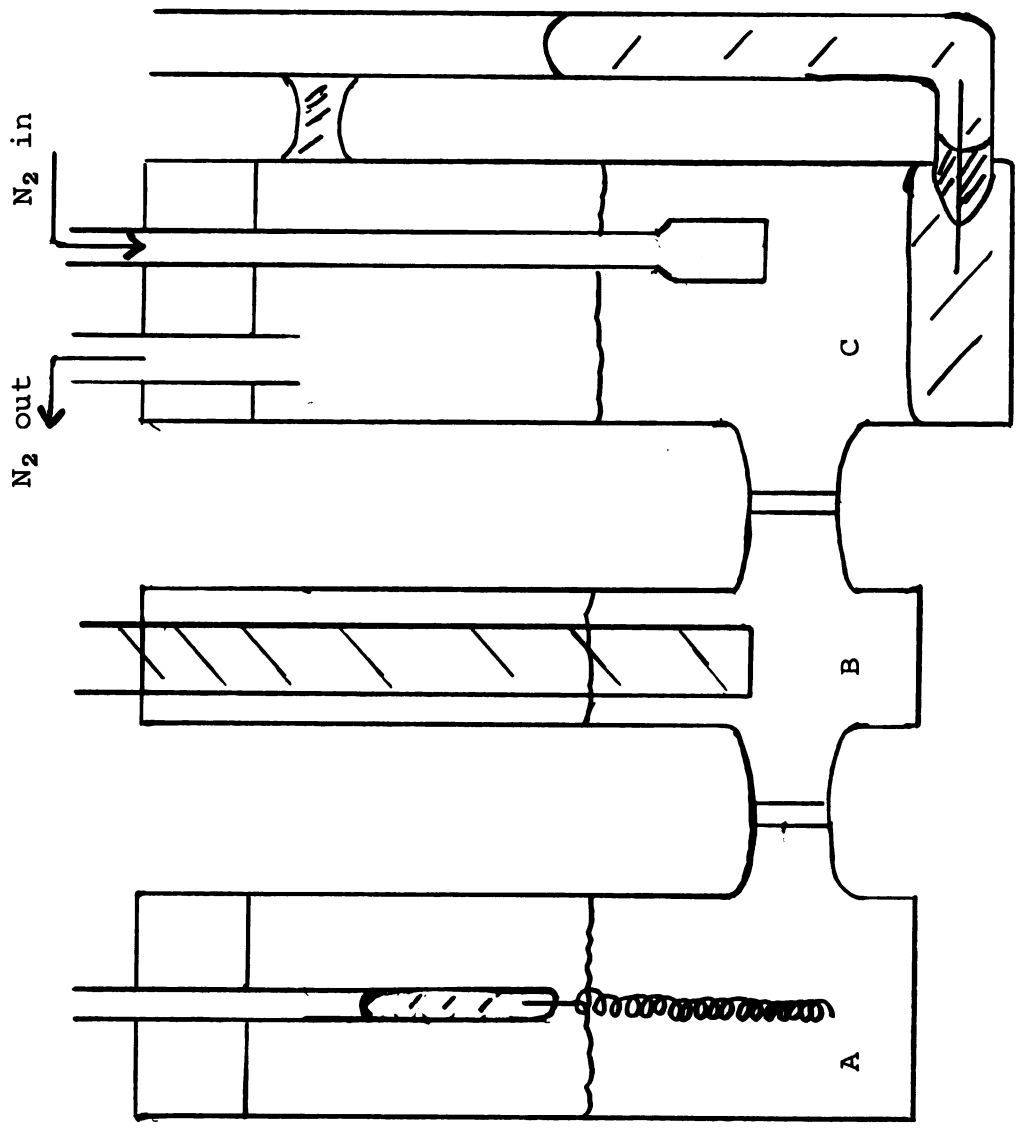


Figure 9. Cell used for prolonged electrolysis.

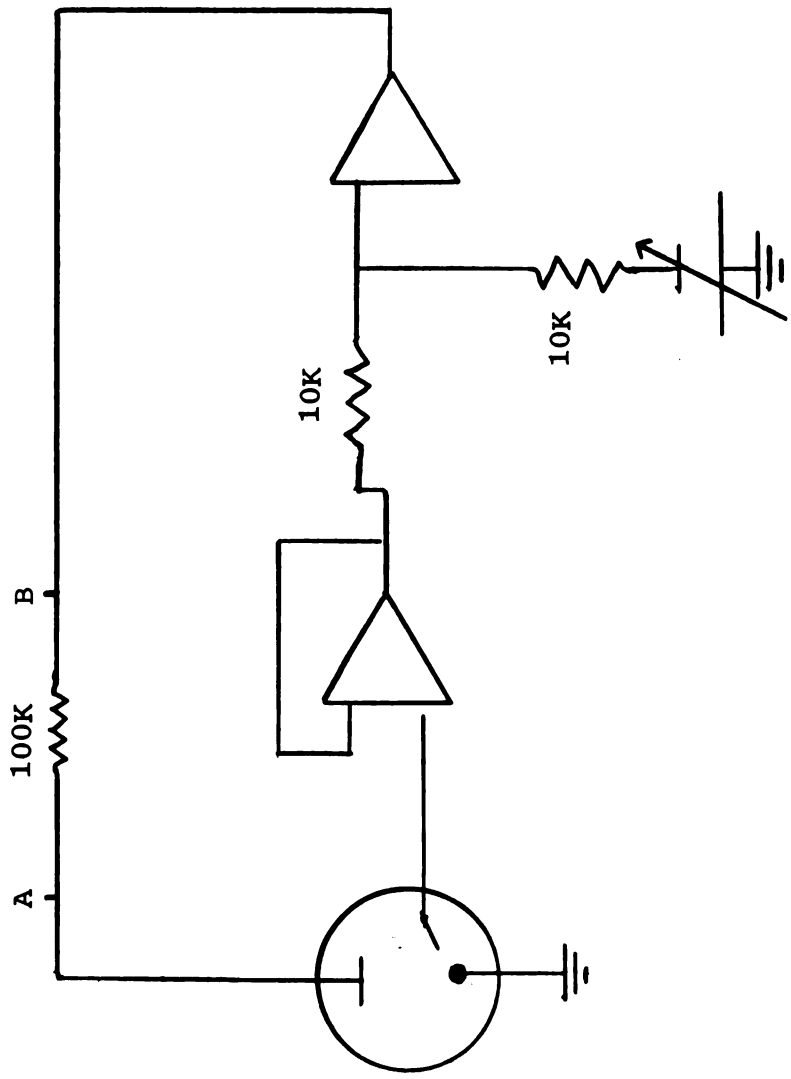


Figure 10. Schematic diagram of components for prolonged electrolysis.

At the end of a given electrolysis, before disconnecting the cell, a portion of the cathode solution was drawn off and placed in the polarographic cell for the recording of a polarogram and a portion of the mercury cathode was drawn off, from below the surface, washed with distilled water and lanthanon stripped out by boiling in concentrated hydrochloric acid for two hours. The solution was then taken to dryness and the residue dissolved in approximately 15 ml of water. A test described by Rinehart (40), in which a complex (which absorbs at 550 mμ) is formed between lanthanide ion and Alizarin Red S in an acetic acid-ammonium acetate buffer, was then applied to prove the presence of lanthanon. Blanks were also run on mercury which had been in contact with the solution containing lanthanide ion.

DISCUSSION OF THE RESULTS

Introduction

Although this study is on Dy(III) and Sm(III) in 0.1 M LiCl, polarograms were also recorded for Ho(III) and Pr(III) in this supporting electrolyte as well as polarograms for Dy(III) and Sm(III) in 0.1 M tetra-n-butylammonium perchlorate to determine the effect of supporting electrolyte on $E_{1/2}$ and how closely $E_{1/2}$ values obtained in this laboratory agreed with those obtained by Gritzner, Gutmann and Schober (7) for Dy(III) and Sm(III) in 0.1 M tetraethylammonium perchlorate. With the exception of the second wave for Sm(III), the $E_{1/2}$ values are somewhat more positive for LiCl supporting electrolyte. There is good agreement, however, when $E_{1/2}$ values for Dy(III) and the first Sm(III) wave are compared in quaternaryammonium perchlorate supporting electrolytes. The $E_{1/2}$ value obtained for the second Sm(III) wave is more negative in 0.1 M tetra-n-butylammonium perchlorate.

These results are summarized in Table II.

Characteristics of the Dysprosium Wave

Irreversible Nature of the Wave

Plots of log $i/(i_d - i)$ vs. $E_{d.e.}$ are shown in Figure 11. These plots show curvature and are not symmetrical about the zero log intercept. The slope is 108 mv which yields an αn_a value of 0.546 or a n_d value of 0.546, the latter result being unreasonable.

Table II. Comparison of $E_{1/2}$ values in various supporting electrolytes at 25°.

Compound	Supporting Electrolyte	$E_{1/2}$ volt vs. SCE
$HoCl_3$	0.1 M LiCl	-2.01
$DyCl_3$	0.1 M LiCl	-2.06
$PrCl_3$	0.1 M LiCl	-2.11
$SmCl_3$	0.1 M LiCl	-2.00
	0.1 M LiCl	-2.18
$DyCl_3$	0.1 M Bu_4NClO_4	-2.08
$SmCl_3$	0.1 M Bu_4NClO_4	-2.03
	0.1 M Bu_4NClO_4	-2.14
$HoCl_3$	0.1 M Et_4NClO_4*	-2.09 (Ref. 7)
$DyCl_3$	0.1 M Et_4NClO_4*	-2.08 (Ref. 7)
$PrCl_3$	0.1 M Et_4NClO_4*	-2.20 (Ref. 7)
$SmCl_3$	0.1 M Et_4NClO_4*	-2.12 (Ref. 7)

*temperature 21°.

These three observations demonstrate the irreversibility of the electrode process. Assuming the rate-determining step is the transfer of one electron, α would be 0.546.

Variation of Wave Height with h_{eff} and $(h_{eff})^{1/2}$

Figures 12 and 13 show the effect of mercury pressure on wave height for different concentrations of Dy(III). In general a combination of both diffusion and adsorption

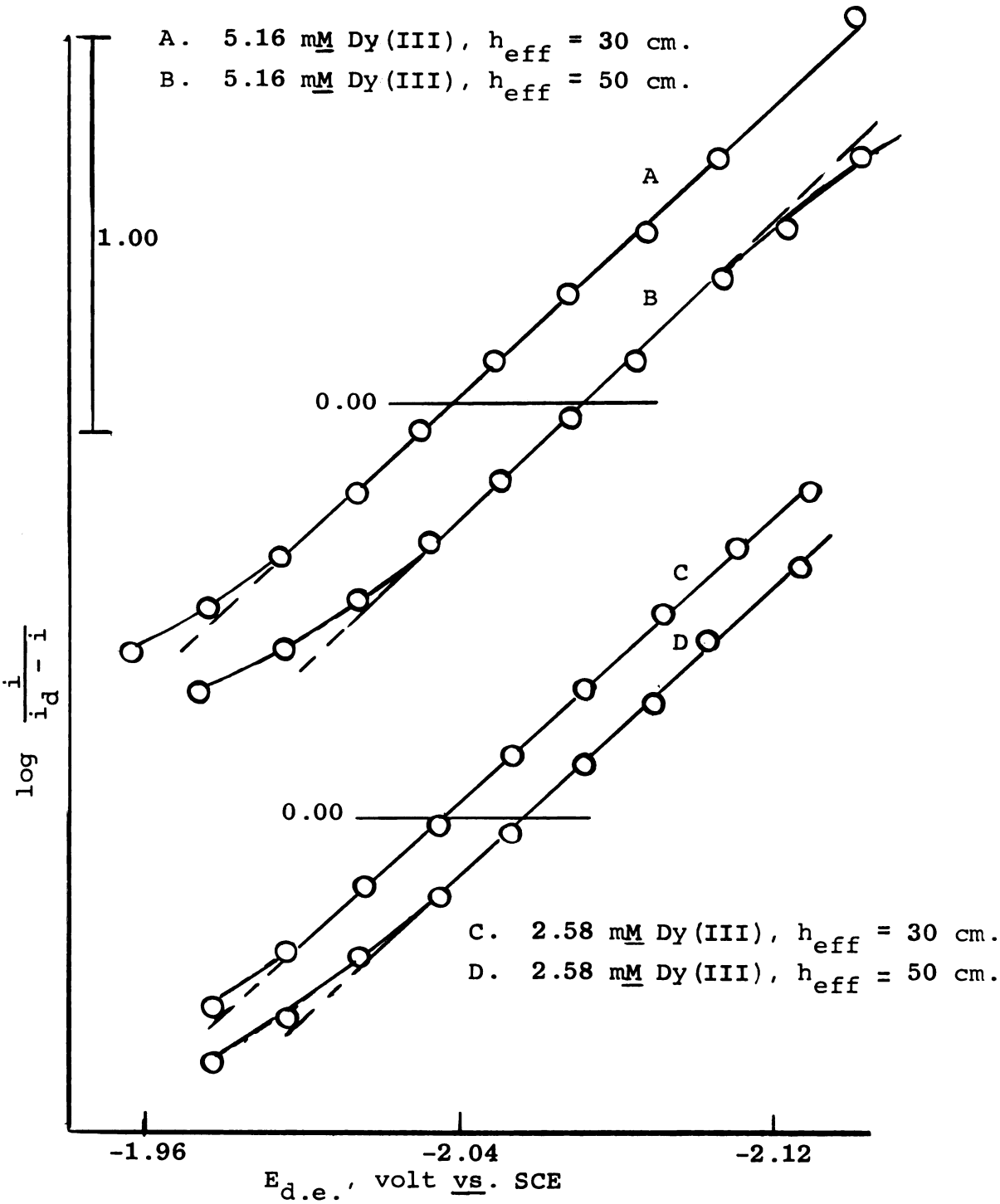


Figure 11. Variation of $\log \frac{i}{i_d - i}$ with $E_{d.e.}$ for Dy(III) in 0.1 M LiCl at 25.0°.

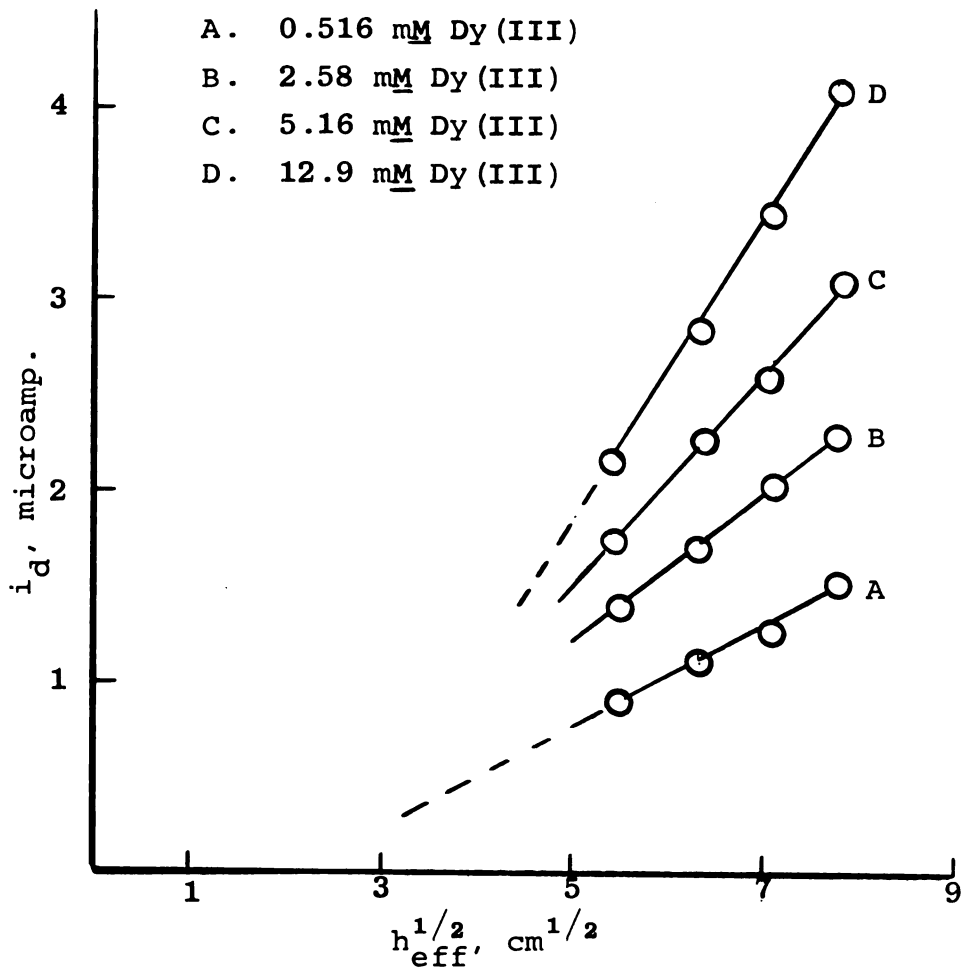


Figure 12. Variation in i_d with changes in h_{eff} for Dy(III) in 0.1 M LiCl at 25.0°.

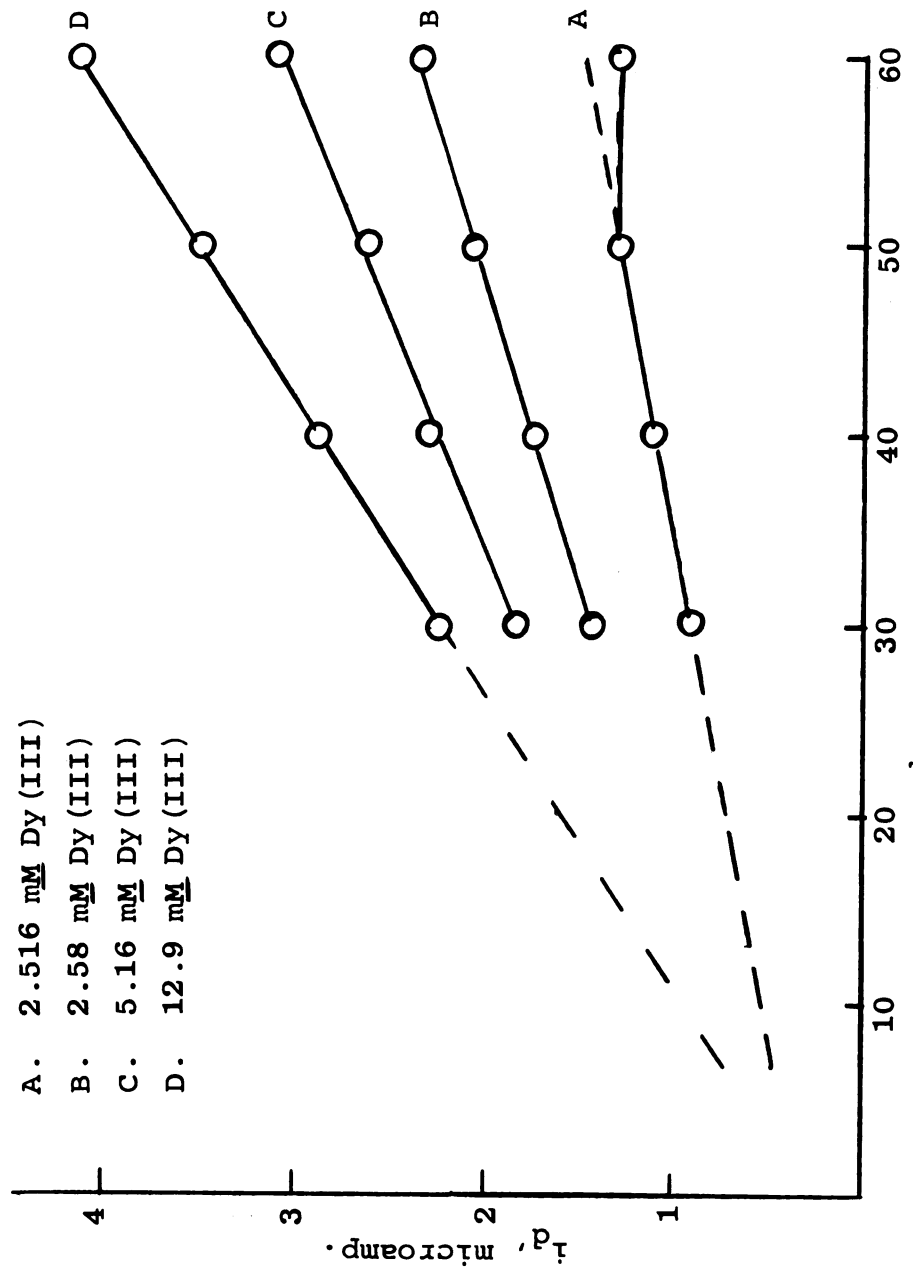


Figure 13. Variation in i_d with changes in h_{eff} for Dy(III) in 0.1 M LiCl at 25°.

control is indicated by a comparison of these results with curves d, f, g, and i, in Figure 1. Lower concentrations favor diffusion control, but the lowest concentration investigated did not yield results consistent with complete diffusion control.

Current-Time Curves for Various Regions of the Wave

Current-time curves for various regions of the wave are quite reproducible and are shown in Figure 14. Comparison with curves a and d in Figure 2 shows some diffusion control in the toe region of the wave, but i - t curves developed on the plateau of the wave are clearly indicative of adsorption of the electroactive species.

Kuta and Smoler (18) theorized that the i - t curves for irreversible waves should demonstrate whether the rate-determining step is a slow electron transfer or a more complicated process. These authors interpreted the change in shape of the i - t curves through the rising portion of the wave developed from solutions of Ni^{+2} in 0.1 N $NaNO_3$ as evidence for a complicated mechanism.

Since a more definite explanation of the exact nature of such a complicated mechanism is still lacking, it can only be concluded that the mechanism for the reduction of Dy(III) appears more complicated than slow electron transfer.

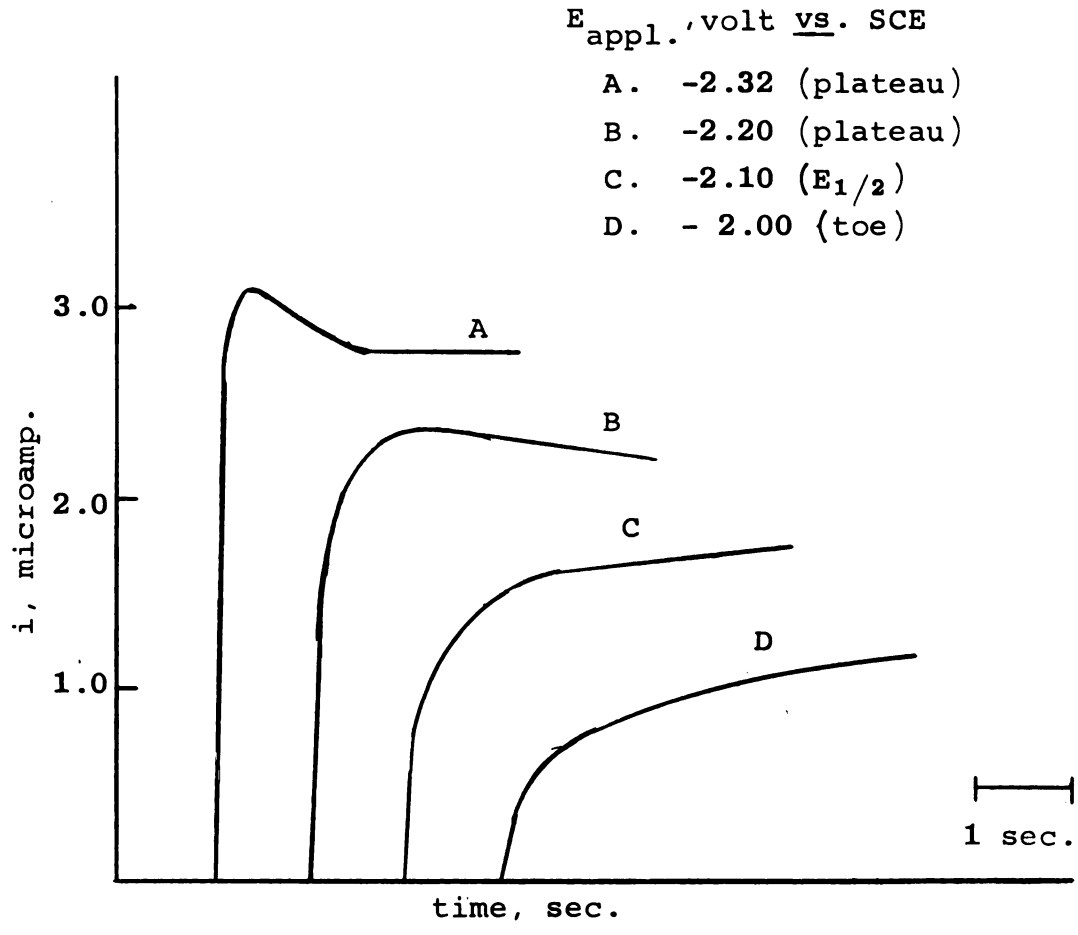


Figure 14. Current-time curves at various applied potentials for Dy(III) in 0.1 M LiCl at 25.0°.

The Effect of Temperature on i_d and $E_{1/2}$

The influence of temperature on i_d and $E_{1/2}$ is summarized in Table III.

Table III. Effect of temperature on $E_{1/2}$ and i_d values of Dy(III).

Temperature (^{0}C)	$-(E_{1/2})_{corr}$ volt vs. SCE	i_d microamp.
25	2.06	2.61
36	1.99	2.76
46	1.95	3.06

The temperature coefficient for the wave height is 0.7% which eliminates kinetic or catalytic control. The temperature coefficient for $E_{1/2}$ is +6 mv per degree which is indicative of an irreversible electrode process.

Using equation (2) for an irreversible wave, and with the conditions that the rate constant for the electrode process obeys the Arrhenius equation and the process is diffusion controlled, Vlcek (58) defined expressions from which the activation energy of the electrode process may be calculated. One of these expressions demonstrates that a plot of log $i/(i_d - i)$ against $1/T$ should be linear. Such a plot for Dy(III) was found to exhibit curvature which leads to the conclusion that the electrode process is not diffusion controlled, and furthermore, no activation energies could be calculated.

Variations of i_d with Dysprosium(III) Concentration

Figure 15 shows the effect on wave height (measured at E_{appl} = -2.24 volt *vs.* SCE) of increasing amounts of dysprosium(III).

The result obtained suggests intermediate behavior. The process cannot be completely adsorption controlled since a limiting value should be reached, and the curvature at higher concentrations eliminates a completely diffusion controlled process. The development of a second wave, characteristic of adsorption control is not likely to be observed at such negative potentials.

Using data obtained for the lowest concentration investigated, 0.516 m*M* Dy(III), and assuming a value of n_d = 3, a diffusion coefficient of 1.56×10^{-6} $cm^2 sec^{-1}$ was calculated.

Variation of i_d and $E_{1/2}$ with Water Concentration

The influence of increasing water concentration on i_d for a 10 m*M* Dy(III) system is shown in Figure 16. The influence of several factors was considered in an attempt to explain the observed initial decrease in i_d with increasing water concentration.

At an applied potential of -2.24 volt *vs.* SCE, mt was found to be 10.57 mg (t = 5.32 sec, m = 1.99 mg/sec), in an aqueous 0.1 *M* LiCl solution for the electrode used in this study. By comparison, the mt value for DMSO (Table I)

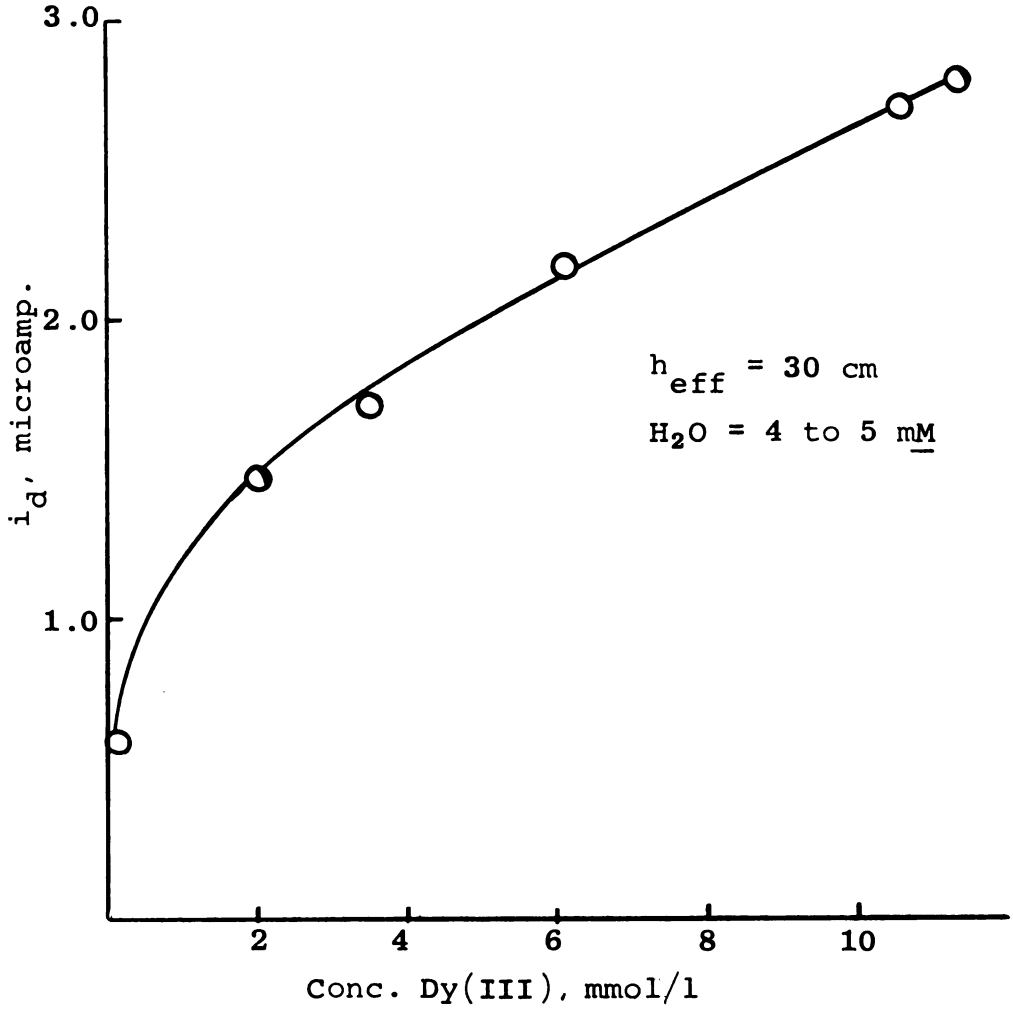


Figure 15. Variation in i_d with Dy(III) concentration at 25.0^0.

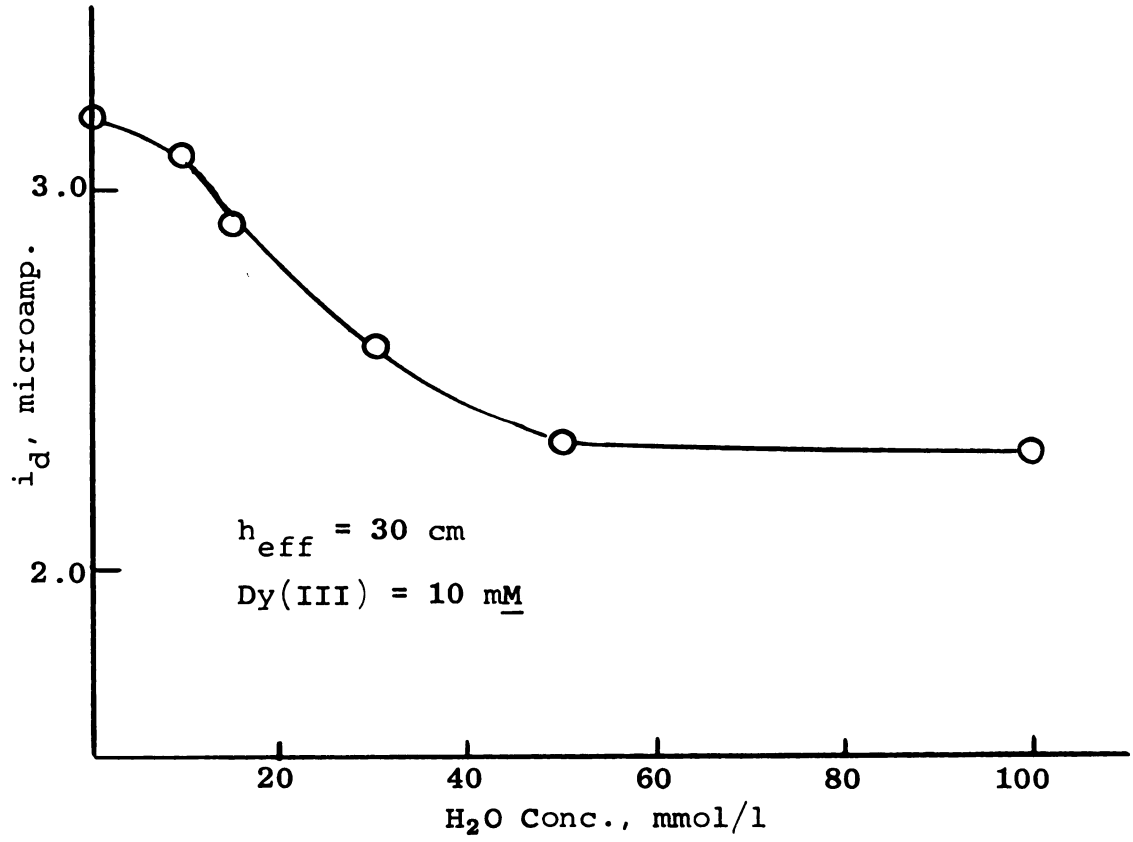


Figure 16. Variation in i_d with water concentration at 25.0°.

is 2.87 (t = 3.66 sec, m = 0.784 mg/sec) which reflects a 2.68-fold increase in the interfacial tension, σ, when the solvent changes from DMSO containing 4-5 mM water to pure water.

Changes in current are related to changes in m and t. For either diffusion or adsorption control, the current is proportional to $m^{2/3}$. Thus the increase in m should cause a proportionate increase in current. For diffusion control the current is proportional to $t^{1/6}$ while for adsorption control it is proportional to $t^{-1/3}$. Thus an increase in t should increase the current if diffusion controlled or decrease the current if adsorption controlled.

These are expected changes in currents influenced by m and t changes when comparing the DMSO system containing only a small amount of water to a pure water system.

The experimental results shown in Figure 16, reflect a current decrease as the water content was varied from 4 mM to 60 mM and then remained relatively constant as the water content was increased to 100 mM. Only variations in t were determined in this experiment. When the water content was increased from 4 mM to 60 mM, t decreased from 3.5 sec to 2.8 sec. This would reflect diffusion control but the 0.7 sec decrease in t does not account for the 1.0 μa decrease in current. The experimental results provide only further evidence that the current is neither purely diffusion controlled, nor purely adsorption controlled if changes in

electroactive species composition is ignored as water content in DMSO is varied.

Changes in current may also be related to changes in the viscosity of the solvent system, since viscosity influences diffusion. The viscosity of water at 25^0 is 0.894 cP while that reported (4) for DMSO at 25^0 is 1.96 cP. If current is diffusion controlled in two solvent systems, m and t are identical in the two solvents, and if there is no change in species composition in the two solvents, the currents vary inversely with the square root of the viscosities. Assuming that only the viscosity in the DMSO system would decrease as the water content is increased, the current should have increased with increasing water content. Experimentally the reverse effect was observed.

In the individual considerations of interfacial tension and viscosity effects on current as the water content in DMSO is increased, all influencing factors, including changes in electroactive species composition were ignored. It is apparent that neither interfacial tension nor viscosity changes account for the experimental observations, and thus it must be concluded that either a change in chemical species or a change in mechanism or both occur as the water content in DMSO is increased from 4 to 60 mM. Beyond this concentration region, the effect of increasing water in DMSO on i_d is relatively constant.

To examine the effect of water content on $E_{1/2}$, measured quantities of 0.1 M aqueous LiCl were added to 20 ml of 10 mM

Dy(III) in DMSO which was also 0.1 M in LiCl. The water concentration was varied from 4.1 to 3890 mM and $E_{1/2}$ varied as shown in Figure 17. The greatest rate of change in $E_{1/2}$, approximately 2 mv/mM, occurred as the water content changes from 4 to 32 mM, the next greatest rate, approximately 0.11 mv/mM, over the concentration range 2.92 to 3.89 M, and the least rate, 0.014 mv/mM over the concentration range 32 to 2500 mM.

This shift in $E_{1/2}$ to more positive values on increasing water concentration could reflect the change in liquid junction potential, or the formation of an aquo-complex, or an influence of water on a chemical reaction preceding the electrode reaction.

As was stated previously, the DMSO-H_2O liquid junction potential has been estimated to be approximately 120 mv. If increasing the water concentration merely changes the magnitude of the liquid junction potential, then $E_{1/2}$ should become more positive by less than 120 mv as the water content in the DMSO is changed from 4 to 3890 mM. Although the liquid junction potential undoubtedly changes, this change alone cannot account for the experimentally observed $E_{1/2}$ change of 200 mv.

Assuming that water is a stronger base than DMSO towards Dy(III), the formation of an aquo-complex would shift $E_{1/2}$, but the interpretation of the shift in $E_{1/2}$ with change in concentration of a complexing agent to yield information on the nature of the complex formed cannot be directly ac-

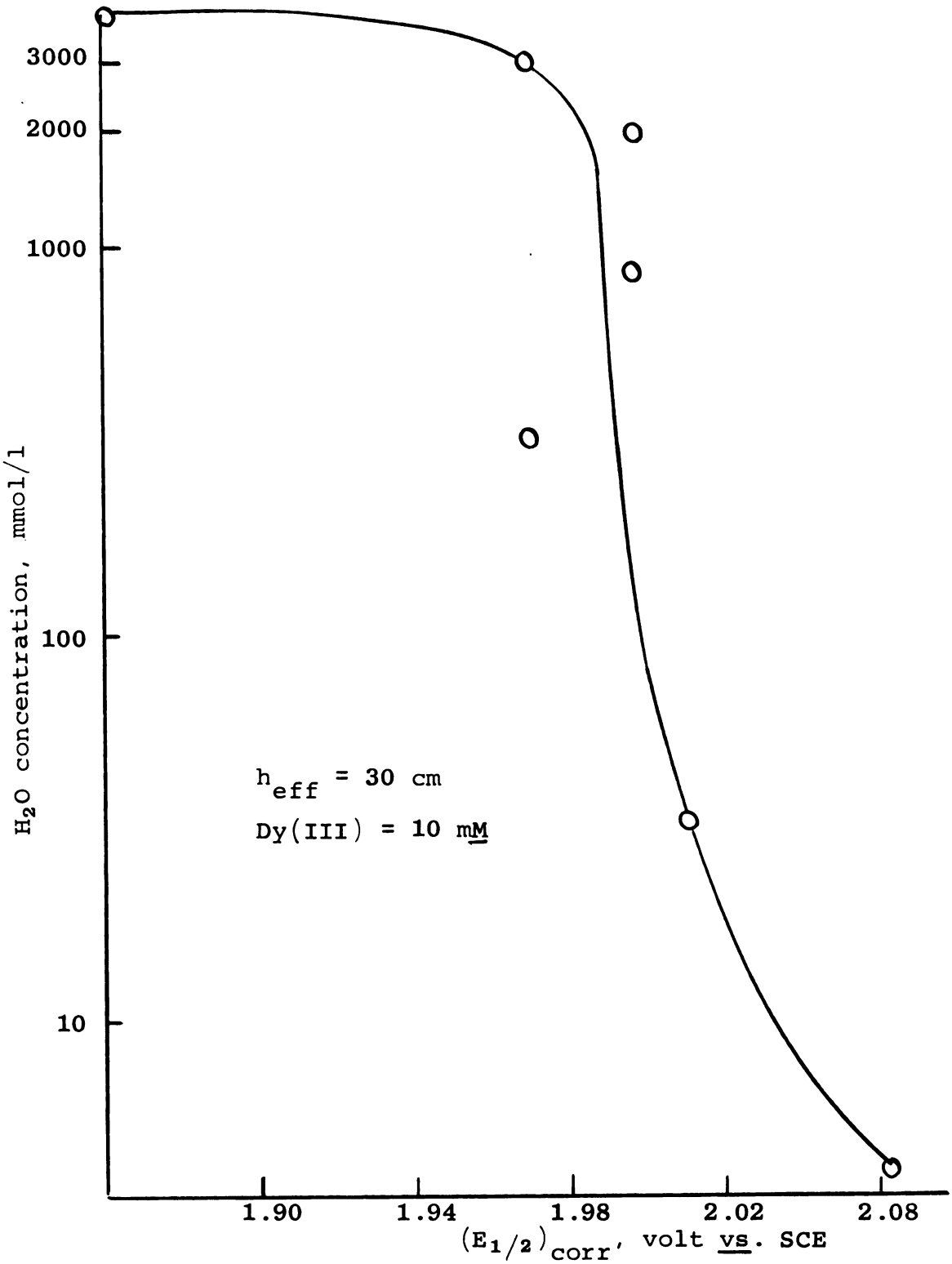


Figure 17. Variation of $E_{1/2}$ with water concentration at 25.0^0.

complished if the electrode process is irreversible. Since $E_{1/2}$ does shift with increasing water concentration, it may be concluded that an aquo-complex is formed. When the concentration of water reaches the 4 M level, $E_{1/2}$ is -1.86 volt vs. SCE which is only 0.05 volt more negative than $E_{1/2}$ for the wave due to the presence of Dy(III) in aqueous medium of pH 3. This could reflect the conversion of the solvated Dy(III) species present in DMSO to the electroactive species present in water.

No clear evidence is obvious to suggest what changes occur which might influence chemical reactions associated with the electrode process. It was previously stated that the addition of water could convert some of the solvated species present in DMSO to those present in aqueous media. The addition of water also would increase the dielectric constant which could effect ionization and dissociation, which may be important reactions associated with the electrode process. Since it was concluded that the liquid junction potential change with change in water content could not account completely for the 200 mv shift in $E_{1/2}$, part of the $E_{1/2}$ change must be due to the influence of water on chemical reactions associated with the electrode process. The observation is that the overall process occurs at more positive potentials when water is present but i_d decreased to 1.2 microamps when the water content in the system was increased to 3.89 M.

Variation of Current-Time Curves with Water Concentration

The general shape of the i - t curves developed on the plateau of the wave was shown by curves A and B in Figure 14. That the shape of this curve is affected by increasing water concentration is shown in Figures 18 and 19. Comparison with theoretical curves, shown in Figure 2, suggests the adsorption of the electroactive species up to approximately 2 M water concentration. There is no precedent found in the literature for i - t curves of the type observed when the water concentration is increased to 2920 mM as shown by curve F in Figure 19. However irregularities in i - t curves of this type were observed (20) for the wave due to the presence of Dy(III) in aqueous media. Large (20) theorized that the irregularity might be the result of one or more of the following phenomena: an abnormal mode of supply of depolarizer to the electrode surface, an abnormal increase in the size of the drop as a result of a change in surface tension, or an abnormal change in the charging rate of the drop as reflected by changes in the double layer capacitance.

The experimental observation is that as the water content in DMSO is increased, i-t curves developed on the plateau of the wave change from the type indicative of adsorption control to a type similar to that observed for the wave due to the presence of Dy(III) in aqueous media.

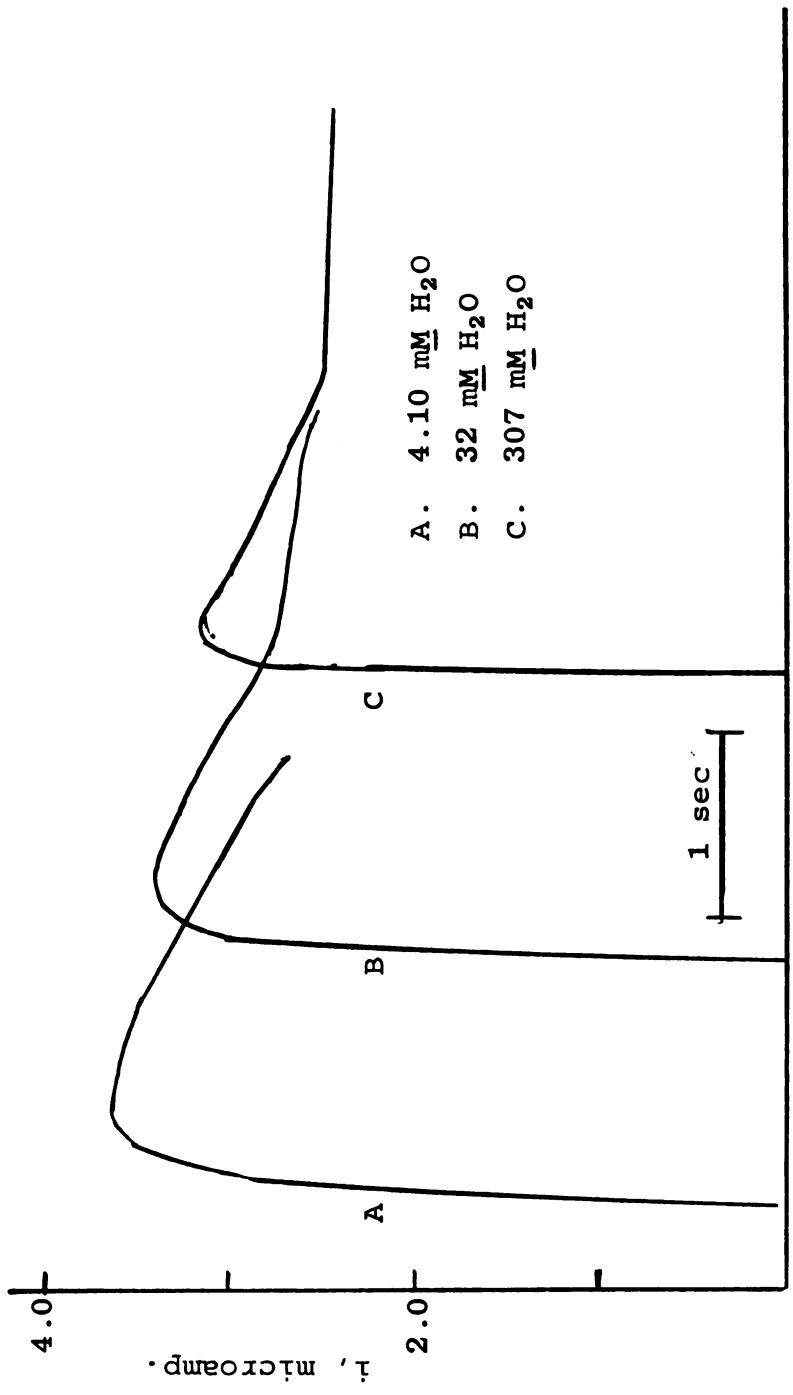


Figure 18. Effect of increasing water concentration on i - t curve at applied potential corresponding to i_d region for 10 mM Dy(III).

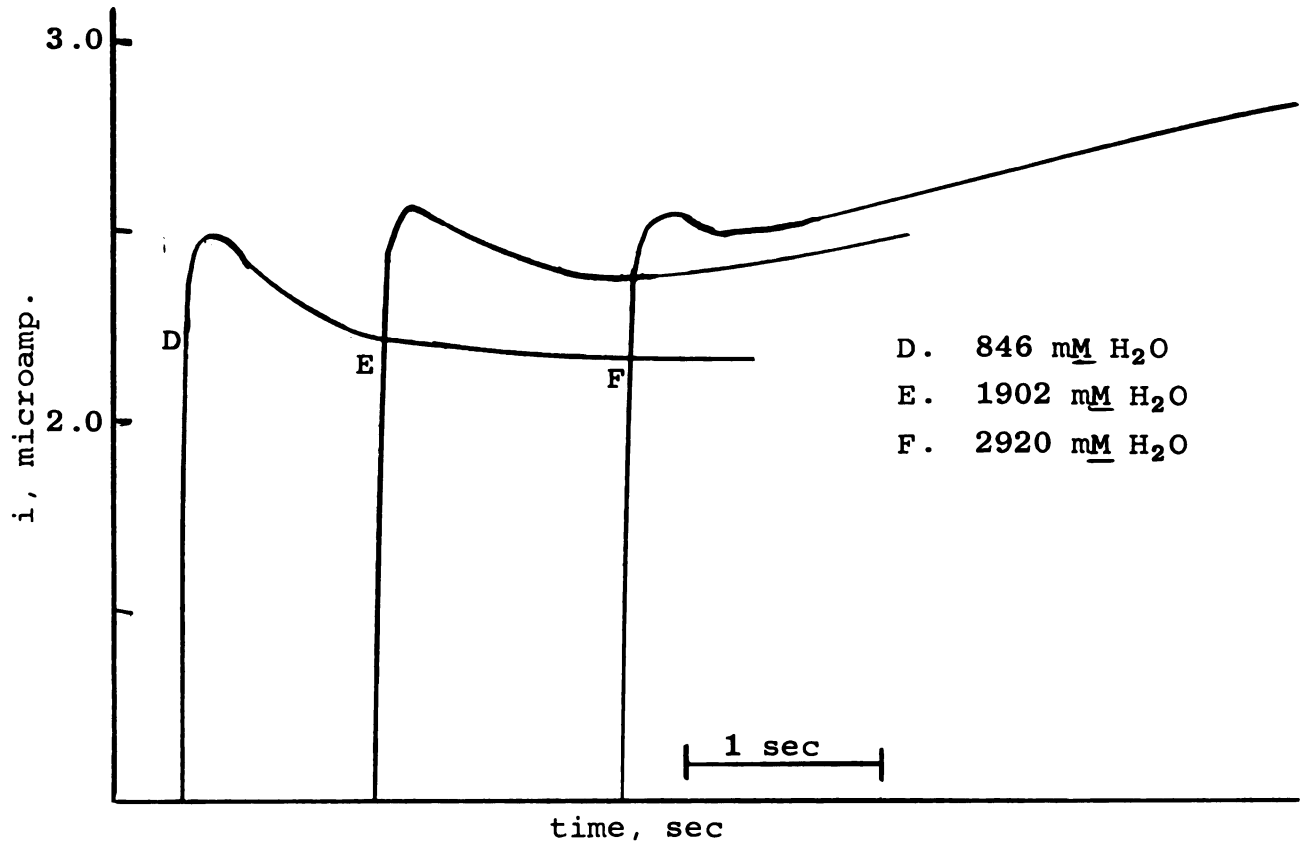


Figure 19. Effect of increasing water concentration on i - t curve at applied potential corresponding to i_d for 10 mM Dy(III).

Prolonged Electrolysis Studies

Solutions containing 10.6 mM Dy(III), 6.6 mM H_2O, 0.1 M LiCl were electrolyzed for various periods of time at E_{appl} = -2.22 volt vs. SCE. Figure 20 summarizes the current-potential curves which were obtained after electrolysis. Although some distortion in the curve occurs after 47 hours of electrolysis, diffusion currents decreased. Positive chemical tests for dysprosium present in the mercury cathode were obtained. These two analytical methods demonstrated that Dy(III) is reduced to the metal.

The Effect of the Addition of DMSO to an Aqueous Dy(III) Solution on i_d, $E_{1/2}$ and i - t Curves

To determine the effect of the addition of DMSO to 3 mM Dy(III) in aqueous 0.1 M LiCl, 0.01% gelatin, pH 3.5, measured volumes of DMSO which was 0.1 M in LiCl were added, i_d and $E_{1/2}$ were evaluated and i - t curves, developed on the plateau of the wave, were recorded.

The $E_{1/2}$ value was found to remain constant at -1.81 volt vs. SCE, which confirms the previous conclusion that water could possibly be a stronger base towards Dy(III) than DMSO since up to 3 M DMSO does not affect $E_{1/2}$.

Below 3 M DMSO the i - t curves suggest diffusion control when compared with curve A, Figure 2. At very high DMSO concentrations, the i - t curve is similar to the unexplainable curve F, Figure 19.

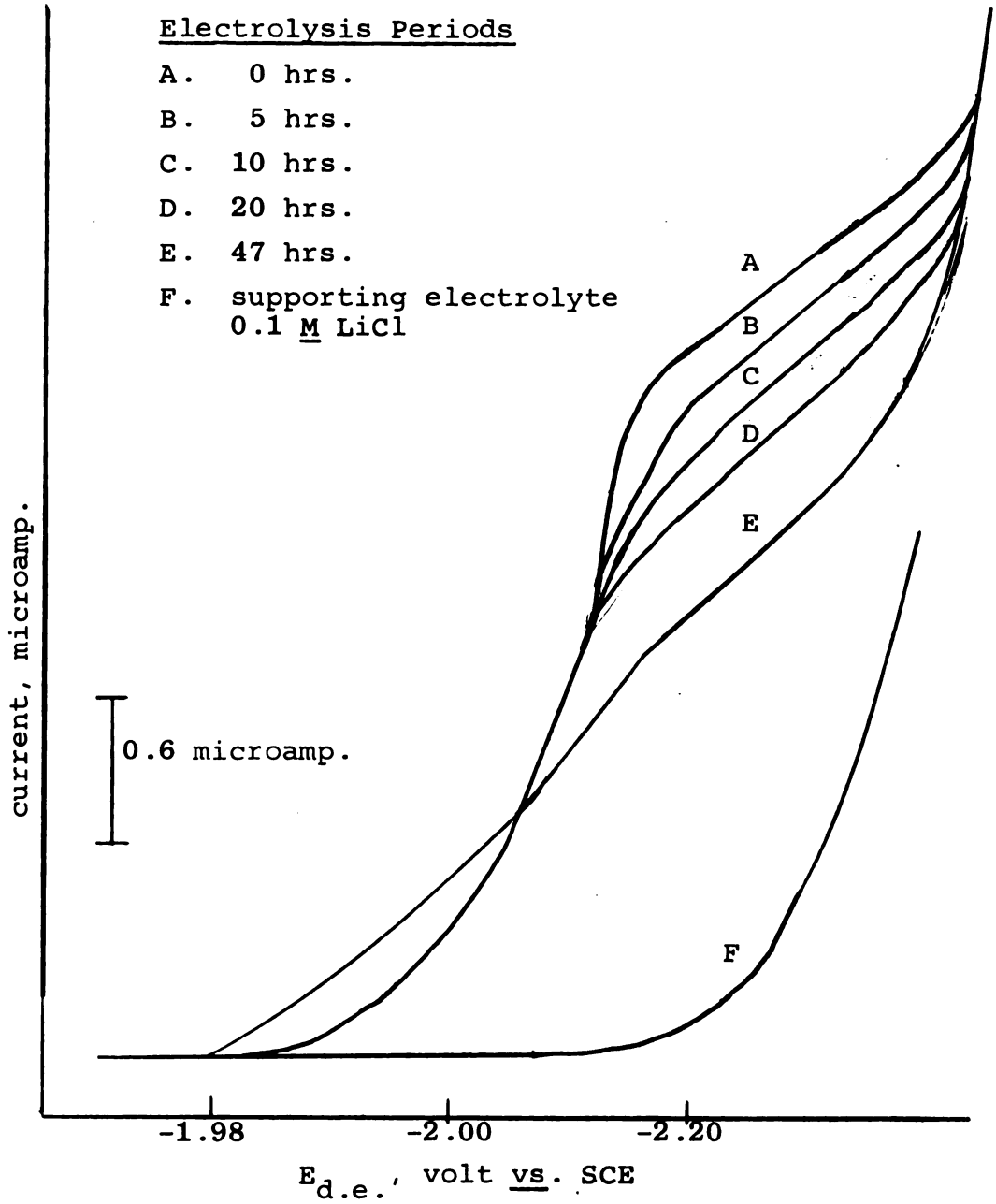


Figure 20. Current-potential curves for 10.6 m$\underline{M}$ Dy(III), 0.1 $\underline{M}$ LiCl, 6.6 m$\underline{M}$ H_2O after various periods of electrolysis.

The expected linear decrease in i_d with increasing DMSO concentration is observed as shown in Figure 21.

Characteristics of the Samarium Waves

Irreversible Nature of the Waves

Results obtained when log $i/(i_d - i)$ is plotted against $E_{d.e.}$ are given in Figures 22 and 23. Both waves show some curvature, and are not symmetrical about the zero log intercept. The slope of the first wave is 109 mv and for the second wave is 127 mv which yield αn_a or n_d values of 0.539 and 0.464 respectively. Again, it is unreasonable to interpret these as n_d values.

These three observations demonstrate the irreversibility of the electrode process. Assuming the rate-determining step involves the transfer of one electron, α values would be 0.539 and 0.464 respectively for the first and second wave.

Variation of Wave Heights with h_{eff} and $(h_{eff})^{1/2}$

Unlike the dysprosium case, Figures 24 and 25 demonstrate that the electrochemical reaction for both the polarographic waves developed for solutions of Sm(III) is diffusion controlled, since these plots are similar to the idealized ones shown as d and g in Figure 1.

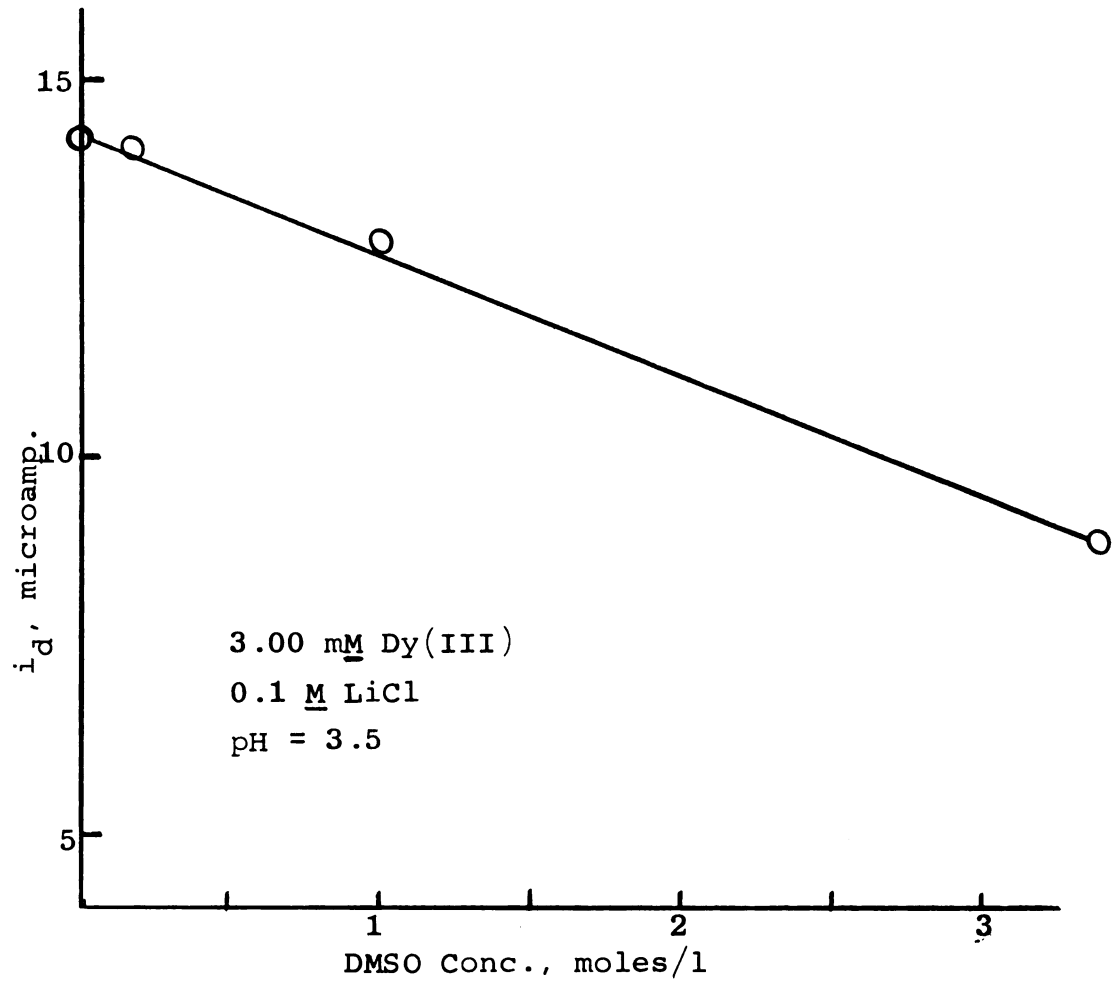


Figure 21. Variation in i_d with DMSO concentration for the first wave of Dy(III) in water.

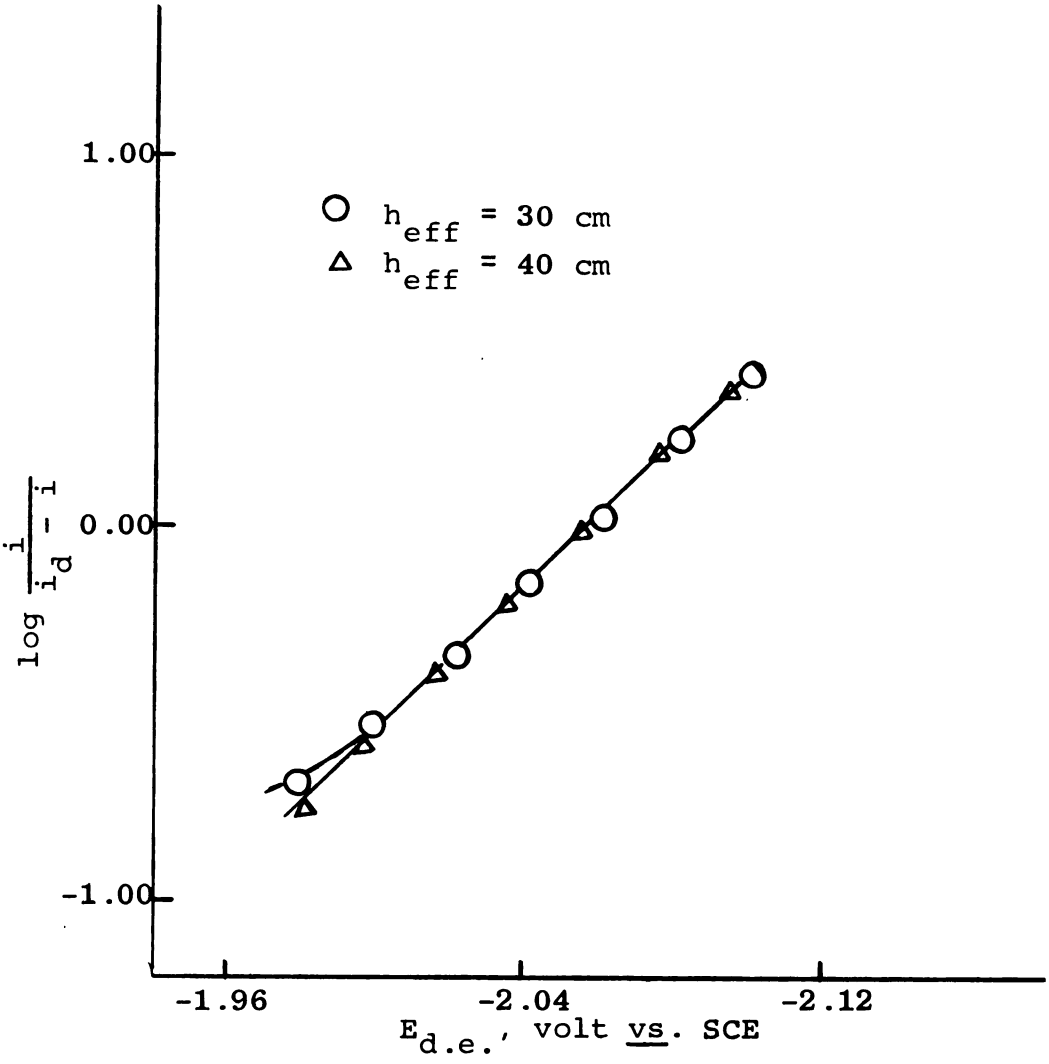


Figure 22. Variation of log $\frac{i}{i_d - i}$ with $E_{d.e.}$ for first Sm(III) wave in 0.1 M LiCl at 25.0°

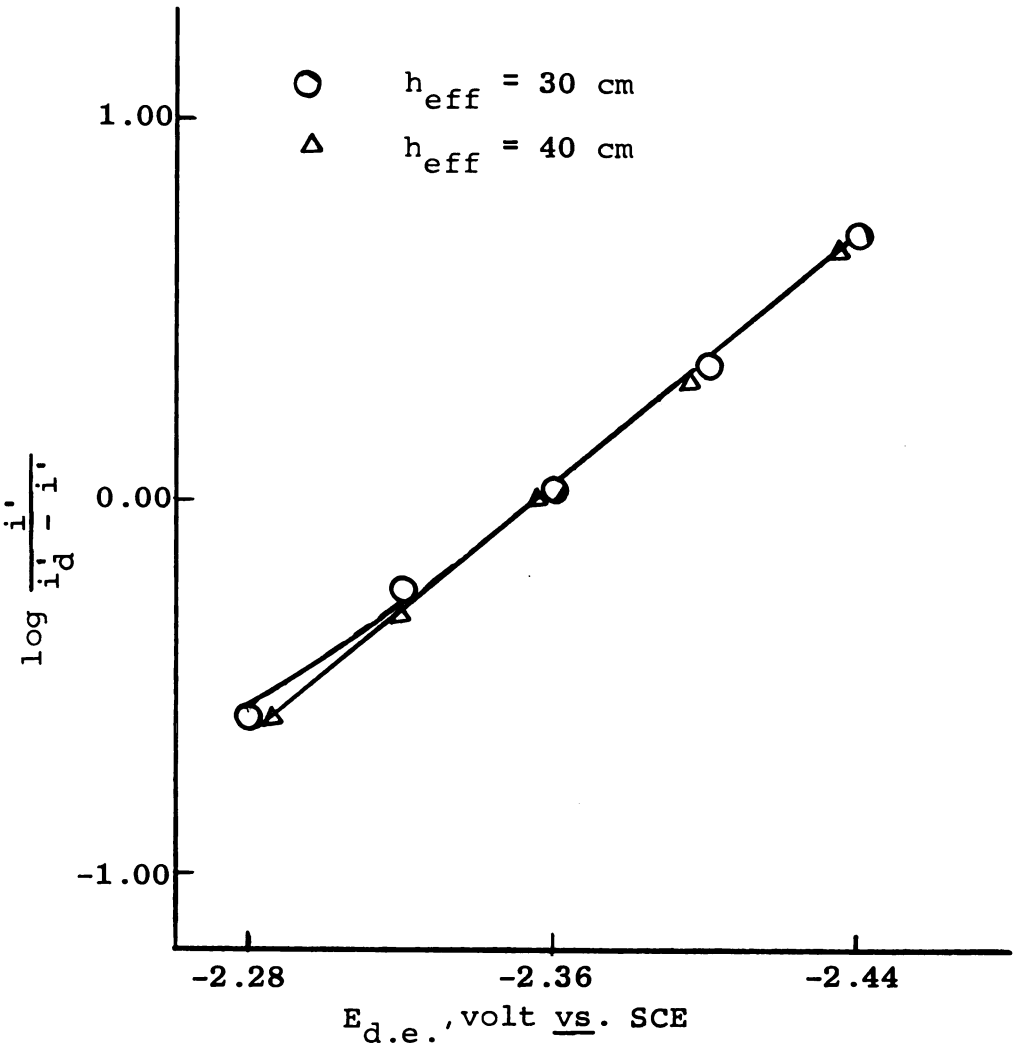


Figure 23. Variation of $\log \frac{i'}{i'_d - i'}$ with $E_{d.e.}$ for second Sm(III) wave in 0.1 M LiCl at 25.0°.

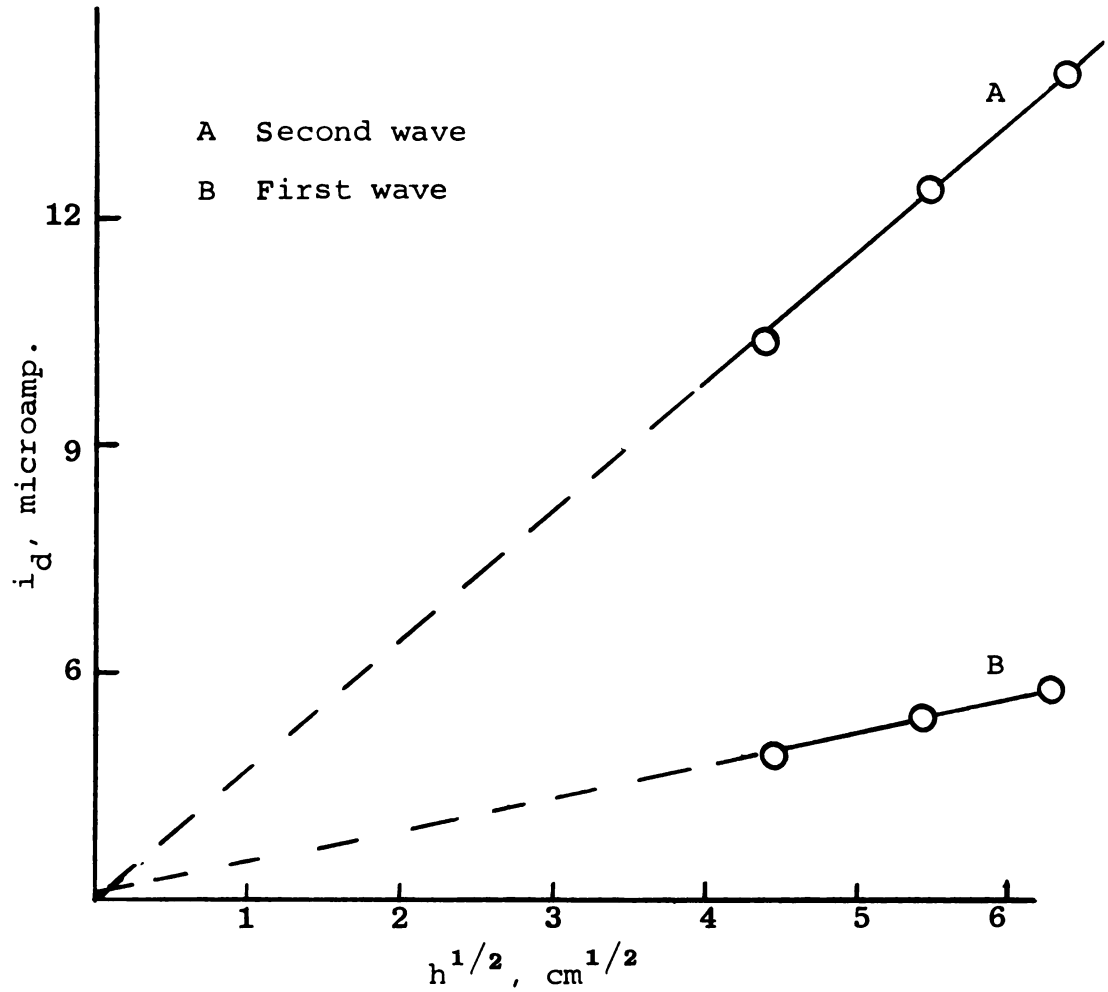


Figure 24. Variation in i_d with changes in h_{eff} for Sm(III) in 0.1 M LiCl at 25.0°.

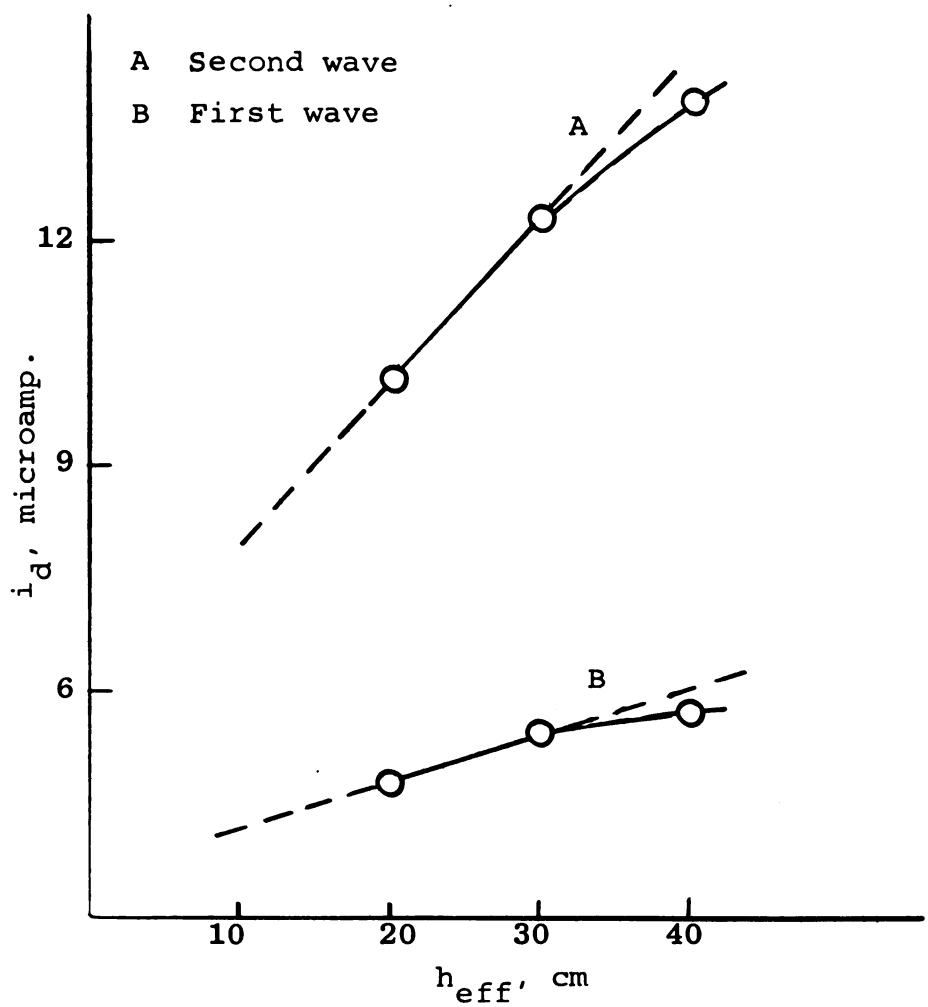


Figure 25. Variation in i_d with changes in h_{eff} for Sm(III) in 0.1 M LiCl at 25.0°.

Current-Time Curves for Various Regions of the Waves

Current-time curves for various regions of the first and second wave developed for Sm(III) solutions are given in Figures 26 and 27.

By comparison with curve a in Figure 2, the i - t curves shown in Figure 26 resemble the current-time relationship ascribed to diffusion control. The i - t curve developed on the plateau of the first wave was therefore analyzed more carefully. As shown in Figure 28, the log i *vs*. lot t plot yields a straight line with a slope of 0.115 which is somewhat smaller than the theoretical 0.167 obtained for diffusion control. Since this slope is not characteristic of any other mode of control and since all of the ideal (54) conditions (m = 2 mg/sec, t = 3 sec, $D = 2 \times 10^{-5}$ cm^2/sec) were not experimentally attained, it is concluded that the first Sm(III) wave is indeed diffusion controlled.

The i - t curves developed for the second wave change in shape for various regions of the wave, and a more complicated mechanism than slow electron-transfer is indicated (18). By comparison with idealized curves shown in Figure 2, the shape of these curves could indicate interference in the electrode process by some adsorption, but the process is not totally adsorption controlled.

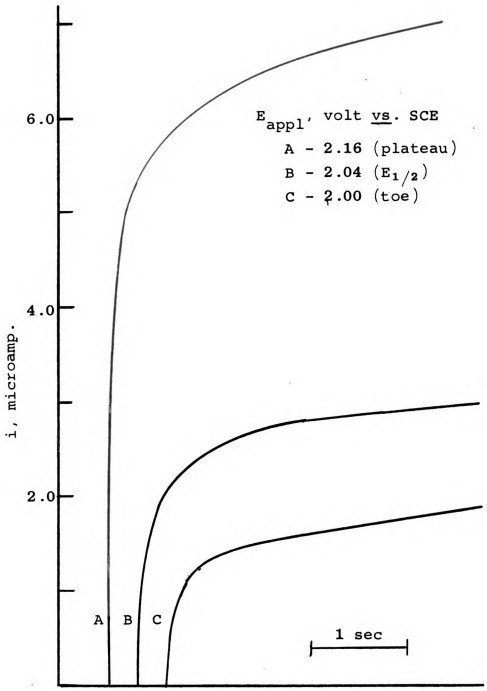


Figure 26. Current-time curves at various applied potentials for first Sm(III) wave in 0.1 M LiCl at 25.0°.

E_{appl}, volt vs. SCE

A - 2.64 (plateau)

B - 2.52 (plateau)

C - 2.36 ($E_{1/2}$)

D - 2.28 (toe)

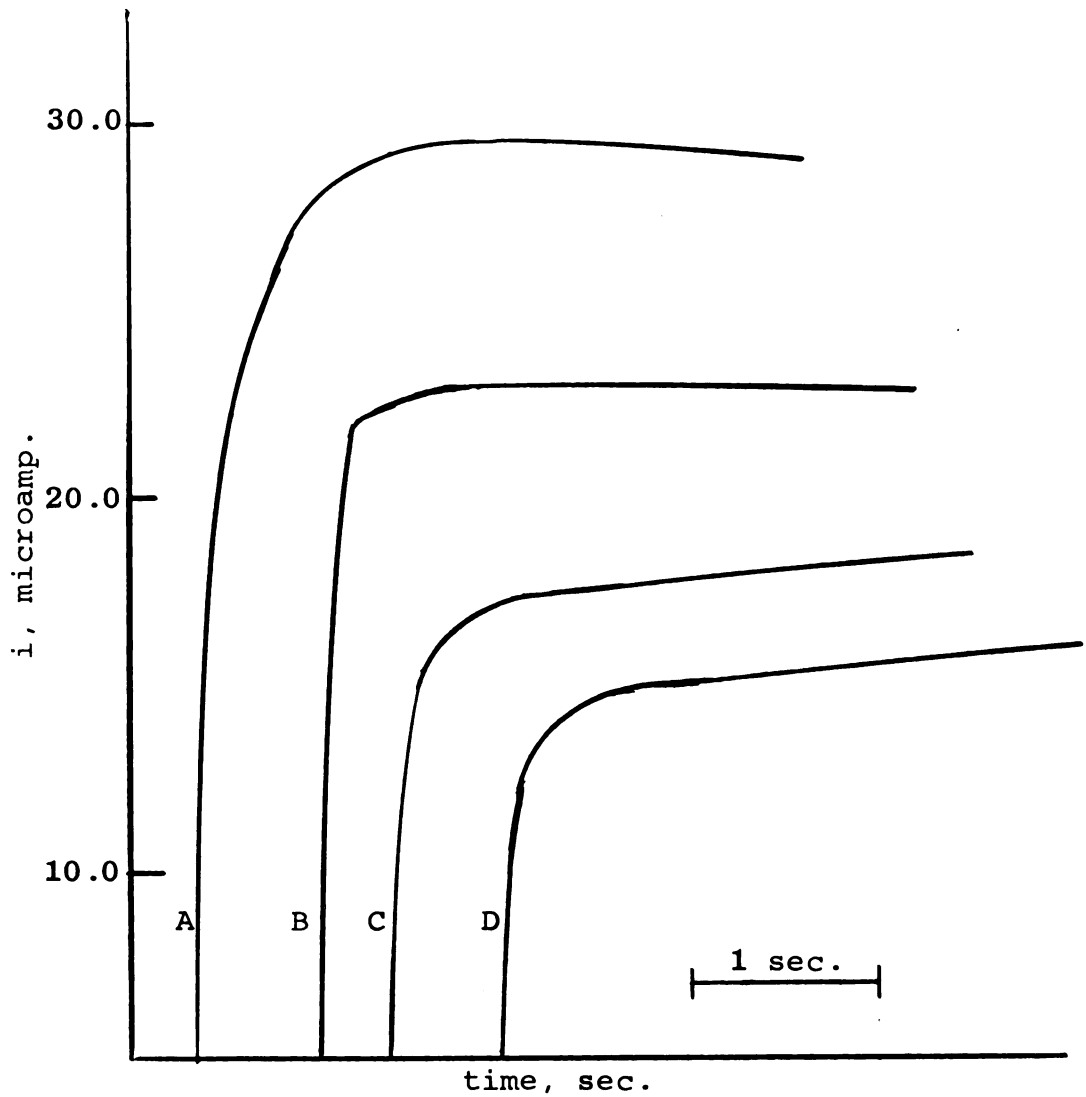


Figure 27. Current-time curves at various applied potentials for second Sm(III) wave in 0.1 M LiCl at 25.0° .

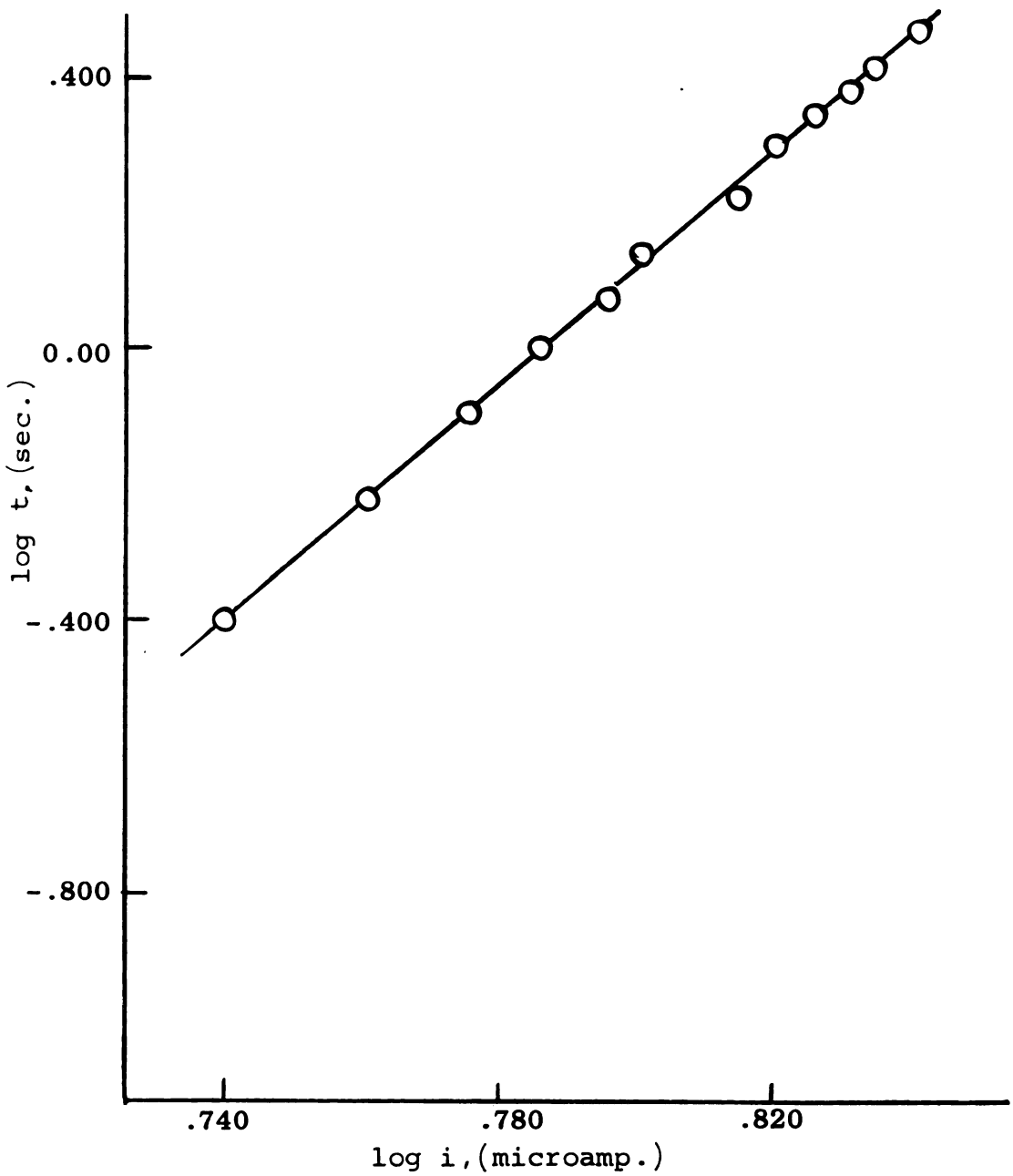


Figure 28. Variation in log i with log t at applied potential corresponding to i_d for first Sm(III) wave.

The Effect of Temperature on i_d, and $E_{1/2}$ Values

The influence of temperature on i_d and $E_{1/2}$ for the first and second waves is summarized in Table IV.

Table IV. Effect of temperature on $E_{1/2}$ and i_d values for Sm(III)

Temp. °C	$-(E_{1/2})_{corr.1}$ volt vs. SCE	$-(E_{1/2})_{corr.2}$	i_d microamp.	i_d'
25	2.01	2.18	7.95	12.75
34	1.99	2.15	8.55	12.90
37	1.99	2.15	9.00	13.95

The temperature coefficient for i_d is calculated as 1.04% and for i_d' as 0.75% which eliminates kinetic or catalytic control for the second wave.

The temperature coefficient for $E_{1/2}$ is +1.7 and +2.5 mv per degree for the first and second wave respectively. While these values in themselves suggest reversibility, the possibility that they indicate irreversibility cannot be excluded.

Variations in i_d and i_d' with Samarium(III) Concentration

The effect of increasing Sm(III) on i_d (measured at -2.16 volt vs. SCE) for the first wave is shown in Figure 29. Although there is very slight curvature at higher concentrations, the data suggest diffusion control as shown in the

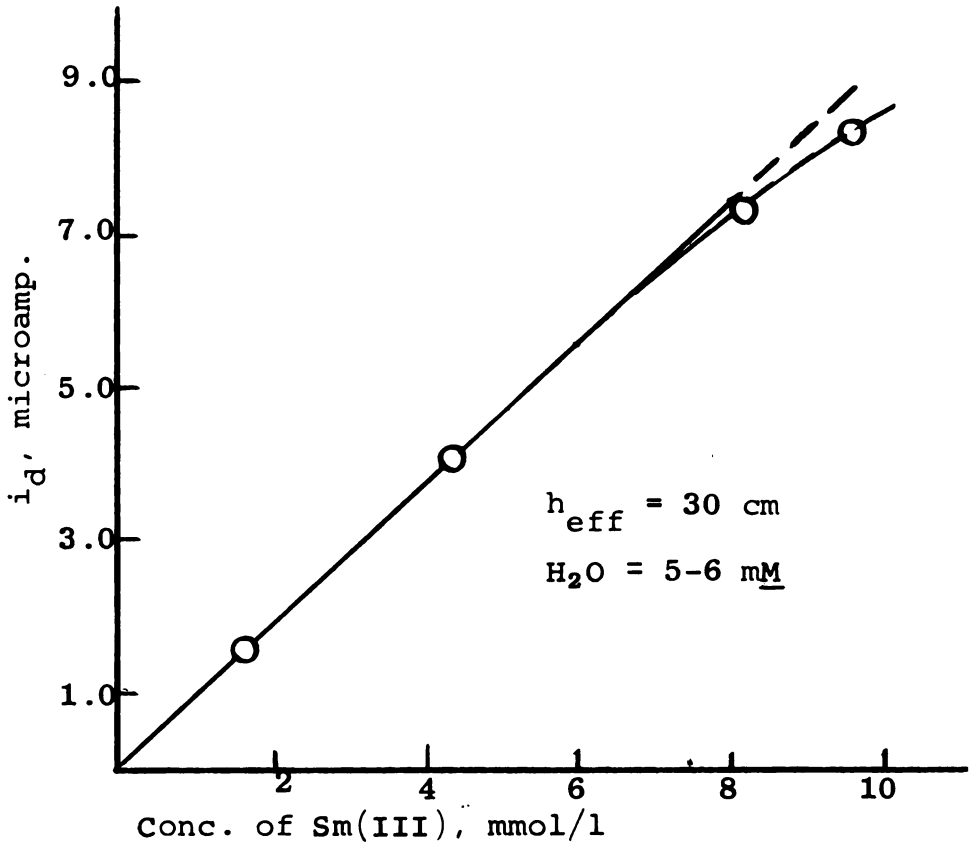


Figure 29. Variation in i_d of first wave with changes in Sm(III) concentration at 25.0°.

idealized curve a, Figure 1.

While a similar plot is not shown for i_d', it also changed linearly, the average ratio of i_d'/i_d being 1.89 ± 0.04 for Sm(III) concentrations from 1.6 to 9.6 m<u>M</u>.

The diffusion current constant, $I = i_d/C\ m^{2/3}\ t^{1/6}$, for the first wave was calculated as 1.038. Assuming a one electron reduction a value of 2.92×10^{-6} cm^2 sec^{-1} is obtained for the diffusion coefficient.

The ratio of i_d'/i_d suggests that the second wave is due to a two electron reduction step if the first wave is assumed to involve a one electron reduction.

Since the diffusion coefficients appear to be of the correct order and magnitude, the assumption that the first step is a one-electron process and the second step a two-electron process is confirmed.

Variations of i_d and $E_{1/2}$ Values with Water Concentration

The influence of increasing water concentration on i_d and i_d' for a 9.6 m<u>M</u> Sm(III) system is shown in Figure 30. The influence of several factors were considered in an attempt to explain the observed constancy of i_d and the initial curvature in i_d' as the water content in the system was increased.

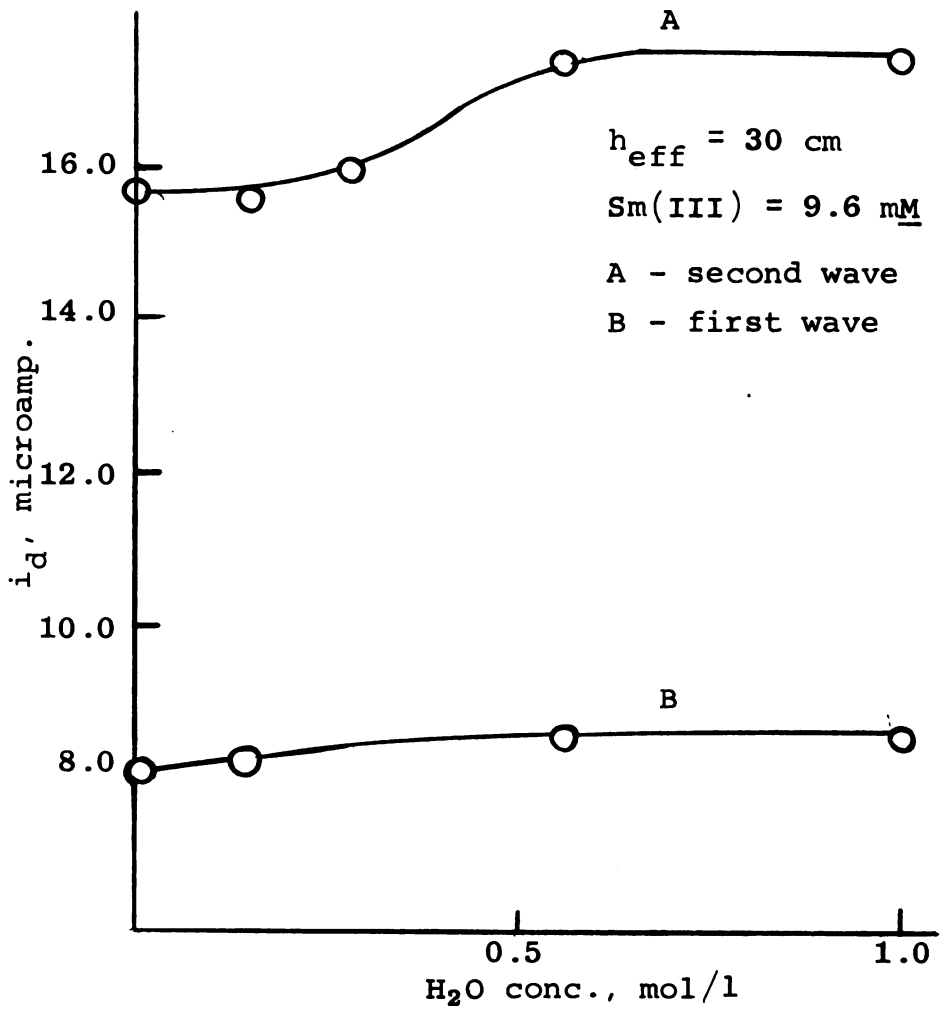


Figure 30. Variation in i_d with water concentration at 25.0°.

As previously stated, the addition of water will change the interfacial tension and thus effect m and t. In these experiments only the change in t was noted. On increasing the water content to 0.55 M, t changed from an initial value of 3.8 sec to 2.1 sec for the first wave. For a similar water concentration change, t varied from 3.38 to 2.00 sec for the second wave. For a diffusion controlled process, i_d should increase as t increases and i_d should increase as t decreases if adsorption controlled. The relative increases in i_d and i_d' are approximately 5 and 10 percent respectively as the water content is increased to 0.55 M. This indicates that the processes are at least in part adsorption controlled.

On increasing the water content from 0.55 to 1.0 M, t for the second step remained at 2.00 sec and no change in i_d' was observed. In the first step i_d did not change even though t decreased to 1.98 sec when the water concentration was 1.0 M. No definite conclusion regarding diffusion or adsorption control can be deduced from this behavior.

If only the effect of viscosity change is considered, i_d and i_d' should increase as the water content is increased since the addition of water lowers the viscosity if the current is diffusion controlled. Up to 0.55 M water concentration i_d and i_d' do increase but the constancy in i_d and i_d' as the water concentration is increased to 1.0 M would not be expected.

Neither the consideration of interfacial tension change nor the viscosity change on altering the water content in the system leads to definite conclusions regarding diffusion or adsorption control in the electrode process.

To examine the effect of water content on $E_{1/2}$, measured quantities of 0.1 M aqueous LiCl were added to 9.6 mM Sm(III) in DMSO which was also 0.1 M in LiCl. The water concentration was varied from 5.4 to 1000 mM and the $E_{1/2}$ values as shown in Figure 31.

The value for $E_{1/2}$ for the first wave remained constant at -2.00 volt vs. SCE. From this observation, and the observation that i_d does not change significantly, it can be concluded that the addition of water does not influence the electrode process associated with the first wave.

The value for $E_{1/2}$ for the second step changed linearly, becoming more positive at a rate of 0.06 mv/mM as the water content was increased up to 1.0 M. This suggests that water affects the electrode process associated with the second step. A change in liquid junction potential to account for this potential shift as the water content is increased cannot be assumed, since it would also have shifted $E_{1/2}$ for the first step an equal amount.

Variation of Current-Time Curves with Water Concentration

The i - t curve developed on the plateau of the first wave, as shown in Figure 32, retains the form associated

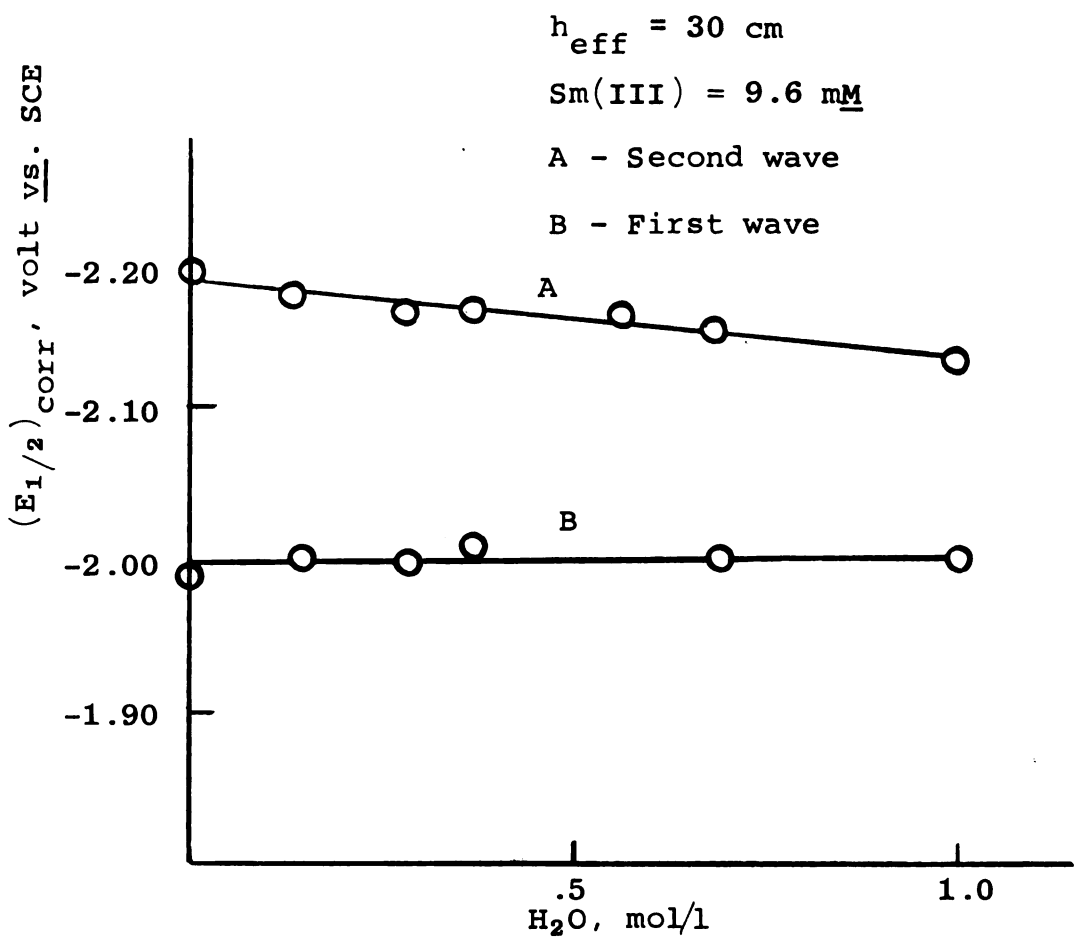


Figure 31. Variation of $E_{1/2}$ with water concentration at 25.0°.

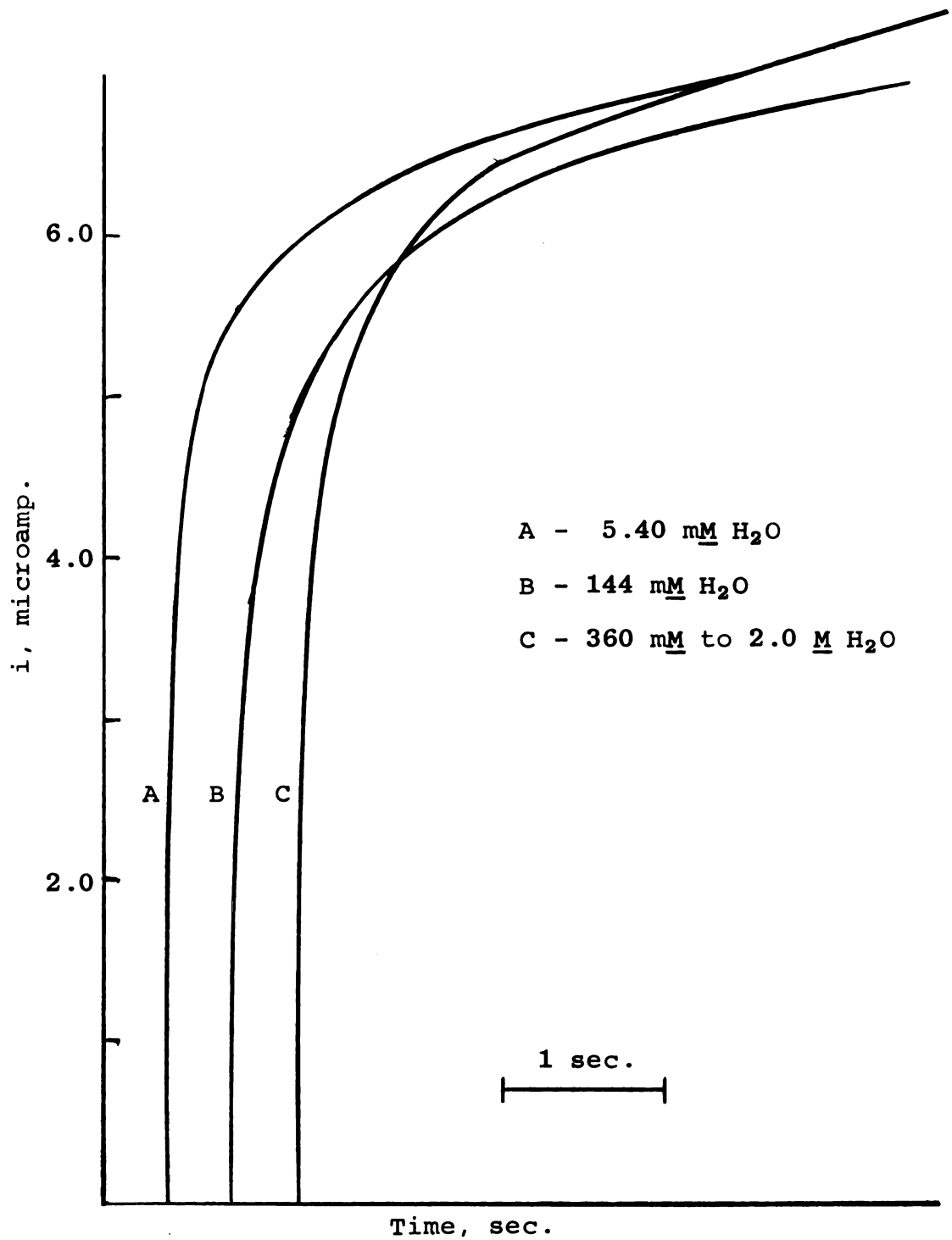


Figure 32. Effect of increasing water concentration on i - t curve at applied potential corresponding to i_d region of first wave for 9.6 mM Sm(III).

with diffusion control as the water concentration is increased from 5.4 to 2000 m*M*.

Increasing water concentration does, however, affect the i - t curves developed on the plateau of the second wave as shown in Figure 33. By comparison with curves shown in Figure 2, a transition in control appears to occur as the water content is increased. At the highest water concentration, the appearance of a small maximum in the i - t curve suggests some adsorption influence on the electrode process, although curve C in Figure 33 is unlike any of the theoretically predicted types.

Prolonged Electrolysis Studies

Solutions containing 8.2 m*M* Sm(III), 5.6 m*M* H_2O, 0.1 *M* LiCl were electrolyzed for various periods of time at various potentials identified in Figure 34 and the current-potential curves which were obtained after various periods of electrolysis are shown in this figure.

The first wave remained unaffected by electrolysis at any of the applied potentials selected, even after 162 hours of electrolysis.

After 3 hours of electrolysis at a potential, -2.45 volt *vs*. SCE, corresponding to the plateau of the second wave, an increase in wave height is observed; however, after 162 hours at the same applied potential the second wave is drawn out and poorly developed and what could be considered the wave height is considerably decreased.

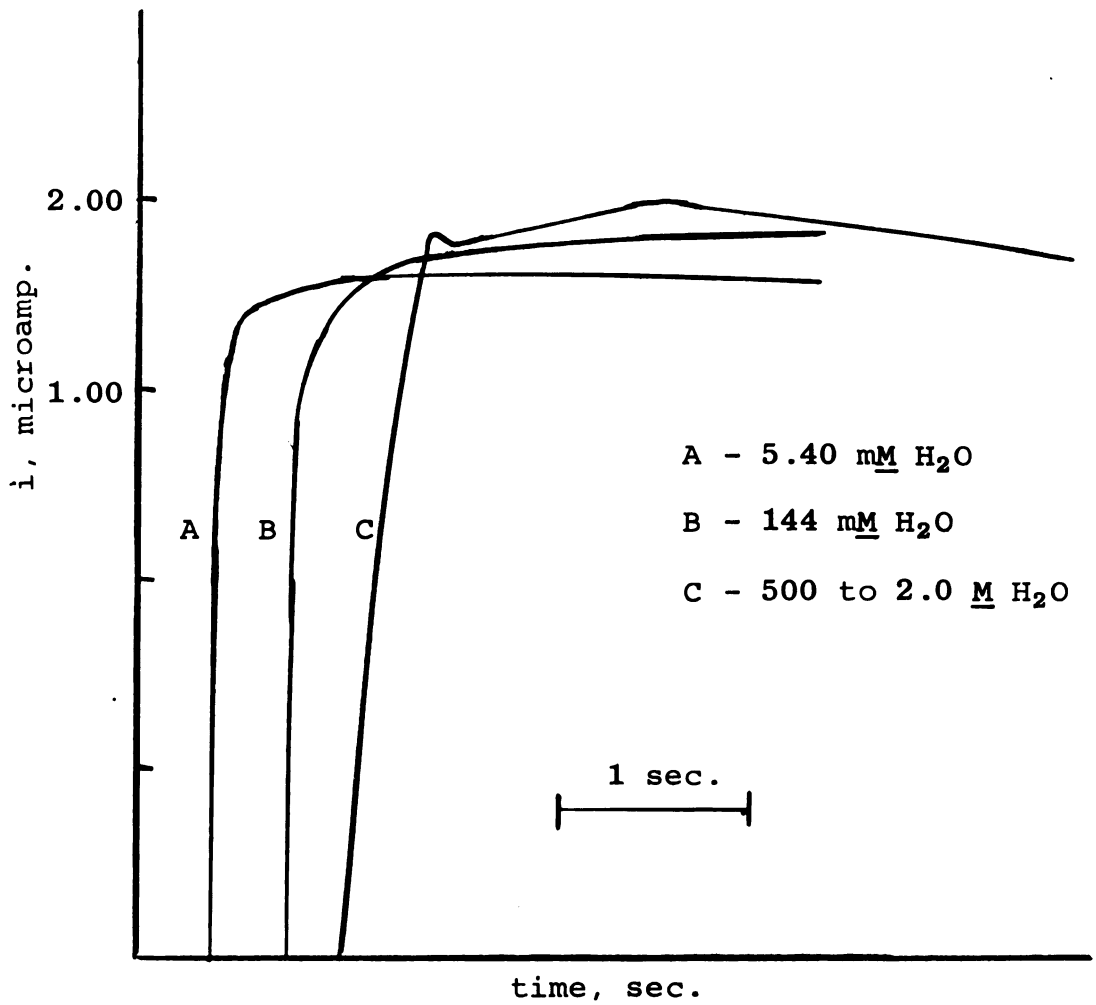


Figure 33. Effect of increasing water concentration on i - t curve at applied potential corresponding to i_d region of second wave for 9.6 mM Sm(III).

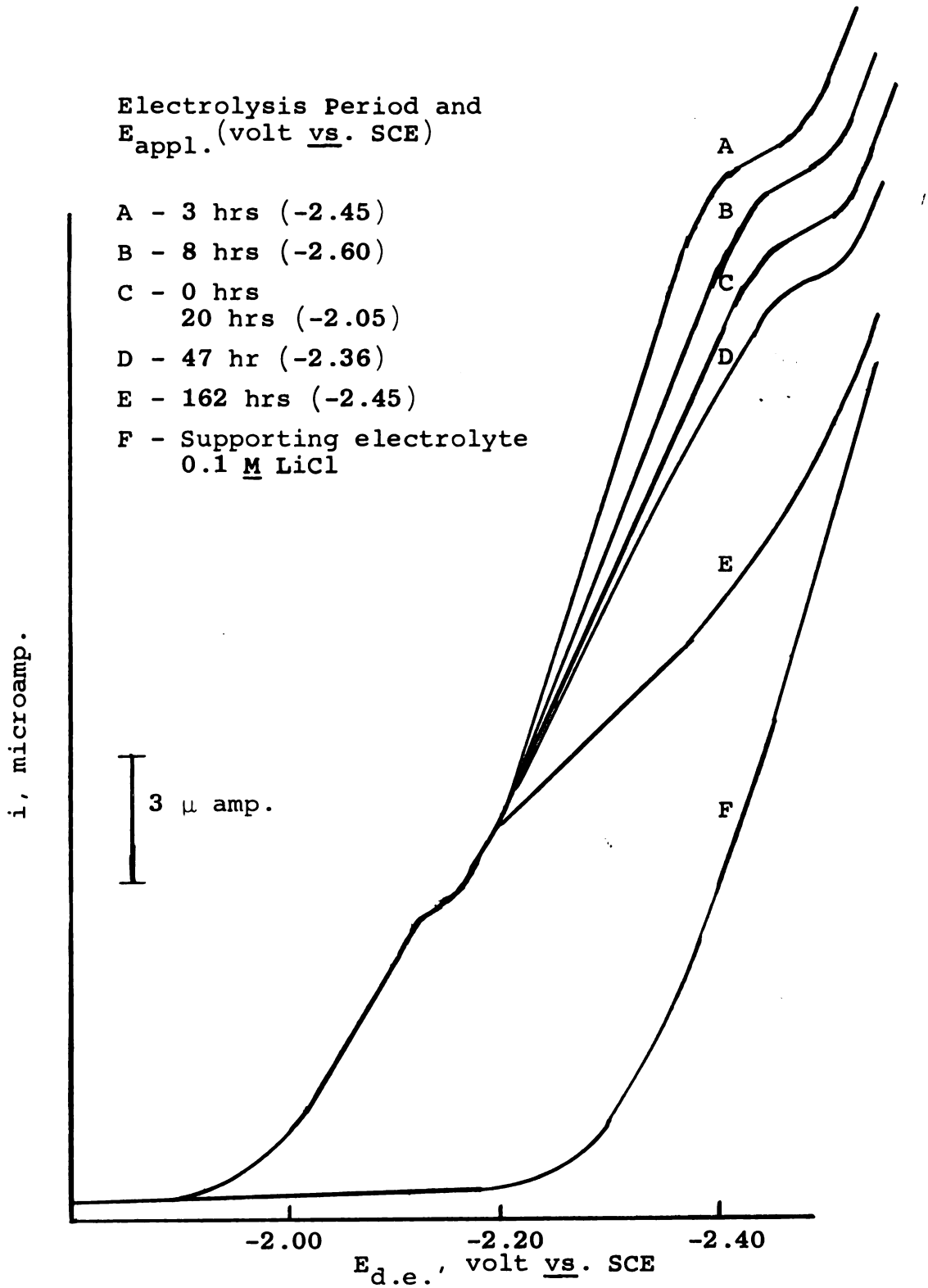


Figure 34. Current-potential curves for 8.2 mM Sm(III), 0.1 M LiCl, 5.6 mM H_2O after various periods of Electrolysis.

After 8 hours of electrolysis at an applied potential, -2.60 volt vs. SCE, beyond the plateau of the second wave, the wave height also increased, but to a lesser extent than that observed after the three hour electrolysis.

After electrolysis of 47 hours at an applied potential of -2.36 volt vs. SCE, the wave height decreased.

Current-time curves for various regions of the second wave obtained after 162 hours of electrolysis at an applied potential of -2.45 volt vs. SCE are shown in Figure 35. Since the shape of the i - t curves changes for various regions of the wave a complex mechanism (18) is indicated. The i - t curve developed at an applied potential corresponding to the plateau of the wave indicates adsorption control by comparison with idealized curve d shown in Figure 2.

Current-time curves for various regions of the first wave are not shown since they did not change in shape even after 162 hours of electrolysis.

Beyond 8 hours of electrolysis a pale greenish color developed in the solution. An absorption spectrum recorded for the solution, which had been electrolyzed for 47 hours at -2.36 volt vs. SCE, against a DMSO blank consisted of a broad band which extended to 450 mμ into the visible region but the peak was so high that it could not be recorded. On dilution of this solution with DMSO, only a single peak, falling in the near uv spectral region, with a maximum at 260 mμ was discernable. The reported maximum for dimethyl

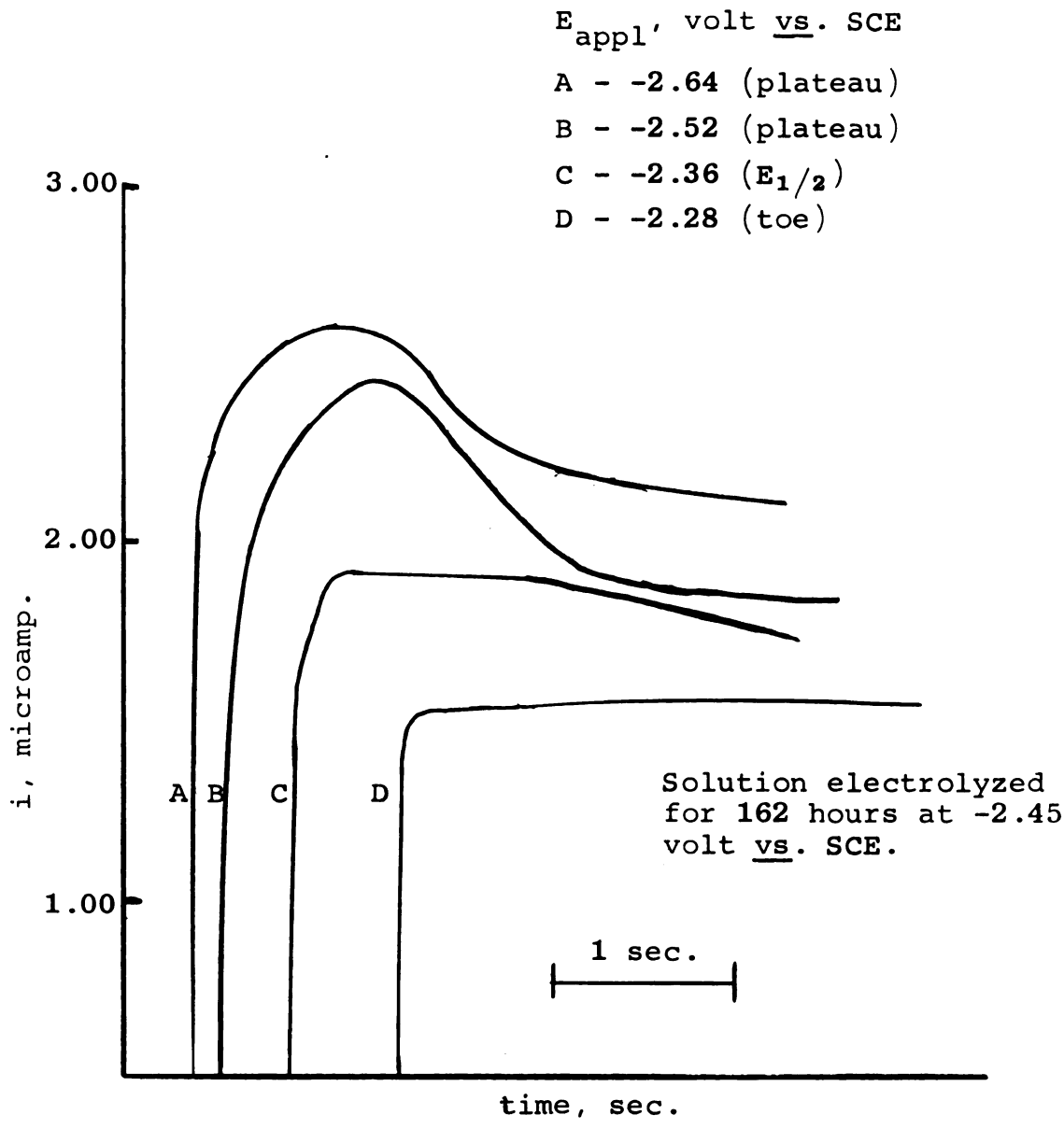


Figure 35. Current-time curves at various applied potentials for second Sm(III) wave after prolonged electrolysis.

sulfide in cyclohexane and ethanol is 254 and 256 mμ respectively which suggests that one product of the electrolysis is dimethyl sulfide.

The above electrolyzed solution was compared to pure DMSO by vpc. A small peak preceding that for DMSO was observed. This peak is located in the same position as the peak which appeared when some of the DMSO obtained for the earlier studies was tested by vpc prior to purification. Since DMSO is made by the oxidation of dimethyl sulfide, it was concluded that the small peak observed for the DMSO obtained for the early work was due to dimethyl sulfide. Furthermore, when the compound giving rise to the small peak emerged from the vpc exit port, a strong sulfide-like odor was detected. From the above correlation of the vpc results it is proposed that a product formed on electrolysis could be dimethyl sulfide.

As further support that Sm(III) is not reduced to the metal, chemical tests for samarium in the mercury cathode were negative.

Since two polarographic steps are observed when Sm(III) is present in DMSO, and since the ratio of step-height is approximately 1:2, and since no samarium was detected in the cathode after prolonged electrolysis, it is proposed that the first step is due to the reduction of Sm(III) to Sm(II), and the second step is due to the reduction of DMSO coordinated with Sm(III) to dimethyl sulfide. On prolonged electrolysis the concentration of Sm(III) would be

expected to decrease which would result in a decrease in the height of the first step. Since this is not observed, the Sm(III) concentration level could be maintained at a constant level by a cyclic reoxidation process, DMSO being reduced by Sm(II) which would return to the +3 state. The irregular behavior of the wave height for the second step after varying periods of electrolysis cannot be explained without additional information about the products which are formed during electrolysis.

SUMMARY AND CONCLUSIONS

An investigation of the polarographic behavior of the tripositive lanthanide ions in DMSO containing 0.1 M LiCl and the effect of water in the system was carried out using Dy(III) and Sm(III) as representative of each of the two types of lanthanide ions, those which exist only in the tripositive state and those which can also exist in the dipositive state. One wave results from the presence of Dy(III) with $E_{1/2}$ = -2.06 volt vs. SCE, whereas two waves with $E_{1/2}$ = -2.00 and -2.18 volt vs. SCE respectively result from the presence of Sm(III). None of the waves possessed a maximum and thus no maximum suppressor was required.

The wave related to Dy(III) in DMSO, which is 4-5 mM in H_2O, is shown to be irreversible by the curvature and dissymmetry observed in the plot of log $i/(i_d - i)$ vs. $E_{d.e.}$, by the slope of 108 mv in this plot, and by the high temperature coefficient of +6 mv per degree for $E_{1/2}$.

Positive chemical tests for dysprosium in the mercury cathode after prolonged electrolysis at -2.22 volt vs. SCE and the decrease in wave height in the polarograms recorded after such electrolysis demonstrate that the ultimate product is dysprosium. Assuming the rate-determining step involves a one electron transfer, the transfer coefficient obtained from the slope of log $i/(i_d - i)$ vs. $E_{d.e.}$ plot is found to be 0.546.

Although a complicated electrode process is inferred from the change in shape of i - t curves developed at applied potentials corresponding to various positions on the

wave, evidence for a combination of diffusion and adsorption control was obtained from the effect of mercury pressure on wave height, the form of i - t curves, and the curvature in the plot of i_d against Dy(III) concentration. Furthermore, the temperature coefficient for the wave height, 0.7%, eliminates kinetic or catalytic control for which the temperature coefficient would be greater than 2%. The diffusion coefficient, 1.56×10^{-6} cm^2 sec^{-1}, calculated from data obtained for the lowest Dy(III) concentration investigated, is reasonable in its order of magnitude.

The shift in $E_{1/2}$ to more positive values as the water content was varied from 4 to 3890 m<u>M</u> was not linear. Three rates of change occur, 2 mv/m<u>M</u>, 0.014 mv/m<u>M</u>, and 0.11 mv/m<u>M</u> for water content intervals 4 to 32, 32 to 2500 and 2900 to 3890 m<u>M</u> respectively.

The experimentally observed shift of 200 mv in $E_{1/2}$ cannot be entirely due to the liquid junction potential change on increasing the water content to 3.89 <u>M</u>, since the liquid junction potential between DMSO and water is estimated to be only 120 mv.

When the concentration of water reaches the 4 <u>M</u> level, $E_{1/2}$ is -1.86 volt <u>vs</u>. SCE which is only 0.05 volt more negative than $E_{1/2}$ for the wave due to the presence of Dy(III) in aqueous medium. This is evidence that on the addition of water, the solvated Dy(III) species present in DMSO are converted to the electroactive species present in water.

The decrease in i_d as water concentration is varied from 4 to 60 m$\underline{M}$ in 10 m$\underline{M}$ Dy(III) cannot be explained by considering the individual effects that water would have on the interfacial tension or viscosity.

A 0.7 sec decrease in t, due to the change in interfacial tension as the water content was increased from 4 to 60 m$\underline{M}$ does not account for the 1.0 μa current decrease but the direction of change in t is evidence for diffusion control.

Since the addition of water lowers the viscosity of the medium and therefore facilitates diffusion, an increase in current is expected if the process is purely diffusion controlled. The observed decrease in i_d implies that the process is not purely diffusion controlled.

From the form of the i - t curves, it may be concluded that the role of adsorption decreases as the water content is increased.

Since the individual influences that water could have on $E_{1/2}$ and i_d do not in themselves explain the experimentally observed changes in these quantities, it may only be concluded that in addition to the effect of water on interfacial tension, viscosity, and liquid junction potential, water must be chemically involved in the electrode process. From the tendency of $E_{1/2}$ to approach that of $E_{1/2}$ for the aqueous medium as the water content in the DMSO is increased, it is concluded that water is a stronger base toward Dy(III) than DMSO. Thus the addition of water alters the

species which are present, and alters the dielectric constant which would affect solvation, ionization and dissociation, which probably are significant chemical reactions associated with the electrode process.

The waves related to Sm(III) in DMSO, which is 4-5 m*M* in H_2O, are also shown to be irreversible by the curvature and dissymmetry observed in the plot of log $i/(i_d - i)$ *vs.* $E_{d.e.}$ and by the slopes of 109 and 127 mv in this plot for the first and second waves respectively. Although temperature coefficients of +1.7 and +2.5 mv per degree for $E_{1/2}$ for the first and second waves respectively suggest reversibility, the possibility that the process is irreversible cannot be excluded.

Since chemical tests for samarium in the mercury cathode after prolonged electrolysis at -2.36, -2.45, and -2.60 volt *vs.* SCE were negative, it must be concluded that the metal is not the ultimate reduction product.

From the ratio of the second to the first wave height of approximately 2 to 1, it is concluded that the second step involves a two-electron and the first step involves a one-electron reduction process. Assuming the rate-determining step in each case involves the transfer of one electron, transfer coefficients of 0.539 and 0.464 are obtained for the first and second step respectively.

The form of the i - t curves for the first wave does not change when recorded at applied potentials corresponding to various regions of this wave and reflects diffusion

control. Although a plot of log i *vs.* log t is linear, the slope in this plot is 0.115 instead of the expected 0.167.

From the change in the shape of i - t curves developed at various applied potentials corresponding to various positions on the second wave it is concluded that a complicated electrode process is associated with this step. Some effects of adsorption control are apparent from the shape of the i - t curve recorded at a potential corresponding to the plateau for the second wave.

That both waves are principally diffusion controlled is concluded from the effect of mercury pressure on each wave height, and the linearity in the plots of i_d and i_d' against Sm(III) concentration. Furthermore, the temperature coefficients for the wave heights, 1.04% and 0.75%, for the first and second wave respectively, eliminate kinetic of catalytic control for the second wave. The diffusion coefficient for Sm(III) is 2.9×10^{-6} cm^2 sec^{-1}, calculated assuming a one electron reduction. The diffusion current constant for the first wave is 1.038.

The concentration from 5.4 to 1000 m*M*, water does not influence the electrode process associated with the first step since $E_{1/2}$ remains constant at -2.00 volt *vs.* SCE. Within the same concentration interval, the $E_{1/2}$ for the second step changes linearly, becoming more positive at a rate of 0.06 mv/m*M*. Since the change in liquid junction potential, which would cause an equal shift to occur for

both $E_{1/2}$ values, cannot account for this observation, it can only be concluded that water affects the electrode process responsible for the second step.

Neither a consideration of interfacial tension change nor the viscosity change accounts for the increase in wave heights, of approximately 5 and 10 percent for the first and second waves respectively, as the water content is varied from 5.4 to 550 m$\underline{M}$. Furthermore these factors do not account for the constancy in i_d and i_d' as the water content is increased from 0.55 to 1.0 $\underline{M}$. However i - t curves recorded at applied potentials corresponding to the plateau of the first wave retain their form, associated with diffusion control, even though the water content is increased from 5.4 to 1000 m$\underline{M}$. The form of the i - t curves recorded at applied potentials corresponding to the plateau of the second wave is retained for water concentrations from 5.4 to 550 m$\underline{M}$, and changes at 550 m$\underline{M}$ water to a shape unlike any of the "ideal" forms. This latter shape, which is retained up to 2.0 $\underline{M}$ water, indicates a different type of adsorption influence.

On the basis of the effect on $E_{1/2}$, i_d and i - t curves it is concluded that the effect of increasing water concentration on the electrode process associated with the first step is negligible; however, increasing water concentration does affect the electrode process associated with the second step by interference with the adsorption associated with this step beyond 0.55 $\underline{M}$ water.

When a solution containing 8.2 m$\underline{M}$ Sm(III), 5.6 m$\underline{M}$ H_2O, 0.1 $\underline{M}$ LiCl was electrolyzed for 47 hours at an applied potential of -2.36 volt $\underline{vs}$. SCE, a product is formed as concluded from spectral and vpc analysis on the electrolyzed solution. The intense spectral band which initially extended into the visible region, yielded only a single peak in the near uv region, with a maximum at 260 mμ, upon dilution with DMSO. This peak was ascribed to dimethyl sulfide through correlation with the peaks at 254 and 256 mμ reported for dimethyl sulfide in cyclohexane and ethanol respectively. The small vpc peak preceding that for DMSO was similar to one which had been ascribed to dimethyl sulfide in earlier work associated with the purification of DMSO.

It is proposed that the first step is due to the reduction of Sm(III) to Sm(II) and the second step is due to the reduction of DMSO coordinated with Sm(III) to dimethyl sulfide. It is further proposed that the Sm(II) produced in the first step is re-oxidized by DMSO accounting for the fact that the height of the first wave remained constant after electrolysis periods of up to 162 hours. Since this re-oxidation would constitute a catalytic process, a catalytic current contribution would be expected which could result in some curvature in the i_d $\underline{vs}$. Sm(III) concentration plot if the concentration of the catalyst is varied. Since the catalyst, DMSO, is present in large excess, its concentration can be assumed constant. Under such conditions, as stated on page 19, the catalytic current

contribution would be proportional to the Sm(III) concentration. Also, the temperature coefficient for i_d, 1.04%, which is 1.5 times that for the second wave, could reflect some catalytic control.

The irregular behavior of the wave height for the second step after varying periods of electrolysis cannot be explained without additional information about the products which are formed during electrolysis.

SUGGESTIONS FOR FURTHER WORK

Evidence has been presented for the reduction of Dy(III) in DMSO to the metal at a mercury electrode. Controlled potential coulometry should be applied to determine the electrolysis efficiency and if it is not 100% the identity of side products should be sought.

The cell could be re-designed so that electrolysis products could be recovered and exact product analysis after prolonged electrolysis of Sm(III) in DMSO should be undertaken. Reference samples of possible reduction products should be procured for analytical comparison with the recovered products.

Since it appears that even vacuum drying of lithium chloride did not remove all of the water, some procedure should be developed for preparing anhydrous lithium chloride.

It is obvious that classical polarography cannot separate all the factors influencing the electrode process in the systems examined. It would be interesting to apply the more modern diagnostic methods such as a.c. polarography or cyclic voltammetry to establish whether by their application the various contributing factors could be resolved.

It would further be interesting to determine how properties such as viscosity, interfacial tension and dielectric constant are altered on mixing water with DMSO.

Since it has been proposed that on adding water to DMSO solutions of lanthanides, the species present in DMSO are converted to aquo-complexes, evidence for such a conversion could possibly be observed by nmr.

LITERATURE CITED

1. Barnard, A. J., Jr., Broad, W. C., Flaschka, H., Chemist-Analyst, 45, 86, 111 (1956).

2. Ibid., 46, 18, 46, 76 (1957).

3. Brdicka, R., Hanus, V., Koutecky, J., "Progress in Polarography", P. Zuman, ed., Vol. I, Interscience, New York, (1962), p. 145.

4. Butler, J. N., J. Electroanal. Chem., 14, 89-119 (1967).

5. Coetzee, J. F., Siao, W., J. Inorg. Chem., 2, 14 (1963).

6. Estee, C. R., Glockler, G., J. Am. Chem. Soc., 96, 1344 (1948).

7. Gritzner, G., Gutmann, V., Schober, G., Mh. Chem., 96, 1056 (1965).

8. Gutmann, V., Schober, G., Z. Anal. Chem., 171, 339 (1959).

9. Hall, L. C., Flanigan, D. A., Anal. Chem., 35, 2108 (1963).

10. Hamaguchi, H., Hashimoto, J., Hosohara, K., Bull. Chem. Soc. Japan, 33, 562 (1960).

11. Holleck, L., Z. Anal. Chem., 126, 1 (1943).

12. Iwase, A., Nippon Kagaku Zasshi, 78, 1656 (1957); C.A. 52, 16090 (1958).

13. Ibid., 81, 1266 (1960); C.A. 55, 21913 (1961).

14. Ibid., 81, 95 (1960); C.A. 54, 13983 (1960).

15. Kolthoff, I. M., Coetzee, J. F., J. Am. Chem. Soc., 79, 870, 1852 (1957).

16. Kolthoff, I. M., Lingane, J. J., "Polarography", Vol. II, second ed., Interscience, New York (1952).

17. Kolthoff, I. M., Reddy, T., J. Electrochem. Soc., 108, 980 (1961).

18. Kuta, J., Smoler, I., "Progress in Polarography", P. Zuman, ed., Vol. I, Interscience, New York (1962) p. 43.

19. Laitinen, H. A., Taebel, W. A., Ind. Eng. Chem., Anal. Ed., 13, 825 (1941).

20. Large, R. F., Ph.D. Thesis, Michigan State University, (1963).

21. Large, R. F., Timnick, A., Anal. Chem., 36, 1258 (1964).

22. McMasters, D. L , Dunlap, R. B., Kuempel, J. R., Kreider, L. W., Shearer, T. R., Anal. Chem., 39, 103 (1967).

23. Meites, L. "Polarographic Techniques", second ed., Interscience, New York (1965).

24. Meites, L., "Treatise on Analytical Chemistry", I. M. Kolthoff and P. J. Elving, ed., Part 1, Vol. IV, Interscience, New York (1963) p. 2303.

25. Meites, L., Israel, Y., J. Am. Chem. Soc., 83, 4903 (1961).

26. Misumi, S., Ide, Y., Bull. Chem. Soc. Japan, 32, 1159 (1959); C.A. 54, 16230 (1960).

27. Ibid., 33, 836 (1960).

28. Misumi, S., Iwase, A., Nippon Kagaku Zasshi, 76, 1231 (1955); C.A. 51, 12706 (1957).

29. Ibid., 77, 640 (1956); C.A. 51, 17527 (1957).

30. Moeller, T., Cullen, G. W., J. Inorg. Nucl. Chem., 10, 148 (1959).

31. Moeller, T., Galasyn, V., J. Inorg. Nucl. Chem., 12, 259 (1959).

32. Moeller, T., Zimmerman, P. A., J. Am. Chem. Soc., 75, 3940 (1953).

33. Muller, O. H., "The Polarographic Method of Analysis". Chemical Education Pub. Co., Easton, Pa., (1951) p. 187.

34. Noddack, W., Bruckl, A., Angew. Chem., 50, 362 (1937).

35. Onstott, E. F., "Rare Earth Research", Macmillan, New York (1961) p. 51.

36. Powell, A. R., Schoeller, W. R., "Analysis of Minerals and Ores of the Rarer Elements", third ed., C. Griffen, London (1955).

37. Purushottam, A., Raghava Rao, Bh. S. V., Current Science (India) 25, 358 (1956); C.A. 51, 5590 (1957).

38. Purushottam, A., Raghava Rao, Bh. S. V., Anal. Chem. Acta., 12, 589 (1955).

39. Reddy, T. B., Ph.D. Thesis, University of Minnesota (1960); L. C. card No. Mic.-60-5606.

40. Rinehart, R. W., Anal. Chem., 26, 1820 (1954).

41. Ryabchikov, D. I., Sklyarenko, Y. W., Stroganova, N. S., Zhur. Neorg. Khim., 1, 1954 (1956); C.A. 51, 5595 (1957).

42. Ibid., 4, 1985 (1959); C.A. 54, 11576 (1960).

43. Ibid., 4, 2682 (1959); C.A. 54, 17110 (1960).

44. Sadtler Research Laboratories, Philadelphia, Pa., "The Sadtler Standard Spectra".

45. Sarma, D. V. N., Raghava Rao, Bh. S. V., Current Science (India) 25, 358 (1956); C.A. 51, 5590 (1957).

46. Schober, G., Gutmann, V., Monatsh., 90, 897-902 (1959).

47. Schober, G., Gutmann, V., "Advances in Polarography: Proceedings Second Internation Congress, Cambridge, 1959", Vol. III, Pergamon Press, London, (1960), p. 940.

48. Schwarzenbach, G., "Complexometric Titrations", Interscience, New York (1957), p. 74.

49. Sears, P. G., University of Kentucky, private communication.

50. Shevedov, V. P., Fu, I., Radiokhimiga, 2, 231 (1960).

51. Strehlow, H., vonStackelberg, M., Z. Electromchem., 54, 51 (1950).

52. Swensen, A. W., Glockler, G., J. Am. Chem. Soc., 71, 1641 (1949).

53. Taylor, J. K., Smith, S. W., J. Research Nat'l. Bur. Standards, 42, 387 (1949).

54. Treindl, L., Collection Czechoslov. Chem. Communs., 24, 3389 (1959).

55. Timnick, A., Ph.D. Thesis, State University of Iowa (1947).

56. Timnick, A., Glockler, G., J. Am. Chem. Soc., 70, 1347 (1948).

57. Vlcek, A. A., Collection Czechoslov. Chem. Commun. 22, 1736 (1957).

58. Ibid., 24, 3538 (1959).

59. Vlcek, A. A., "Progress in Inorganic Chemistry", F. A. Cotton, ed., Vol. V, Interscience, New York (1963) p. 211.

60. Vlcek, A. A., "Progress in Polarography", P. Zuman, ed., Vol. I, Interscience, New York (1962) p. 269.

61. Yakubson, S. I., Kastromina, N. A., Zuhr. Neorg, Khim., 2, 349 (1957); C.A. 51, 16149 (1957).

62. Zuman, P., "Progress in Polarography", P. Zuman, ed., Vol. II, Interscience, New York (1962) p. 583.