

THE POLAROGRAPHIC BEHAVIOR OF
AQUEOUS SOLUTIONS OF DYSPROSIUM (III)

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Robert Franklin Large
1963

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ABSTRACT

THE POLAROGRAPHIC BEHAVIOR OF AQUEOUS SOLUTIONS OF DYSPROSIUM(III)

by Robert Franklin Large

An investigation of the polarographic behavior of the tripositive lanthanide ions having no stable dipositive state in aqueous solution was conducted employing the dysprosium(III) ion as a representative of the group.

Two waves related to the lanthanide ion were observed, the characteristics of which were quite dependent on the pH of the solution. The $E_{\frac{1}{2}}$ of the first wave shows a shift to more negative potentials with an increase in hydrogen ion concentration of approximately 90 mv. per pH unit, with a value of $E_{\frac{1}{2}}$ of -1.791 v. vs. S.C.E. obtained at a pH of 3.20 in 0.1 M LiCl with 0.01% gelatin.

The i_d of the first wave decreases with increasing hydrogen ion concentration, but is proportional to the concentration of dysprosium(III) over the range 0.2 to 5.0 moles per milliliter at a constant pH value.

The i_d values experimentally observed were approximately five-sixths of those calculated by the Ilkovic equation, employing a value of 3 for n , experimentally determined m and t values, and a calculated value of $5.85 \times 10^{-6} \text{ cm.}^2 \text{ second}^{-1}$ for the diffusion coefficient for the dysprosium(III) ion.

The first wave was shown to involve the reduction of hydrogen ion by employing D_2O as a solvent and noting marked shifts in $E_{\frac{1}{2}}$ to more negative potentials.

The first wave was shown to be partially kinetic controlled by the nature of the plots obtained when i_d is plotted against $(h_{eff})^{\frac{1}{2}}$.

The current resulting from the second process associated with the lanthanide ion does not vary linearly with the concentration of dysprosium(III), and is dependent on the pH, the current decreasing as the pH decreases. A current was also observed for a suspension of dysprosium hydrous oxide. Gaseous hydrogen was visible around the electrode in the potential region of the maximum current values.

The i-t curves obtained at potentials during the development of both waves show reproducible irregularities of an unprecedented nature, and denote unusual phenomena occurring at the electrode surface. Electrocapillary curves obtained in the presence of dysprosium(III) also show an irregularity in the potential region of the second wave.

The choice of supporting electrolyte was shown not to be of significance by comparison of i-E curves obtained employing LiCl, LiClO₄, Li₂SO₄, and Me₄NI as supporting electrolytes.

A comparison of i-E curves obtained for lanthanum(III), gadolinium(III), and lutecium(III) with those of dysprosium(III) shows a similar behavior for all these ions with a shift in the waves to more negative potentials with increasing basicity of the ion.

From this investigation it was concluded that the polarographic waves observed for aqueous solutions of dysprosium(III) are the result of the reduction of hydrogen ions produced by the hydrolysis of the lanthanide ion in the immediate vicinity of the electrode followed by the adsorption of the lanthanide hydrous oxide produced in the hydrolysis, which results in the reduction of additional hydrogen ions from water associated with the lanthanide hydrous oxide.

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By

Robert Franklin Large

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INTRODUCTION

Since the appearance of the initial report concerning the polarographic behavior of the tripositive lanthanide ions in aqueous solution, numerous reports have appeared in the literature, some of which support the original findings, while others contradict them. In the initial report, stepwise reduction of all available tripositive lanthanide ions was described. Such behavior would be expected for those lanthanide ions capable of existing in the dipositive state in aqueous solution, but not for the remaining ones.

Varied explanations have been presented pertaining to the polarographic behavior of those lanthanides which do not form stable dipositive species in aqueous solution, and none have 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 a hydrogen ion dissociated from a hydrated lanthanide species;
- (d) reduction of hydrogen ion to hydride ion which results in the formation of lanthanide hydrides.

This investigation was undertaken to obtain information which will lead to an elucidation of the electrode processes giving rise to polarographic waves for these lanthanide ions. The dysprosium(III) ion was selected as representative of the group, and most of the experimental work was conducted with solutions of this ion.

HISTORICAL

The initial report pertaining to the polarographic behavior of the tripositive lanthanide ions was that of Noddack and Bruckl (27), who electrolyzed sulfate solutions of all the available lanthanons 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 trivalent 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 for europium and ytterbium. Laitinen and Taebel (17) have demonstrated that europium(III) is reversibly reduced to europium(II) in 0.1M ammonium chloride and the half-wave potential has been reported as -0.671 v. vs. S.C.E. 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 (17) have also shown that ytterbium(III) is reversibly reduced to the divalent state in 0.1M ammonium chloride, and the half-wave potential was reported as -1.169 v. vs. S.C.E. However, this reduction cannot be carried out in an acid medium as the wave due to the discharge of hydrogen ion obscures the ytterbium(III) $\rightarrow$ ytterbium(II) wave. Quantitative determinations of ytterbium based on this process have been reported (7, 17, 30).

Laitinen and Taebel reported that no second wave for either europium or ytterbium was observed in 0.1M ammonium chloride, but

other authors have observed a second wave for both of these ions in other media (9, 22).

The only other lanthanon exhibiting a dipositive state in aqueous solution is samarium, and samarium(II) is quite unstable in aqueous solution. Timnick and Glockler (41) studied the polarographic reduction of samarium(III) and reported a two step wave in either 0.1M tetramethylammonium iodide or 0.1M lithium chloride, with $E_{1/2}$ values of -1.80 v. and -1.96 v. vs. S.C.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 samarium(II) formed in the initial reduction by reaction with water and subsequent precipitation of a portion of the samarium(III) by the hydroxide ion produced in the reoxidation process.

Purushottam and Raghava Rao (31) have also suggested the two step reduction process for samarium.

Iwase (8) has reported only a single wave for samarium(III) employing either lithium chloride or tetramethylammonium iodide as a supporting electrolyte, and has attributed the wave to direct reduction to the metallic state. Yakubson and Kastromina (43) have 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 (31) studied the polarographic waves of yttrium(III), lanthanum(III), praeosodymium(III), neodymium(III), gadolinium(III), dysprosium(III) and reported a double wave for all of these lanthanide ions in 0.1M lithium chloride and attributed the waves to the stepwise reduction process. Sarma and Raghava Rao (36) have also reported a stepwise process for the reduction of holmium(III), erbium(III), terbium(III), thulium(III), lutecium (III).

Swensen and Glockler (39) have reported only a single polarographic wave for praeodymium(III) in either 0.1M lithium chloride or 0.1M tetramethylammonium iodide and attribute the wave to the direct reduction to the metal. Similar observations were noted by Estee and Glockler (5) for neodymium(III) in 0.1M lithium chloride or 0.1M tetramethylammonium iodide, and by Rabideau and Glockler (32) for gadolinium(III) in 0.1M lithium chloride or 0.1M tetramethylammonium chloride.

Iwase (10) has reported only a single wave in 0.1M lithium chloride for gadolinium(III), dysprosium(III), holmium(III), erbium(III), thulium(III) and attributes the wave to the direct reduction to the metal. Misumi and Iwase (24, 25) have reported a single wave for both praeodymium(III) and neodymium(III).

Yakubson and Kastromina (43) have reported only a single wave for lanthanum(III), neodymium(III), and cerium(III) in 0.1M tetramethylammonium iodide and suggest the 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 reduction of a complex ion is observed.

Misumi and Ide (23) have studied the waves obtained for yttrium(III) in tetramethylammonium iodide and lithium perchlorate, and report a double wave in halide medium and only a single wave in perchlorate medium. These authors have suggested that the first wave was due to reduction of hydrogen ion produced by ionization of the hydrated yttrium(III) ion and the second wave in halide medium arising from the same type of reaction for a halocomplex ion.

Treindl (42) has studied the polarographic behavior of lanthanum(III), cerium(III), praeodymium(III), neodymium(III), and samarium(III) and reports 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 supposed that the polarographic reduction of the ions studied involves the formation of lanthanide hydrides.

Considerable interest has been shown in the electrolytic separation of the lanthanons by reduction at mercury or amalgam electrodes (29, 33, 34, 35, 37). 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 (6) have carried out neutron activation analysis on mercury drops collected in a holmium(III) solution at potentials corresponding to the polarographic waves of holmium(III). Much less holmium than would be expected was found in the mercury, and these authors concluded that there is no reduction to the metallic state. However, no precautions were taken in this work to avoid re-dissolution of any holmium that might have been present as an amalgam.

EXPERIMENTAL

INSTRUMENTATION

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

- A Sargent Model XXI Polarograph to obtain recorded current-potential curves;
- A Sargent Number S-30260 Potentiometer in conjunction with the Sargent Model XXI Polarograph to measure the initial potential values;
- A Tektronic Model 504 Oscilloscope in obtaining instantaneous current-time curves during the course of a single mercury drop;
- A Sargent Model M. R. recorder with a pen speed of one second for full scale deflection to obtain maximum current-potential curves;
- A Beckman Zeromatic pH Meter equipped with standard glass and saturated calomel electrodes to obtain all pH readings;
- A Serfass Model RCM 15 Resistance bridge in measuring the resistance of the cell;
- A Polaroid Model 110A camera and Polaroid type 42 or 44 film to record the instantaneous current-time curves displayed on the oscilloscope;
- A Sargent Number S-2770 constant temperature bath to insure temperature control at $25.0 \pm 0.1^{\circ}$ during electrolysis.

OTHER EQUIPMENT

The electrolysis cell employed in this work is shown in Figure 1 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

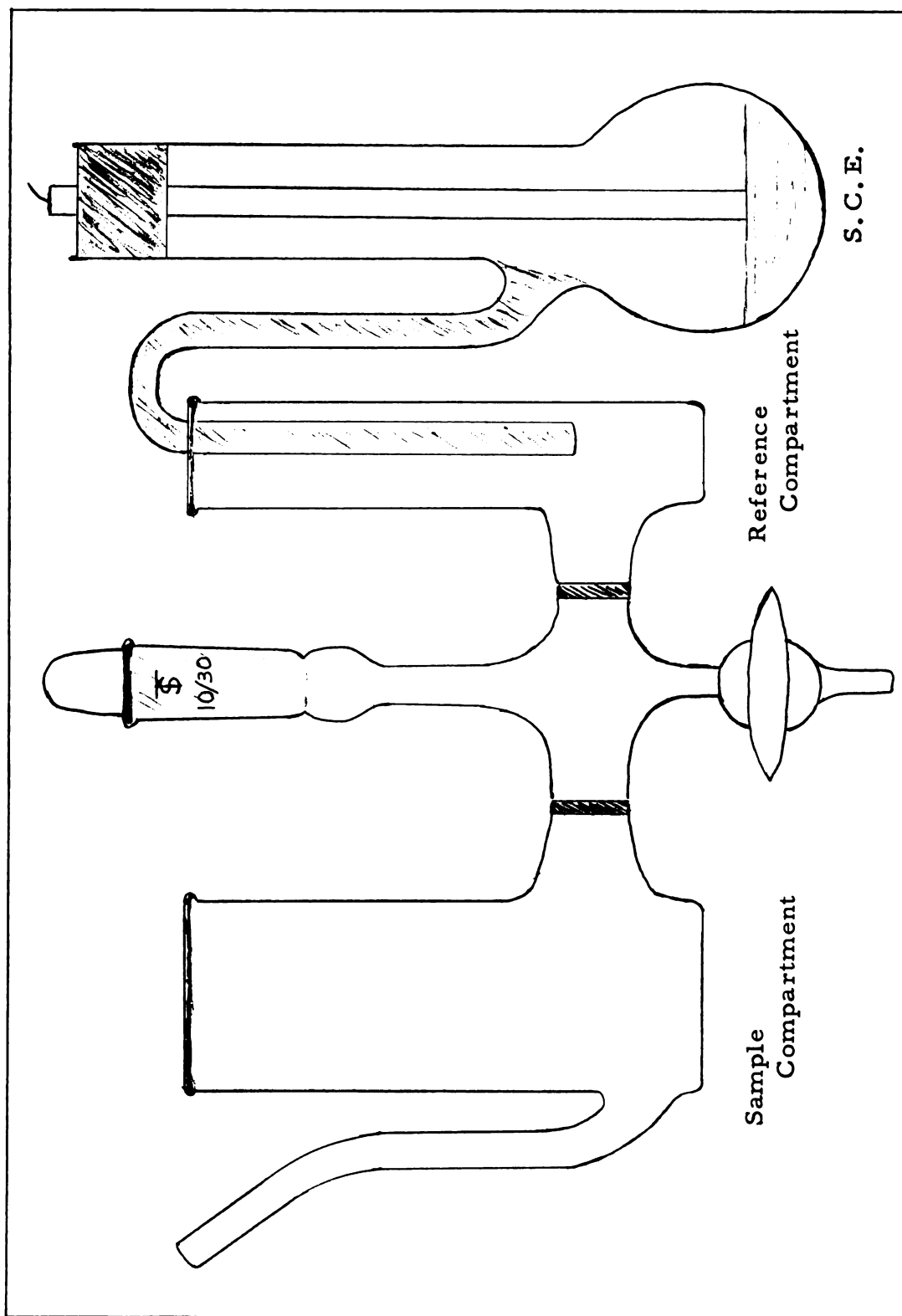


Figure 1. Electrolysis cell and reference electrode.
Actual size.

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 contained saturated KCl to allow connection with the saturated calomel reference electrode. This cell design provides adequate electrical connection while minimizing contamination of the sample solution by foreign ions or by agar from the side arm of the reference electrode. The central and reference compartments were filled with new solution prior to each run.

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

The resistance between a platinum electrode immersed in the inner compartment of the reference electrode and one immersed in the sample compartment of the cell with appropriate solutions in the cell was 350 ohms.

The capillaries employed were constructed from uniform marine barometer tubing and were connected to the mercury reservoir with neoprene tubing previously boiled in KOH solution to remove sulfur.

For recording the instantaneous current-time (i-t) curves a 100 ohm $\pm$ 0.5% resistor was inserted in series with the polarographic cell and the potential drop across this resistor followed with the oscilloscope.

REAGENTS

A number of reagents were employed in this work without further purification. The chemicals, labeled purities and sources are as follows:

Lanthanide sesquioxides	99.9 per cent Michigan Chemical Corporation St. Louis, Michigan
Mercury	Triple distilled A.C.S. F. P. Jay Chemicals, Inc. Waukesha, Wisconsin
Lithium Chloride	Reagent, crystals Matheson Coleman and Bell
Lithium Sulfate	Reagent, anhydrous powder Matheson Coleman and Bell
Lithium perchlorate trihydrate	Reagent G. Frederick Smith Chemical Co. Columbus, Ohio
Perchloric Acid	70-72 per cent Baker's Analyzed Reagent
Deuterium Oxide	99.5 per cent Nichem, Inc. Bethesda, Maryland
Gelatin	Pfanstiehl Chemical ash 1.14%
Sodium Hydroxide	Bakers Analyzed Reagent
Nitrogen	Prepurified, 99.996 per cent The Matheson Company

Tetramethylammonium iodide from Eastman Organic Chemicals was purified by repeated recrystallization from an ethanol-water mixture as suggested by Kolthoff and Lingane (15).

All water employed in this work was redistilled from alkaline permanganate solution. The initial portion of distillate after each charging of the distillation flask was discarded.

EXPERIMENTAL PROCEDURES

Preparation of Lanthanide Perchlorate Stock Solutions

All lanthanide stock solutions were prepared from the oxides which had been previously ignited to constant weight at 750° while contained in a platinum crucible. A weighed portion of the oxide sufficient to yield a 20 mM solution was dissolved in a slight excess of the theoretical amount of perchloric acid, and the dissolution process was aided by heating on a steam bath for approximately two hours. After dilution to the appropriate volume, all solutions were stored in amber glass-stoppered bottles.

Preparation of Gelatin Solutions

All gelatin solutions were prepared just prior to use by dissolving a weighed portion of the solid in water heated to just below boiling, and diluted after complete dissolution to yield a 0.1% solution.

Preparation of Sample Solutions

Sample solutions were prepared the day they were used by dilution of stock solutions of lanthanide perchlorates, perchloric acid if desired, gelatin if desired, and supporting electrolyte in volumetric flasks.

For that portion of the work requiring a solution in D_2O , the following modified procedure was employed. A weighed amount of gelatin corresponding to that necessary to yield a 0.01% solution and a weighed amount of LiCl necessary to yield a 0.1M solution were placed in a volumetric flask and dissolved in a volume of hot D_2O somewhat less than the total required for complete dilution. The desired amounts of lanthanide stock solution and perchloric acid solution were evaporated to a minimum volume in a small beaker and were then diluted by the

solution containing the gelatin and LiCl by repeated decantation and subsequent washing of the beaker with D₂O. The solution was then diluted to the final volume with D₂O.

Dissolved oxygen was removed from all solutions in the electrolysis cell by bubbling a stream of nitrogen through the solution for a period of 15 minutes.

pH Adjustment

To prepare solutions of a desired pH without subjecting them to pH measurement prior to electrolysis, the following procedure was employed.

A solution was prepared containing the same total amount of lanthanide perchlorate, maximum suppressor and supporting electrolyte in the same total volume as required for a desired solution to be electrolyzed. A pH titration was then carried out on this solution avoiding any dilution other than that by the titrating reagent. From the resulting titration curve the volume of acid or base to be added to yield a particular pH value could be determined and then added in the preparation of the solution to be electrolyzed. This procedure yielded solutions within ± 0.01 pH unit of the desired pH. An example of the pH titration curve obtained for 1 mM dysprosium(III) in 0.1M LiCl with 0.01% gelatin is shown in Figure 2.

Recording of Current-Potential Curves

In recording the current-potential curves, extra care was taken to insure that the capillary tip was as clean as possible. Before each use, the capillary, with mercury flowing through it was immersed in concentrated HNO₃ for a few minutes, rinsed thoroughly with distilled water and then immersed in distilled water for approximately 15 minutes.

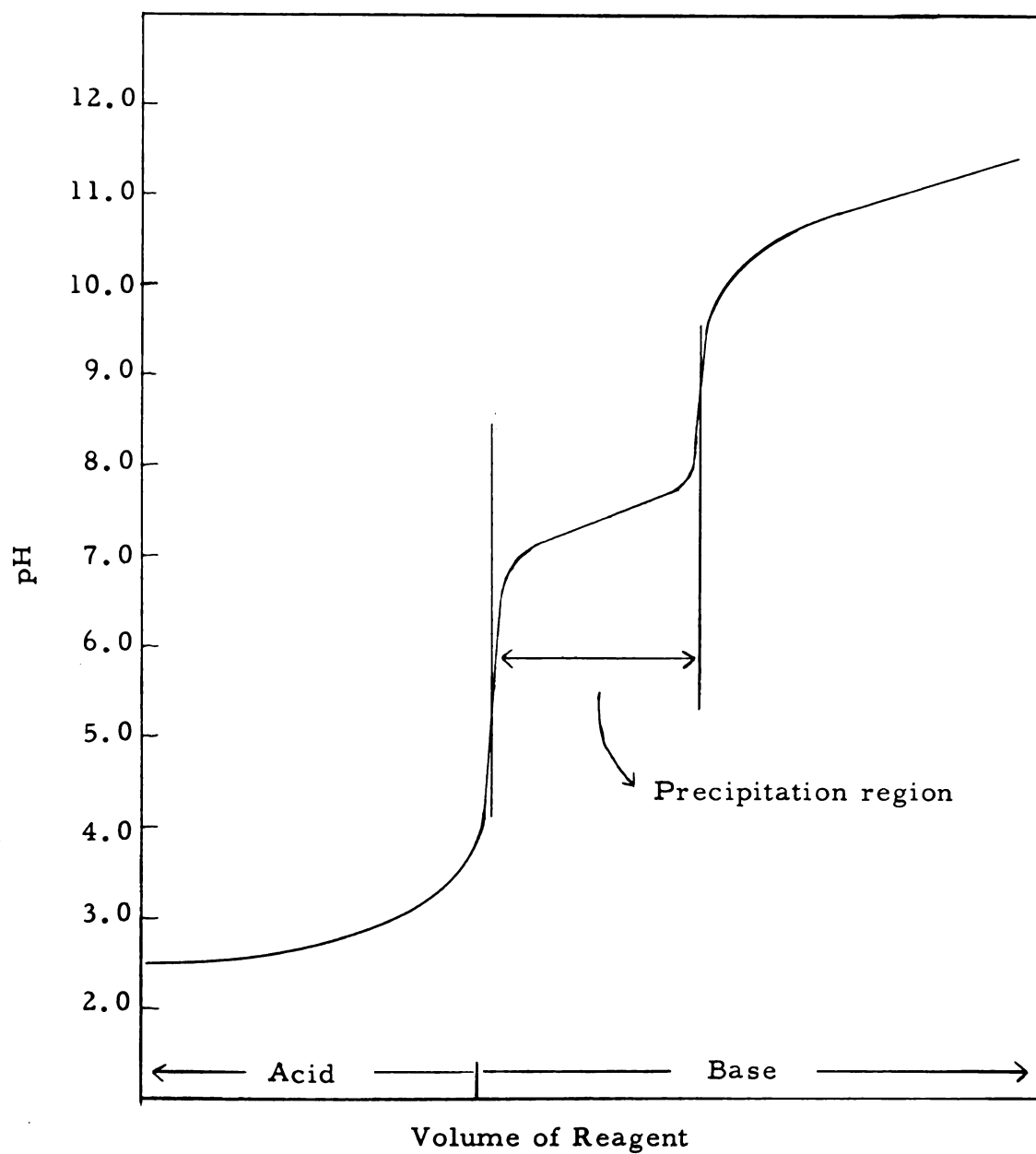


Figure 2. The effect of the addition of perchloric acid or sodium hydroxide on the pH of 1 mM dysprosium(III) in 0.1 M LiCl--0.01% gelatin.

Just prior to insertion into the cell, the capillary was rinsed thoroughly with a stream of redistilled water and the sides wiped dry with absorbent filter paper. If the capillary remained in the cell between recording of additional data on the same solution, care was taken to ensure that all hydrogen bubbles which might have accumulated during the previous electrolysis were removed. A few gentle but quick flicks of a finger against the upper stem of the capillary effectively removed all visible hydrogen.

The majority of the current-potential (i-E) curves were recorded with an initial voltage of -1.00 volts vs. S.C.E. and a span voltage of -1.50 volts vs. S.C.E. 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 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 uncertainty in the reproducibility of the individual potential values of ± 4 mv.

Evaluation of Half-Wave Potentials and Diffusion Currents

Since the i-E curves obtained in this investigation were not symmetrical, an arbitrary procedure had to be developed through which a practical half-wave potential ($E_{\frac{1}{2}}$) and the diffusion current (i_d) values could be reproducibly evaluated from these curves. Zuman (44) has recently described procedures for evaluating polarographic parameters from unsymmetrical i-E curves which are quite similar to the choice made for this work.

As illustrated in Figure 3, to evaluate $E_{\frac{1}{2}}$ for the first lanthanide wave, line AB was drawn through the midpoints of the oscillations on the plateau of the hydrogen wave, line CD 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 and the intersection of lines CD and EF were 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 half-wave potential. It can be seen from the figure that this point does not represent the true point where the current is one-half the diffusion current, but it does represent the most reproducible point of reference. The $E_{\frac{1}{2}}$ values measured by this means were estimated to be 5 mv less negative than the values obtained from the zero intercept of a plot of $E_{d.e.}$ vs. $\log i/i_d - i$. The majority of the $E_{\frac{1}{2}}$ values stated in this work are by no means meant to be true $E_{\frac{1}{2}}$ values, but merely a reproducible point representing $E_{\frac{1}{2}}$ which allows the estimation of potential differences.

To evaluate i_d for the first lanthanide wave, line IJ was drawn through the midpoints of the second lanthanide wave, and the midpoint of the line between the intersection of lines CD and EF and the intersection of lines EF and IJ was used to evaluate the diffusion current. In general this evaluation required measuring the vertical distance between this point and the extension of line AB.

The evaluation of the wave parameters for the second lanthanide wave leaves something to be desired. No plateau is defined, only a drop in current prior to active current rise from discharge of the supporting electrolyte. As a result, the procedure used was to draw a horizontal line through the midpoint of the oscillation giving the highest current value prior to the fall in current. The point of intersection of this line and line IJ was used as a reference point, the potential at

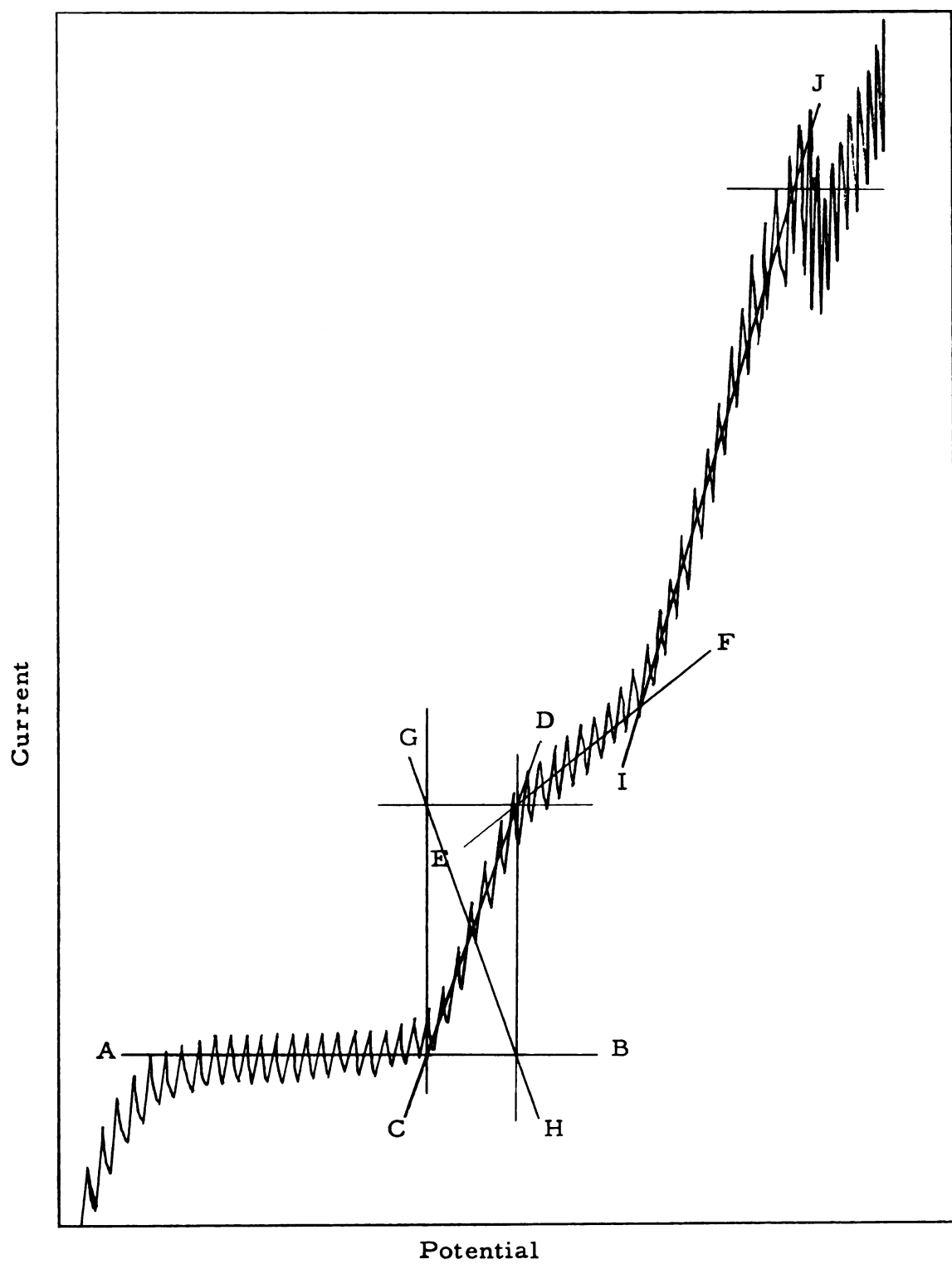


Figure 3. Representation of construction procedures for the evaluation of the wave parameters.

this point being denoted as E_r and the current to this point measured from the diffusion current defined for the first lanthanide wave being denoted as i_r . A considerable portion of this current is due to discharge of the supporting electrolyte, and where possible the current value for the supporting electrolyte at this point was subtracted from the measured i_r value. Because of these complications, the i_r values are not of high accuracy.

The wave parameters for the hydrogen wave were evaluated in the customary manner, with care being taken to evaluate all i_d values at the same potential value whenever comparisons were to be made.

All potential values were corrected for iR drop through the cell and measuring circuit in accordance with the procedure outlined in the operations manual supplied with the Sargent Model XXI Polarograph.

Measurement of Capillary Characteristics

The drop time (t , seconds per drop) at various potentials and mercury head values was evaluated by timing the fall of 10 or 20 drops with a stop watch and calculating an average. For the most precise values, the average obtained from two such measurements on 10 drops was employed. The variations in drop time with change in potential are extreme in the potential region being studied as is shown in Figure 4. 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 that specific composition.

The rate of flow of mercury (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 using previously determined values of t for the same conditions.

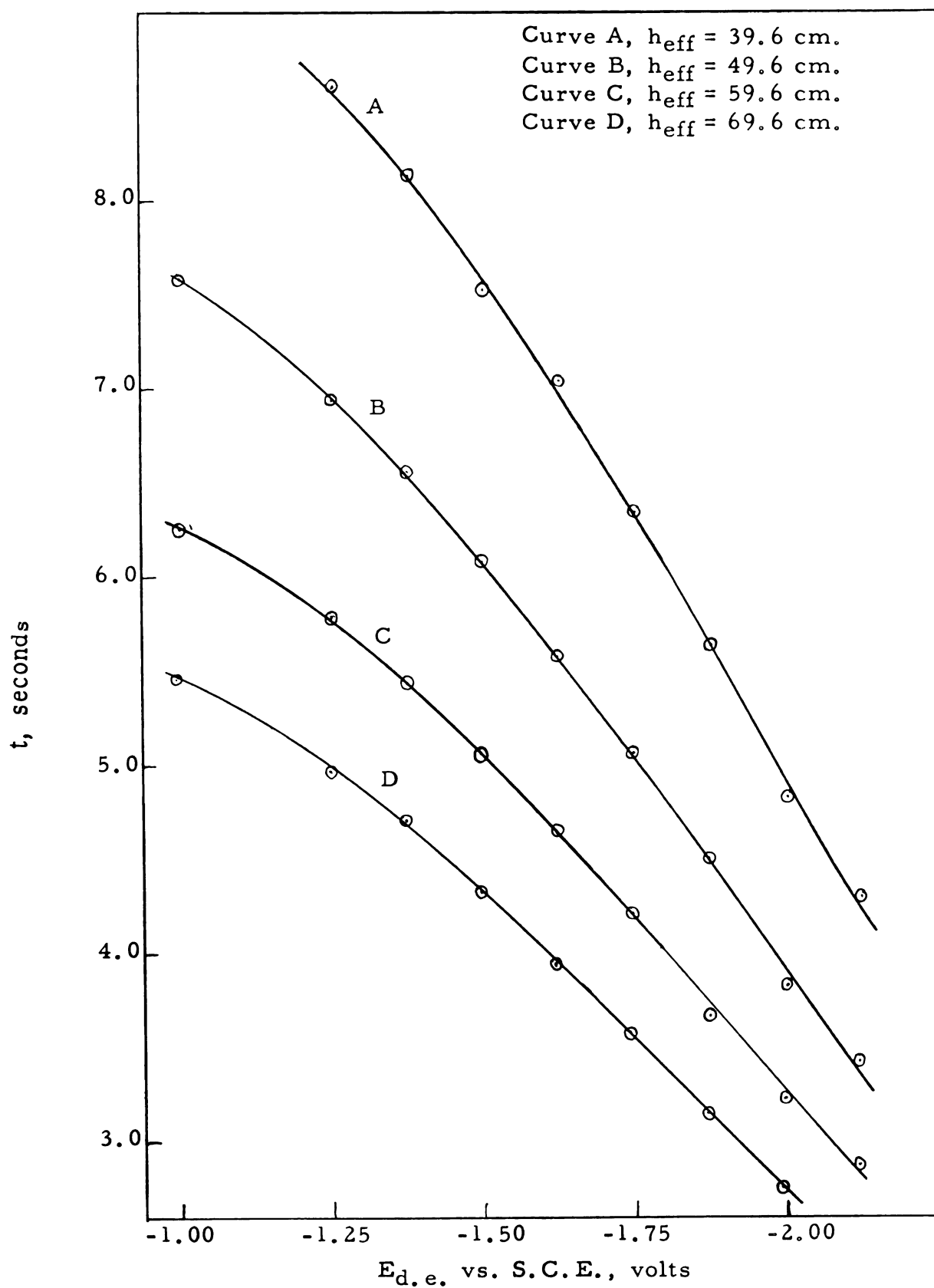


Figure 4. Variation of drop time with potential at selected mercury head values in 0.1 M LiCl--0.01% gelatin.

Measurements Related to the Effect of Mercury Pressure on the Diffusion Current

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. All h values were corrected for back pressure in the customary manner (18) to yield the effective pressure of mercury (h_{eff} , cm.). In the experiments demonstrating the interrelationship between i_d and h_{eff} , very accurate i_d values had to be obtained. Since the measurements of i_d for the lanthanide waves require measurements from the plateau of the hydrogen wave, a correction was employed to account for the decrease in i_d of the hydrogen wave as the potential increased. This decrease in i_d for the hydrogen wave is not the same for all mercury head values as can be seen from the electrocapillary curves shown in Figure 4, and is sometimes obscured by the wave resulting from the lanthanide ion. Therefore a correction factor for each head value employed was determined as follows. The decrease in the height of the plateau of the hydrogen wave was noted by measuring the slope of the plateau of the hydrogen wave obtained for hydrogen ion from HClO_4 under the same solution conditions. This slope value (S) was noted in terms of current divisions per voltage division. The distance (D) on the wave being evaluated between the intersection of the previously defined lines AB and CD and the previously defined point of measurement of i_d was noted in terms of voltage divisions. The height of the wave being evaluated was measured at the point of intersection of lines AB and CD, and the ratio (R) of the height of this wave to that of the reference hydrogen wave at the same potential was noted in terms of current divisions. The product (SDR) gave a correction term in

current divisions to account for the decrease in i_d of the hydrogen wave. This term was then compared to the decrease of the extension of line AB on the wave being measured between the intersection of lines AB and CD and the point of measurement of i_d to find the correction necessary. The actual corrections applied to the current values were small (typically 1 to 2% of the total) and somewhat approximate, but they did allow a better definition of the i_d vs. h_{eff} plots. Due to the magnitude involved, these corrections were not applied to current values employed in other portions of the work.

Instantaneous Current-Time Curves

To obtain instantaneous current-time (i-t) curves, a 100 ohm $\pm 0.5\%$ 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, and the potential values measured with the Sargent Potentiometer. Since no precise potential values were necessary in this portion of the work, only the relative position of the i-t curve on the corresponding i-E curve, no corrections were applied to the potential values for iR drop. The i-t curves as displayed on the oscilloscope were photographed with the Polaroid camera during one complete sweep. The usual operating conditions for the Tektronic Model 504 oscilloscope were; sweep time - 1 cm. per second, triggering-recurrent, sensitivity--between 0.2 and 2 mv per cm; and for the Polaroid Model 110A camera; No. 4 portrait lens type 42 film at f 16 or type 44 film at f 32, shutter release on bulb.

Since the recording of a series of current-time curves is more time consuming than an ordinary i-E curve, the potential was applied to the cell only when recording the curves to prevent unnecessary decomposition of the solution.

Maximum Current-Potential Curves

The maximum current-potential curves were obtained by substitution of the Sargent Model M.R. recorder for the recording system in the Sargent Model XXI Polarograph. This simply involved disconnecting the leads from the D. C. portion of the instrument at the point where they connect to the recording system in the instrument and connecting the leads to the M.R. recorder at this point. The potential bridge was advanced by means of the driving motor to the desired potential value and held constant for recording maximum recorder deflection. Since the maximum current values were used only to obtain E vs. $\log i/i_d - i$ plots of the waves, only maximum recorder deflections were obtained. Generally, five to ten oscillations were recorded, and the average from these was used in the calculations. The potential values were measured and corrected for iR drop as described earlier for average current-potential curves.

DISCUSSION OF RESULTS

INTRODUCTION

Shown in Figure 5 are representations of the i - E curves obtained for 1 mM dysprosium(III) at a pH of 3 (curve A), perchloric acid at a pH of 3 (curve B), and that of the supporting electrolyte, 0.1 M LiCl plus 0.01% gelatin (curve C). Of special interest is the fact that the wave resulting from the reduction of hydrogen ion precedes the waves resulting from the presence of the lanthanide ion. Therefore, in considering the processes involved in the waves due to the lanthanide ion, the fact that another electrochemical reaction is actively taking place prior and during these processes must be kept in mind.

Also of interest is the development of the waves resulting from the lanthanide ion in the presence of varying concentrations of free hydrogen ion. As the pH of the solution is increased, the first wave resulting from the lanthanide ion becomes less well-defined and difficulties in measurement of the wave parameters are the result. This same behavior was noted by Timnick (40). Therefore, to assure adequate development of the waves, some excess free hydrogen ion must always be present in the solution. However, if the hydrogen ion concentration is too high the current resulting from the discharge of hydrogen ion is too large to allow accurate measurement of the current due to the presence of the lanthanide ion. Thus for general purposes, the most practical range of hydrogen ion concentrations is that equivalent to the pH range 2.5 to 4.5.

For simplicity in the following discussion, the lanthanide ion induced waves will be separated from the hydrogen wave and identified in order as the first wave and the second wave, and will be discussed separately as far as is feasible.

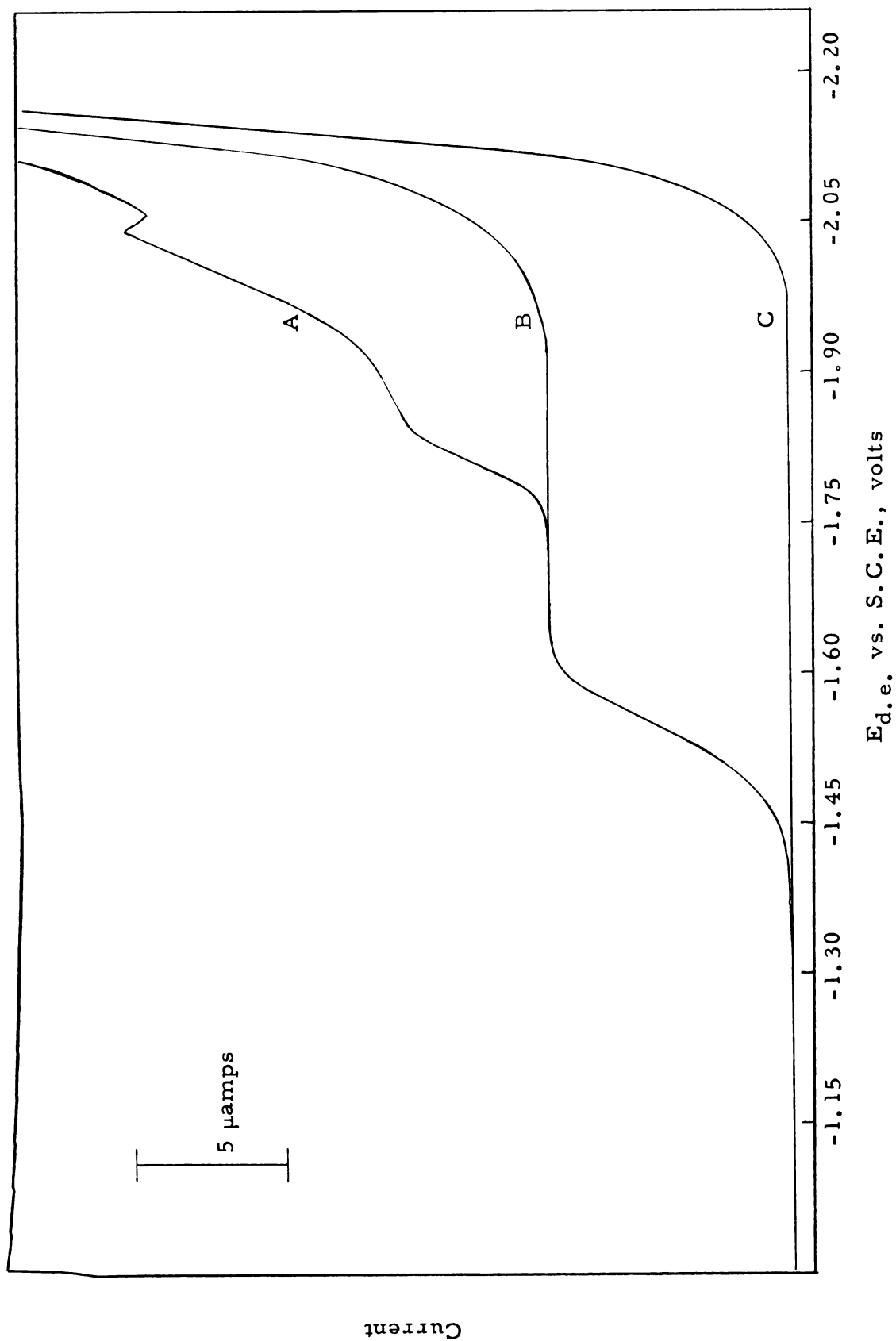


Figure 5. Comparison of the i-E curves obtained for 1 mM dysprosium(III) at a pH of 3, perchloric acid at a pH of 3 and that of the supporting electrolyte, 0.1 M LiCl--0.01% gelatin. Curve A, dysprosium(III); Curve B, perchloric acid; Curve C, 0.1 M LiCl--0.01% gelatin.

CHARACTERISTICS OF THE FIRST WAVE

Irreversible Nature of the Wave

To test the waves obtained for dysprosium(III) in 0.1 M LiCl plus 0.01% gelatin for reversibility, the waves were analyzed by the equation

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{.059}{n} \log \frac{i}{i_d - i}$$

by plotting $E_{d.e.}$ against $\log i/i_d - i$, which for a reversible process should yield a straight line with a slope of $\frac{0.059}{n}$ volts at 25°. Adherence to this equation is the most widely applied test for the reversibility of a wave. As examples of the nature of the first lanthanide wave the results obtained for 1 mM dysprosium(III) at two acidities are shown in Figure 6 and Table I. The plots obtained show curvature, are not symmetrical about the zero log intercept or true $E_{\frac{1}{2}}$, and give non-integral values of n . From these facts, it can be assumed that the process involved is not a reversible one, and in such case, any attempts to predict an n value from the slope of the plots is impossible (19).

Further evidence of the irreversibility of the process giving rise to this wave is the high value, +5 mv per degree, of the temperature coefficient of $E_{\frac{1}{2}}$ obtained over the temperature range 20° to 30°. For a reversible process, the temperature coefficient of $E_{\frac{1}{2}}$ should be much lower, and any value greater than 3 mv per degree is accepted as indicative of an irreversible process (20).

The method described by Meites and Israel (21) for the analysis of irreversible waves employing maximum current values and constructing a plot of $E_{d.e.}$ against $[\log i/i_d - i - 0.546 \log t]$ (where t is the drop time) was applied to this wave. From such a plot αn_a (α is the transfer coefficient, n_a is the number of electrons involved in the rate determining

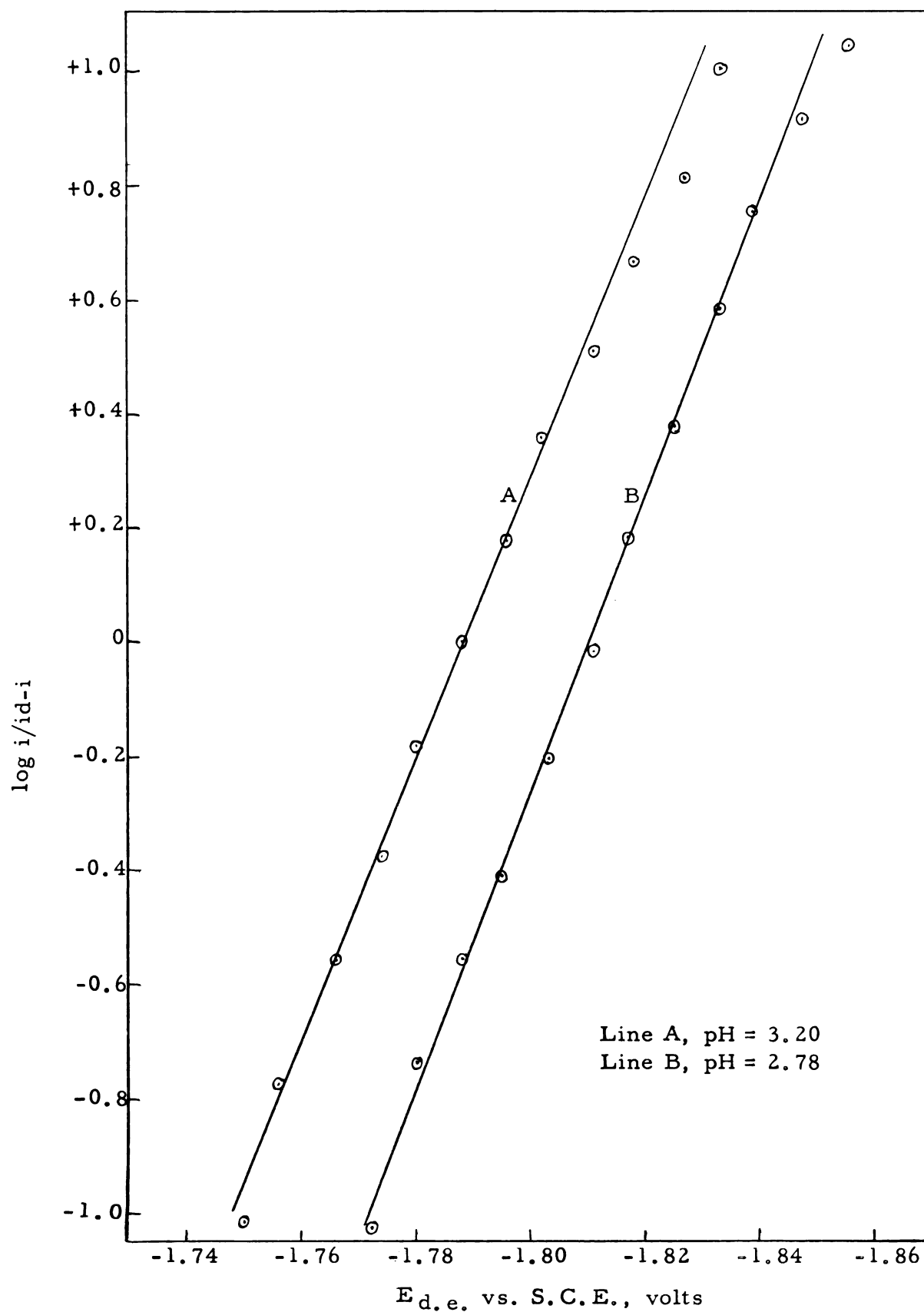


Figure 6. Plots of $E_{d.e.}$ against $\log i/id-i$ for 1 mM dysprosium(III) in 0.1 M LiCl-0.01% gelatin.

Table I. $E_{d.e.}$ versus $\log i/i_d-i$ Values for the First Wave

1 mM Dysprosium(III) in 0.1 M LiCl with 0.01% Gelatin			
at pH = 2.78		at pH = 3.20	
$E_{d.e.}$ (v. vs. S.C.E.)	$\log i/i_d-i$	$E_{d.e.}$ (v. vs. S.C.E.)	$\log i/i_d-i$
-1.764	-1.490	-1.732	-1.410
-1.772	-1.028	-1.741	-1.210
-1.780	-0.737	-1.750	-1.015
-1.788	-0.556	-1.756	-0.773
-1.795	-0.410	-1.766	-0.557
-1.803	-0.204	-1.774	-0.373
-1.811	-0.018	-1.780	-0.182
-1.817	-0.181	-1.788	0
-1.825	+0.378	-1.796	+0.178
-1.833	+0.583	-1.802	+0.357
-1.839	+0.751	-1.811	+0.510
-1.848	+0.913	-1.818	+0.665
-1.856	+1.039	-1.827	+0.814
		-1.833	+1.005
		-1.841	+1.210

process) may be evaluated from the slope, and $k_{f,h}^0$ (the forward heterogeneous rate constant for the electrochemical reaction) may be evaluated from the intercept. Such a plot for a 1 mM solution of dysprosium(III) in 0.1 M LiCl with 0.01% gelatin at a pH of 3.00 yields a straight line with a slope of 34 mv. and an intercept of -1.806 v. vs. S.C.E. However, the applicability of this method to the wave being studied is in question, thus no conclusions were drawn from these values.

Variation of the Wave Parameters with Solution Composition

To study the effect of the concentration of free hydrogen ion on the wave parameters $E_{\frac{1}{2}}$ and i_d , solutions of dysprosium(III) in 0.1 M LiCl plus 0.01% gelatin were prepared varying only in pH and were electrolyzed under similar conditions. The results are shown in Table II and Figure 7.

Table II. Variation of the Current-Potential Characteristics of the First Wave with Change in pH

0.8 mM Dysprosium(III) in 0.1 M LiCl plus 0.01% Gelatin		
pH	$E_{\frac{1}{2}}$ (v. vs. S.C.E.)	i_d (μ amps)
2.59	-1.849	3.42
2.78	-1.828	3.50
2.98	-1.806	3.60
3.18	-1.795	3.78
3.53	-1.768	3.92
4.02	-1.735	4.02

The wave shows a marked pH effect with $E_{\frac{1}{2}}$ becoming more negative with a decrease in pH. The slope of the $E_{\frac{1}{2}}$ vs. pH plot for 0.8 mM dysprosium(III) in 0.1 M LiCl plus 0.01% gelatin as shown in Figure 7 is 82 mv. per pH unit and is representative of all such values obtained. This shift in $E_{\frac{1}{2}}$ with change in pH is in the same direction and of the same order of magnitude as the shift in $E_{\frac{1}{2}}$ with change in concentration observed for a weak acid in unbuffered solutions when the process giving rise to a polarographic wave is the reduction of hydrogen ion produced by the dissociation of the weak acid (14). This behavior may

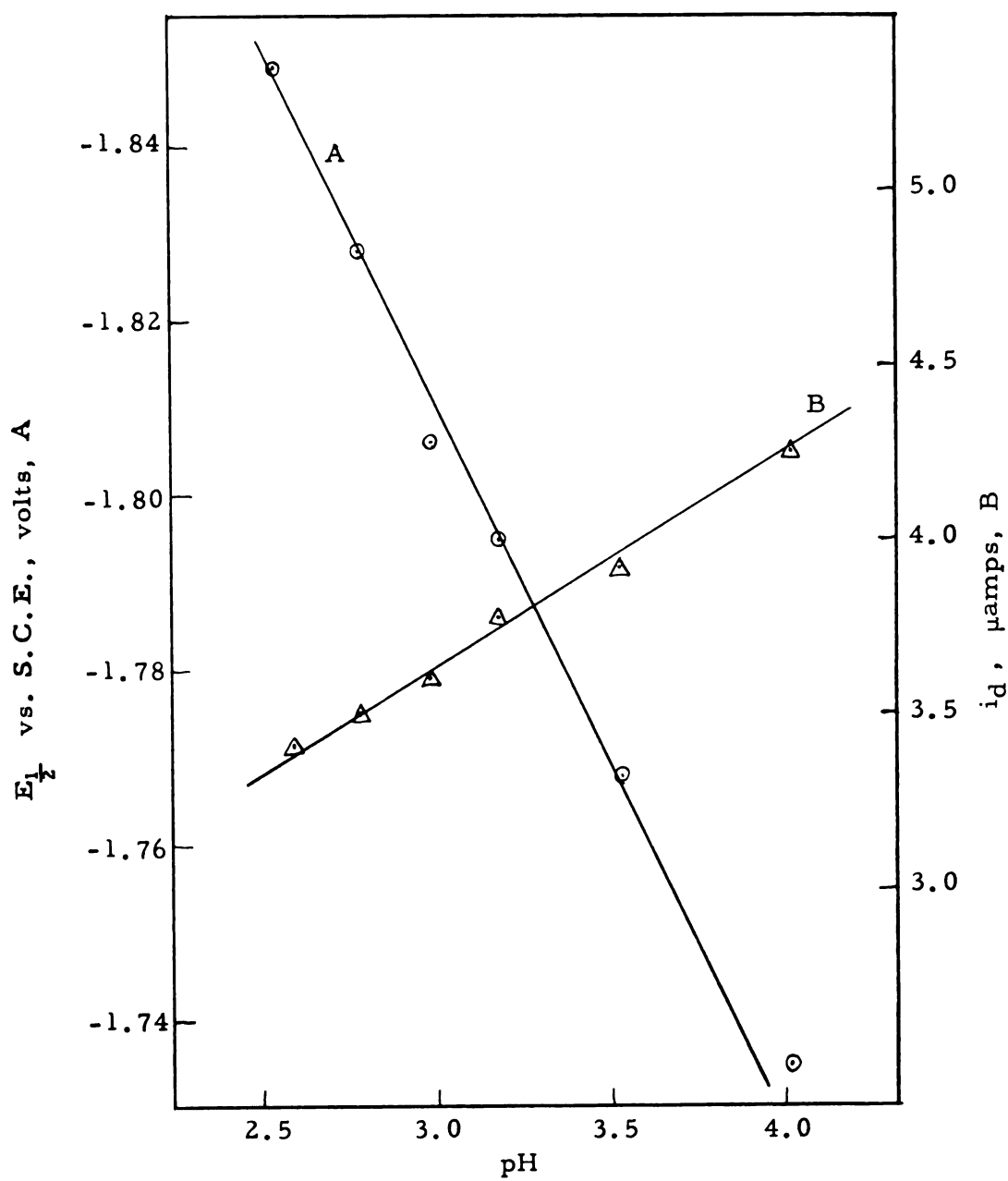


Figure 7. Variation of wave parameters of the first wave with change in pH. 0.8 mM dysprosium(III) in 0.1 M LiCl--0.01% gelatin.

be rationalized for the wave resulting from the presence of the lanthanide ion in the following manner.

The lanthanide ion begins to hydrolyze and form the gelatinous hydrous oxide at a pH between 6 and 7 as can be seen from Figure 2. The conditions at the electrode surface and in the solution in the immediate vicinity of the electrode, which shall be called the reaction layer, are drastically affected by the diffusion controlled reduction of hydrogen ion. With such depletion of the hydrogen ion concentration, the solution conditions in the reaction layer should approximate conditions favorable to hydrolysis of the lanthanide species diffusing into this volume of solution. However, the actual conditions in the reaction layer are determined by the flux of hydrogen ions from the bulk of the solution, and are thus dependent on the hydrogen ion concentration in the bulk of the solution. Changes in the effective free hydrogen ion concentration thus established in the reaction layer would have the same effect on the protolytic dissociation (hydrolysis) of the lanthanide species as changes in concentration of a weak acid would have on the dissociation of the acid, i. e., an increase in concentration of a weak acid represses dissociation, and an increase in the flux of hydrogen ions into the reaction layer represses dissociation of the hydrated lanthanide ion.

Thus, the variation of $E_{\frac{1}{2}}$ with changes in the hydrogen ion concentration suggests that the actual reduction process associated with the lanthanide ion is the reduction of hydrogen ions produced by protolytic dissociation of the hydrated lanthanide ion.

The decrease in i_d with decrease in pH as shown in Table II and Figure 7 is also in keeping with this protolytic behavior. As the flux of hydrogen ions into the reaction layer is increased, the protolytic dissociation of the lanthanide ion is repressed, which results in a lower i_d . This pattern of behavior is indicative of a current controlled by an

antecedent chemical reaction, and is representative of the general classification of polarographic currents known as kinetic currents.

At this point, a comparison of the observed current values to those calculated by the Ilkovic equation which states that

$$i_d = 607 n D^{\frac{1}{2}} c m^{\frac{2}{3}} t^{\frac{1}{6}}$$

where i_d = the diffusion current in μ amps.

n = the number of faradays of electricity required per mole

D = the diffusion coefficient in $\text{cm.}^2 \text{ second}^{-1}$

m = the rate of mercury flow in mgs. per second

t = the drop time in seconds

c = concentration in moles per ml.,

is of interest, and to this end an estimation of the diffusion coefficient of the dysprosium(III) ion is required.

For polarographic purposes, the diffusion coefficient of an ion under the actual conditions employed may be approximated by evaluating the diffusion coefficient at infinite dilution (13). The diffusion coefficient at infinite dilution of an ion may be evaluated by the following Nernst expression,

$$D_o = 2.67 \times 10^{-7} \frac{\lambda_o}{Z} \text{ cm.}^2 \text{ second}^{-1}$$

where D_o = diffusion coefficient at infinite dilution

λ_o = equivalent conductivity at infinite dilution

Z = charge on the ion.

The diffusion coefficient at infinite dilution of dysprosium(III) was calculated to be $5.85 \times 10^{-6} \text{ cm.}^2 \text{ second}^{-1}$, employing the value of the equivalent conductivity at infinite dilution of DyCl_3 of $142.0 \text{ mhos cm.}^{-1}$, as given by Dye and Spedding (4) and the usually accepted value of 76.3 for the equivalent conductivity of the chloride ion at infinite dilution.

Employing the above calculated value of D , experimentally determined values of m and t of 1.12 mgs. per second and 4.05 seconds respectively, and a value of 3 for n , the i_d as calculated by the Ilkovic equation is 6.00 μ amps for 1 mM dysprosium(III) in 0.1 M LiCl plus 0.01% gelatin at a pH of 3.0.

The experimentally determined i_d values are approximately five-sixths of this value, which leads to the assumption that if n is 3, the observed current values are less than the calculated i_d values because of the kinetic character of the processes giving rise to the wave.

The relationship between the wave parameters i_d and $E_{\frac{1}{2}}$ and the concentration of lanthanide ion at constant pH is shown in Table III and Figure 8 for dysprosium(III) concentrations between 0.2 and 5.0 mM in 0.1 M LiCl with 0.01% gelatin at a pH of 3.00. As can be seen from Figure 8, the observed i_d is proportional to the concentration over the range tested at a constant pH value.

Table III. Variation of Current-Potential Characteristics of the First Wave with Change in Dysprosium(III) Concentration at Constant pH

0.1 M LiCl with 0.01% Gelatin at a pH of 3.00		
Conc. (moles/ml)	$E_{\frac{1}{2}}$ (v. vs. S.C.E.)	i_d (μ amps)
0.2	-1.801	1.00
0.5	-1.802	2.48
0.8	-1.803	3.91
1.0	-1.799	5.03
2.0	-1.813	10.79
5.0	-1.815	27.33

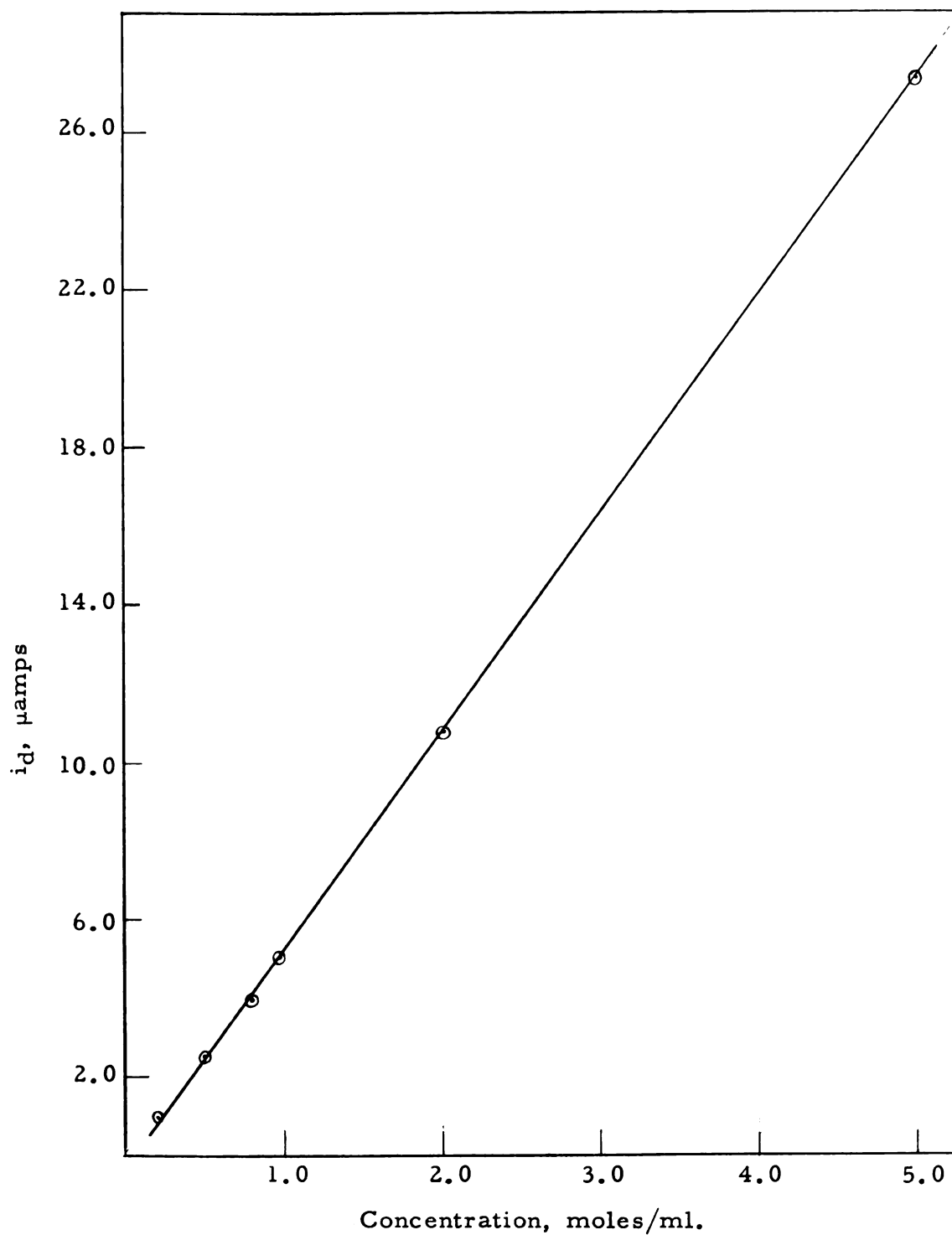


Figure 8. Variation in i_d of the first wave with changes in concentration at a constant pH. Dysprosium(III) in 0.1 M LiCl with 0.01% gelatin at a pH of 3.00.

From Table III it can be seen that there is no variation in $E_{\frac{1}{2}}$ with change in concentration of the lanthanide ion at constant pH other than that to be expected in measurements over such a concentration range. Thus the concentration of the lanthanide ion has little or no effect on $E_{\frac{1}{2}}$ as compared to that of pH, and control of the flux of hydrogen ions from the bulk of the solution into the reaction layer by keeping the pH at a constant value as the concentration varies serves as a "buffer" to level any effect on the dissociation process by the concentration of the lanthanide ion.

Novak (28) has shown that the $E_{\frac{1}{2}}$ for the reduction of the deuterium ion from DCl in D_2O is more negative than that for the reduction of an equal concentration of hydrogen ion from HCl in H_2O , and has also noted that the extent of the shift of $E_{\frac{1}{2}}$ to more negative potentials is determined by the relative amount of H_2O present in the D_2O . The values of the potential shift for particular solvent compositions were as follows: 87 mv. more negative in 99.6% D_2O , 80 mv. in 99.1% D_2O , 63 mv. in 94.6% D_2O , 31 mv. in 76.5% D_2O . Furthermore, he established that such shifts in $E_{\frac{1}{2}}$ to more negative potentials were not observed for processes not involving the reduction of hydrogen(deuterium) ion. Thus, if the reduction process associated with the lanthanide ion wave actually involves the reduction of hydrogen ions, a shift of $E_{\frac{1}{2}}$ to more negative potentials should be observed if the process is carried out in D_2O .

Solutions of dysprosium(III) were prepared as described in the experimental section containing the same concentrations of dysprosium(III), $HClO_4$, supporting electrolyte and gelatin as a reference solution in H_2O , and were electrolyzed under identical conditions. A comparison of the $i-E$ curves obtained for these solutions in D_2O to the reference solutions in H_2O is shown in Figure 9. A marked shift along the potential axis is evident in the waves.

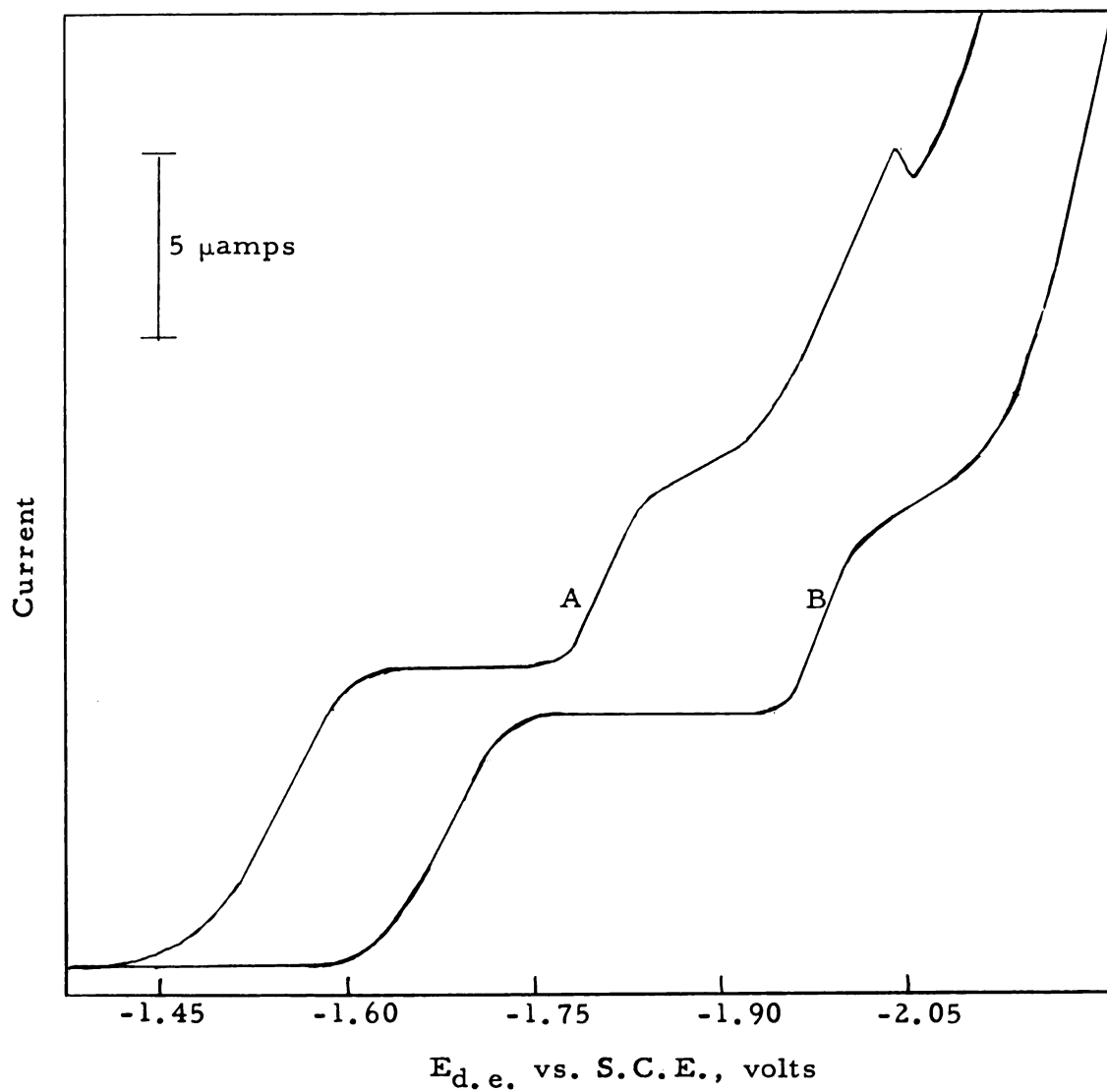


Figure 9. Comparison of the i - E curve obtained in D_2O to that of the reference solution in H_2O . Curve A, - 1 mM dysprosium(III) in 0.1 M LiCl--0.01% gelatin at pH = 3.0, Curve B, - similar solution in D_2O .

Two attempts were made and the value of the shift obtained in the first attempt was 60 mv. while the value obtained in the second was 140 mv. However, in the first attempt, the exact dilution of the D_2O with H_2O was not known, but the sample was considerably more dilute than the second attempt. In the second attempt, the solution preparation and handling technics were improved and the electrolysis was carried out immediately after preparation, thus the D_2O content of the sample was much higher than the first.

A value of the potential shift in $E_{\frac{1}{2}}$ of greater than the 80 mv. value obtained by Novak is not unexpected if the reduction process is preceded by a chemical reaction as the D_2O would certainly have an effect upon the rate of any chemical reaction, which in turn would give rise to an additional shift to more negative potentials.

It was also found that changing the solvent composition by the addition of a slight amount of water shifts the wave to more positive values than are observed with high D_2O content.

The solutions in D_2O , as initially prepared, were estimated to be approximately 98% D_2O at best, and were of course continually being contaminated with H_2O while in the cell. On this basis, determinations of precise values of the $E_{\frac{1}{2}}$ shifts involved are impossible.

As is shown in Figure 9, the most striking observation in the comparison of the i - E curves is the disappearance of the second wave. However, the shift to more negative potentials puts this process into a potential region where the discharge of the supporting electrolyte gives a considerable current, and it is probable that the second process blends in with that of the supporting electrolyte and thus no second wave is observed.

Solutions were prepared employing various salts as supporting electrolyte at the same concentration and with the same concentrations of dysprosium(III) and gelatin. Two waves related to the lanthanide ion

were obtained in all cases. The choice of supporting electrolyte has no particular effect on the waves as is shown in Table IV which compares the $E_{\frac{1}{2}}$ values obtained in various media to that obtained in LiCl at the same pH.

Table IV. Comparison of $E_{\frac{1}{2}}$ Values in Various Supporting Electrolytes

1.0 mM Dysprosium(III) in 0.1 M Solutions of the Supporting Electrolyte with 0.01% Gelatin		
Supporting Electrolyte	pH	$E_{\frac{1}{2}}$ (v. vs. S.C.E.)
Me ₄ NI	2.92	-1.809
LiCl	2.92	-1.816
LiClO ₄	2.75	-1.835
LiCl	2.75	-1.831
Li ₂ SO ₄	3.18	-1.805
LiCl	3.18	-1.796

The effect of gelatin on the wave is illustrated in Figure 10. As is shown in the figure, the primary effect is on the hydrogen wave, not on the wave induced by the lanthanide ion. In the absence of any gelatin and at hydrogen ion concentrations sufficient to give a well-defined hydrogen wave, the hydrogen wave is quite drawn out due to a prolonged maximum and merges with the wave produced by the lanthanide ion such that there is no visible first wave directly related to the presence of the lanthanide ion. However, the addition of a slight amount of gelatin allows the development of the lanthanide ion first wave. Triton x-100 gives very similar results. At lower hydrogen ion concentrations (pH 3.5), the lanthanide ion wave is visible before the addition

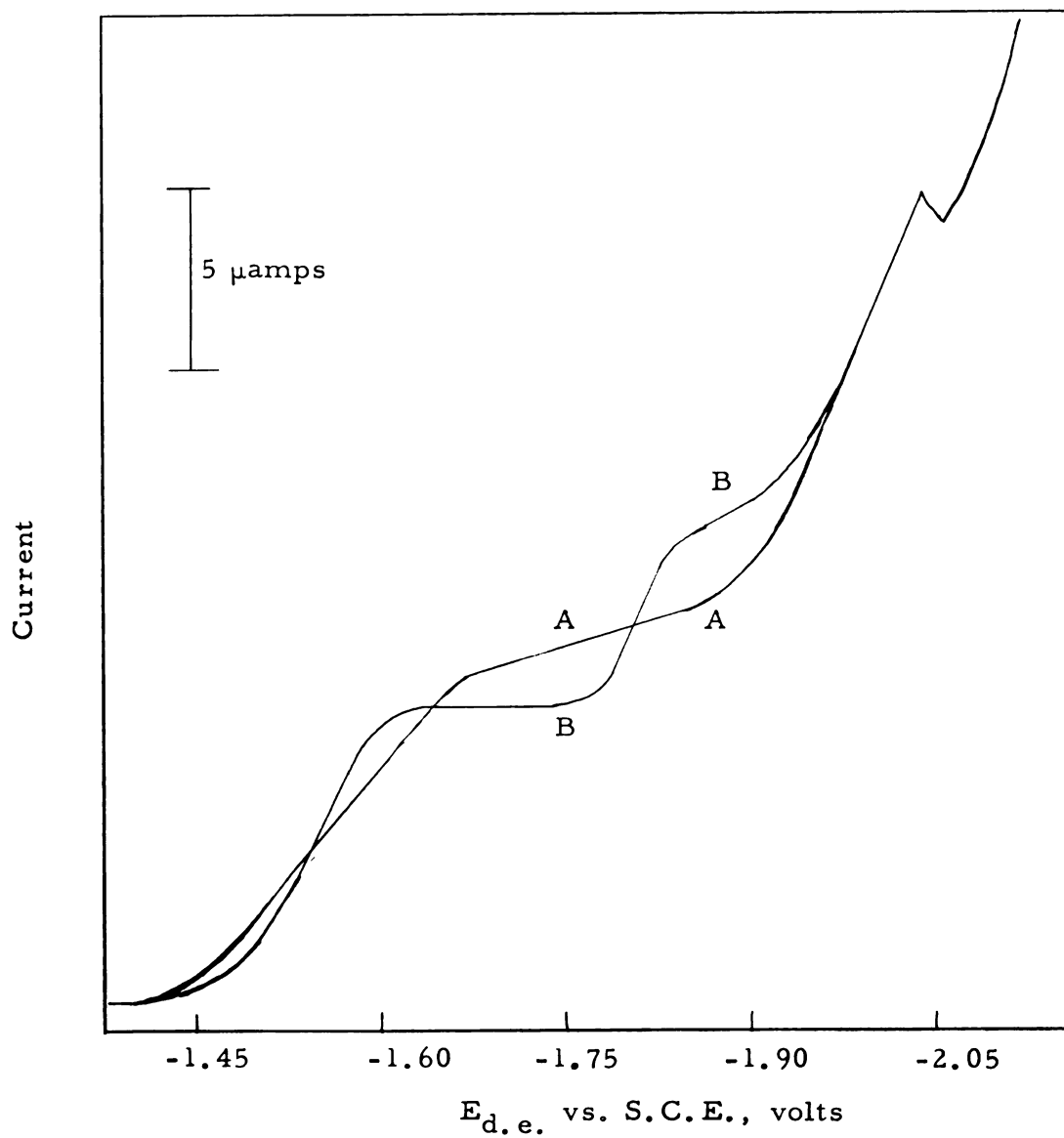


Figure 10. Comparison of the i - E curves obtained for 1 mM dysprosium(III) in 0.1 M LiCl at a pH of 3 in the presence and in the absence of gelatin. Curve A, - no gelatin; Curve B, - 0.01% gelatin.

of gelatin. In either instance, the lanthanide ion wave exhibits a slight maximum until the concentration of maximum suppressor approaches 0.01%.

The observations by other workers (43) concerning the disappearance of polarographic waves for lanthanide ions in the presence of citrate or tartrate ions is consistent with the electrode process presented in this work since complexation of the lanthanide ion would certainly reduce the extent of hydrolysis. The improvement of yields in electrolytic separations of the lanthanide ions in the presence of citrate or tartrate ions can also be explained by consideration of this reduction in the extent of hydrolysis.

Variations in the Diffusion Current with Variations in Mercury Pressure

The relationship between the diffusion current and the pressure of mercury arises from the dependence of the capillary characteristics m and t on the pressure of mercury. The pressure of mercury is a function of the height of the mercury column which is referred to as h_{eff} after the appropriate back pressure correction (18). The rate of mercury flow is directly proportional to h_{eff} and the drop time is inversely proportional to h_{eff} . Combining these two relationships by their effect on i_d , the relationship i_d is proportional to $(h_{\text{eff}})^{\frac{1}{2}}$ is obtained. Thus for a diffusion controlled process, i_d is proportional to the square root of the effective pressure of mercury, and a plot of i_d against $(h_{\text{eff}})^{\frac{1}{2}}$ should yield a straight line which passes through the origin.

Also of interest is the relationship between h_{eff} and the limiting current for a kinetic process. Since in a kinetic process the limiting current is controlled by the rate of a chemical reaction and not by the rate of diffusion, it is independent of h_{eff} and a plot of i_d against

$(h_{\text{eff}})^{\frac{1}{2}}$ gives a straight line parallel to the h_{eff} axis. A combination of both diffusion and kinetic control of an electrochemical reaction results in an intermediate behavior, and a plot of $(h_{\text{eff}})^{\frac{1}{2}}$ against i_d yields a straight line but one which does not pass through the origin.

Plots of i_d against $(h_{\text{eff}})^{\frac{1}{2}}$ for the wave in question are shown in Figures 11 and 12 and the values are tabulated in Table V. For 1 mM dysprosium(III) in 0.1 M LiCl with 0.01% gelatin and with HClO_4 concentrations sufficient to yield a pH of approximately 3, a straight line is obtained which does not pass through the origin and denotes behavior which is intermediate between diffusion and kinetic control. With 2 mM dysprosium(III) in the same medium but with a lower acid concentration, the line begins to approximate that to be expected for diffusion control.

Of particular interest is the variation in the i_d against h_{eff} relationship observed as the pH varies with a 1 mM dysprosium(III) solution. When the pH is decreased from a value of 3.20 to 2.78, the i_d against $(h_{\text{eff}})^{\frac{1}{2}}$ plot obtained for the lower pH value shows less diffusion control than that for the higher value as is illustrated in Figure 12. This behavior is in keeping with the variations of i_d and $E_{\frac{1}{2}}$ with pH previously mentioned and is again indicative of some kinetic control.

A comparison of i_d against $(h_{\text{eff}})^{\frac{1}{2}}$ plot obtained for a solution of dysprosium(III) in D_2O to that obtained for a solution in H_2O of similar composition is shown in Figure 13. As would be expected, the plots obtained for the D_2O solution show a greater kinetic control of the current. The current values are also somewhat less as would be expected.

Brdicka (1) has recently summarized the development of theoretical equations to describe the behavior of kinetic currents, and for a process of the type expressed by the equilibrium $\text{HA} \xrightleftharpoons[k_{-1}]{k} \text{H}^+ + \text{A}^-$ the following equation is applicable:

Table V. Variation in the Diffusion Current with Variations in Mercury Pressure

0.1 M LiCl with 0.01% Gelatin			
$(h_{\text{eff}})^{\frac{1}{2}}, \text{cm.}^{\frac{1}{2}}$	Dy(III) Conc. moles/ml.	pH	$i_d, \mu\text{amps}$
8.35	1.0	2.78	5.24
7.72	1.0	2.78	5.04
7.04	1.0	2.78	4.67
6.68	1.0	2.78	4.52
6.29	1.0	2.78	4.40
8.35	1.0	2.95	5.61
7.72	1.0	2.95	5.19
7.04	1.0	2.95	4.78
6.68	1.0	2.95	4.66
6.29	1.0	2.95	4.40
8.35	1.0	3.20	5.71
7.72	1.0	3.20	5.37
7.04	1.0	3.20	4.85
6.68	1.0	3.20	4.69
6.29	1.0	3.20	4.43
8.35	2.0	3.55	11.64
7.72	2.0	3.55	10.73
7.04	2.0	3.55	9.82
6.68	2.0	3.55	9.17
6.29	2.0	3.55	8.83

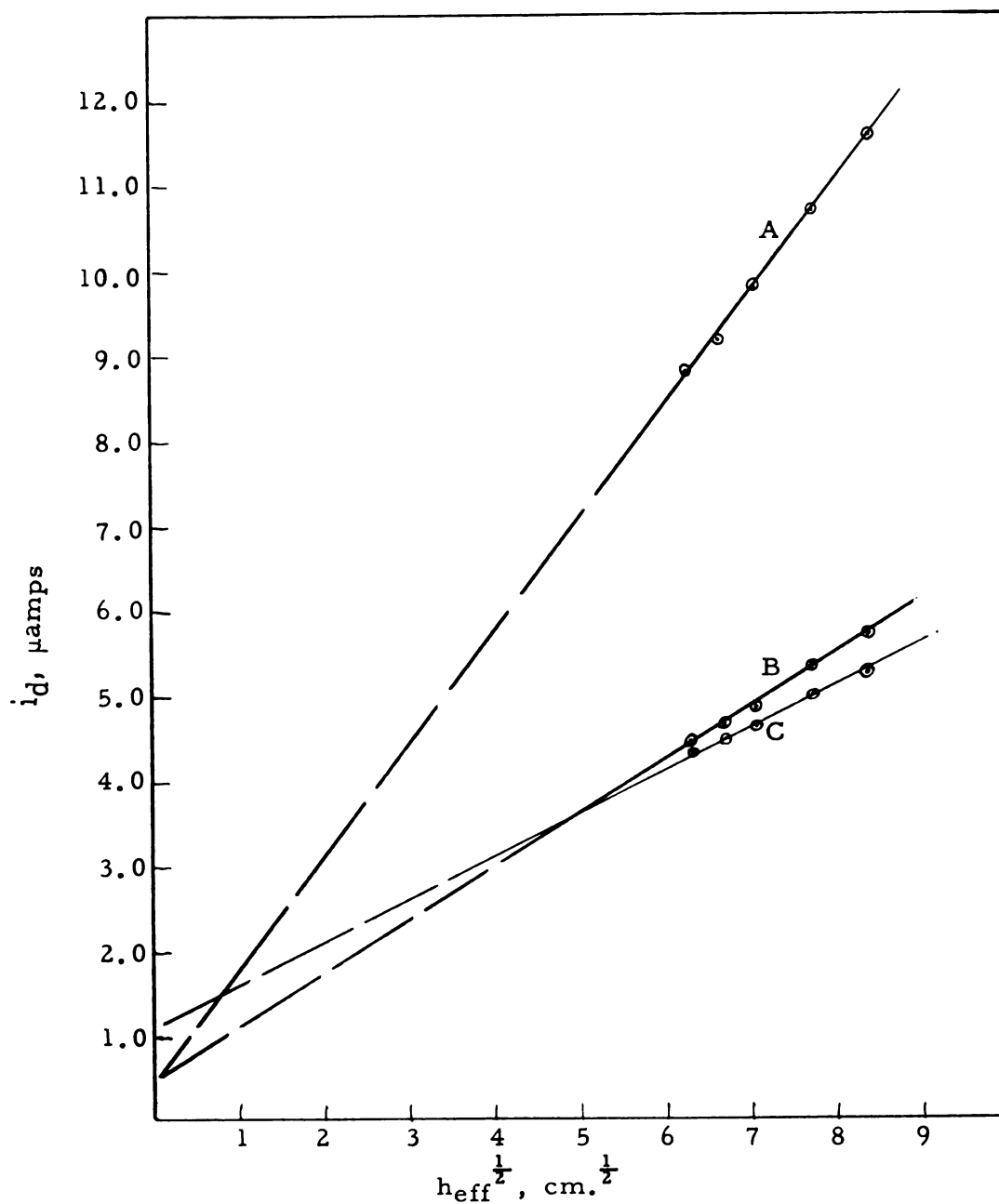


Figure 11. Variation in i_d of the first wave with changes in h_{eff} . Line A, 2 mM dysprosium(III) in 0.1 M LiCl-0.01% gelatin at pH = 3.55; Line B, 1 mM dysprosium(III) in 0.1 M LiCl--0.01% gelatin at pH = 3.20; Line C, 1 mM dysprosium(III) in 0.1 M LiCl-0.01% gelatin at pH = 2.78.

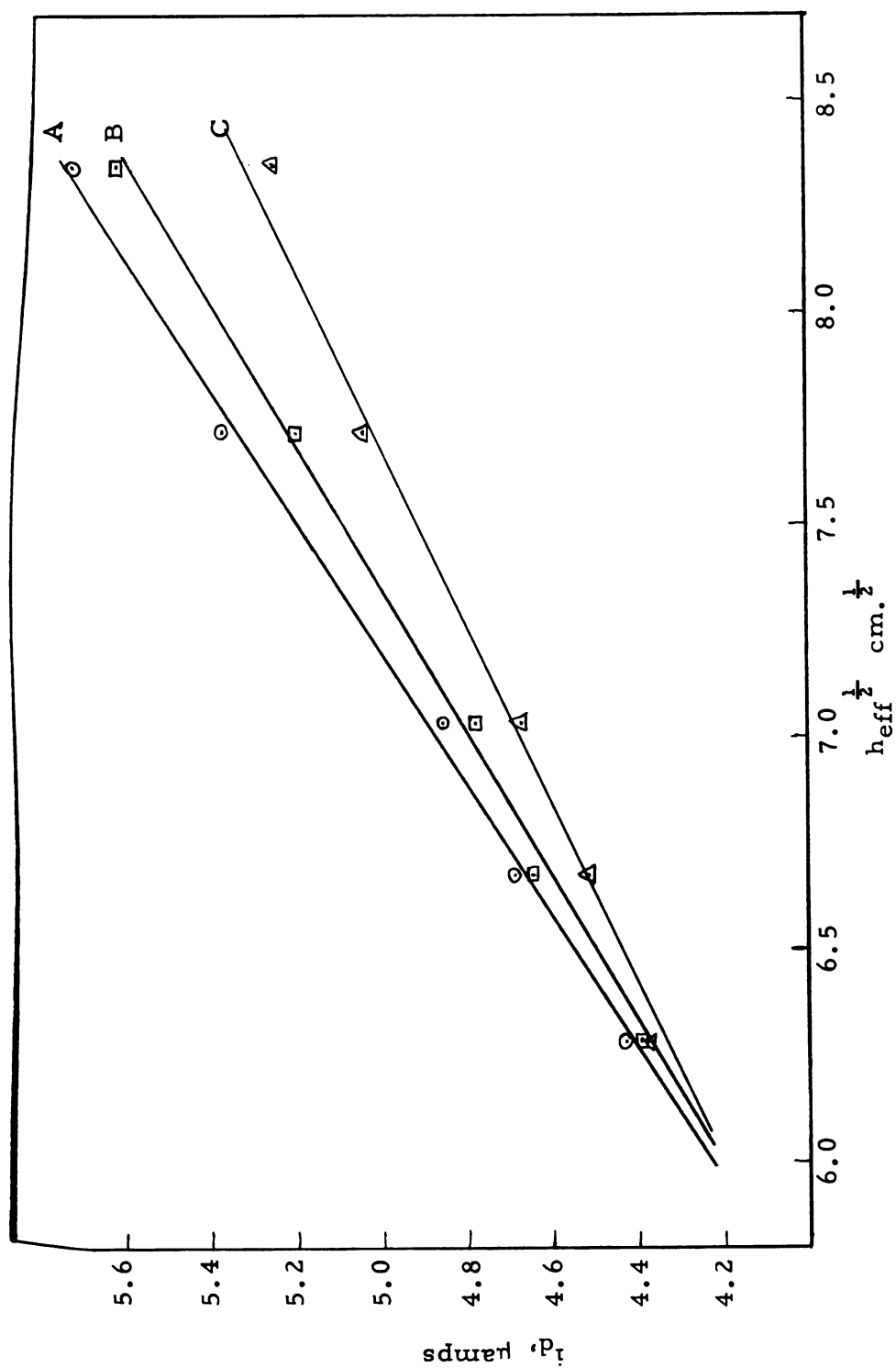


Figure 12. Variation in i_d vs. h_{eff} relationship of the first wave with change in pH. 1 mM dysprosium(III) in 0.1 M LiCl--0.01% gelatin. Curve A, pH = 3.20; Curve B, pH = 2.95; Curve C, pH = 2.78.

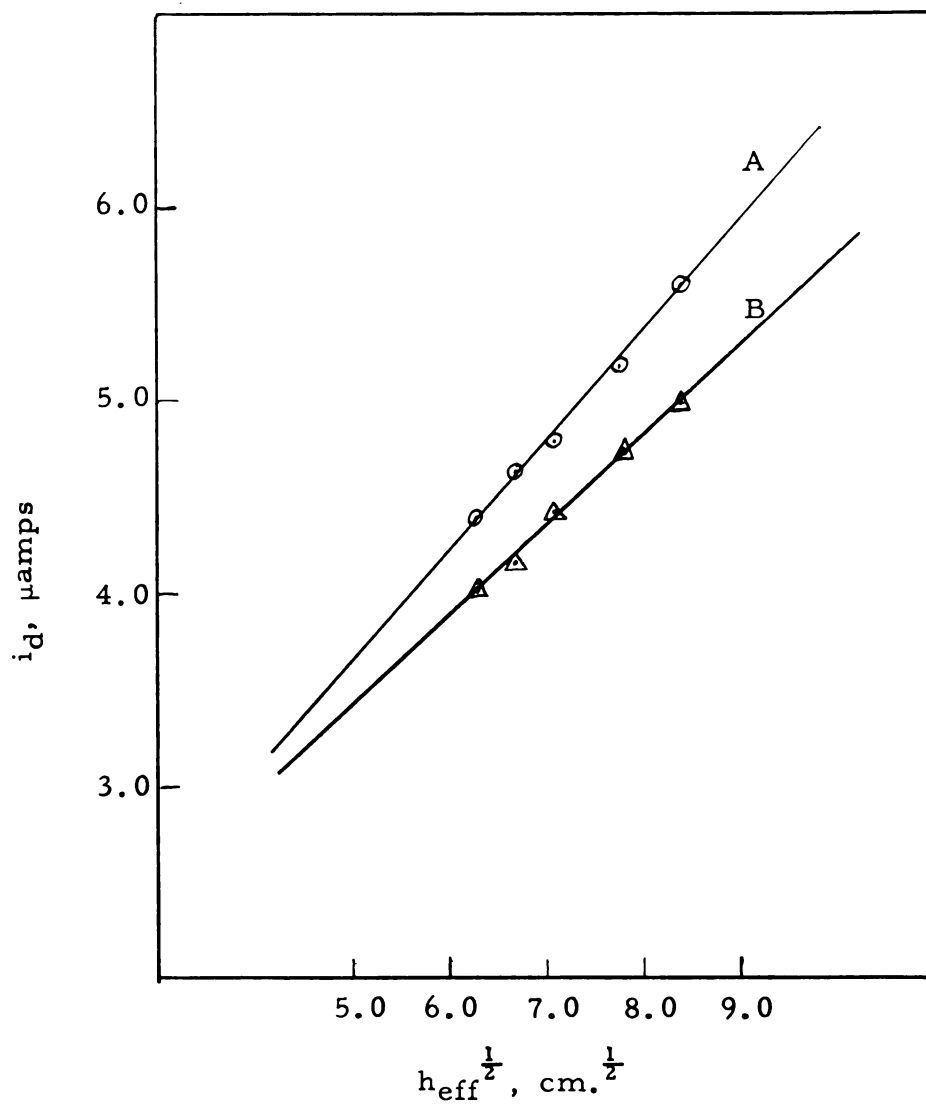


Figure 13. Comparison of the i_d vs. $(h_{\text{eff}})^{1/2}$ plot obtained in D_2O to that of the reference solution in H_2O . Curve A, 1 mM dysprosium(III) in 0.1 M LiCl--0.01% gelatin at a pH of 3 in H_2O ; Curve B, similar solution in D_2O .

$$\frac{y^{\frac{3}{2}}}{1-y} = 0.81 a \sqrt{\frac{\delta K k t}{[HA]}}$$

where y = ratio of observed limiting current to the i_d calculated by the Ilkovic equation

$a = \sqrt{\frac{2n}{1+n}}$, where n is the stoichiometric factor of the electroactive species in the chemical reaction producing this species

$\delta = \frac{D_{H^+}}{D_{HA}} \sqrt{\frac{D_{A^-}}{D_{HA}}}$, where D is the diffusion coefficient

K = the equilibrium constant

k = the formal rate constant for the forward reaction

t = the drop time

This equation has been employed to calculate the k and k_{-1} values for a number of weak acids, and this application appears to be the most interesting aspect of the development of the equation (2). No k and k_{-1} values can be calculated for the dissociation process for the lanthanide ion as no value for K is at hand.

The value of $(kK)^{\frac{1}{2}}$ also gives information pertaining to the diffusion controlled nature of a wave. If the value obtained of $(kK)^{\frac{1}{2}}$ is 5 second ^{$-\frac{1}{2}$} or greater the electrochemical process is considered to be essentially diffusion controlled, if the value of $(kK)^{\frac{1}{2}}$ is 0.05 second ^{$-\frac{1}{2}$} or smaller the process is essentially kinetic controlled and intermediate values of this product denote mixed kinetic and diffusion control (3). The values obtained for the lanthanide ion process assuming $n = 3$, a value of 9.34×10^{-5} cm² second ^{$^{-1}$} for D for the hydrogen ion (12), the value calculated earlier for D for dysprosium(III), the ratio of (D_{A^-}/D_{HA}) to be unity, and calculating i_d by the Ilkovic equation are in the vicinity of 0.65 seconds ^{$^{-\frac{1}{2}}$} . This value is in general agreement with the observed i_d against $(h_{eff})^{\frac{1}{2}}$ behavior.

Current-Time Relationships

As predicted by the Ilkovic equation, the current during the course of a single mercury drop is proportional to the one-sixth power of time. This relationship has been shown to hold over the entire course of a wave for a reversible polarographic process (16). However, for an irreversible process, the current time relationship varies during the course of the wave, the current being proportional to the two-thirds power of time at very small values of the current as compared to the limiting current, and with a gradual decrease over the course of the wave until a current dependence on the one-sixth power of time is attained in the limiting current portion of the wave.

A further effect, which has been conclusively demonstrated by Kuta and Smoler (16), is that the i - t curve for the first drop after application of a potential is quite different from that observed with any subsequent drops due to an inherited concentration depletion of the solution into which the second and further drops grow. Thus for any drop other than the first drop, the current dependence on time will never reach the theoretical value, and the exponent of time varies over the course of the drop.

An additional factor of importance is that the addition of gelatin slightly alters the i - t relationships during the course of the drop, and tends to lower the value of the limiting current. However, with all these deviations from the theoretical behavior combined, the i - t curves experimentally observed for well-defined polarographic processes are still smooth curves which are suggestive of the theoretical behavior.

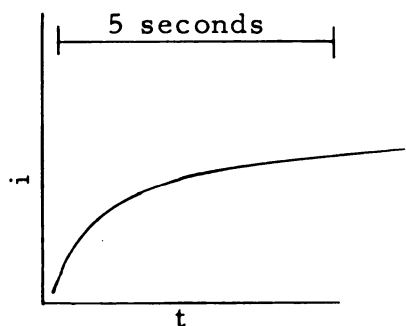
To test the experimental technic employed in this work, i - t curves were obtained for millimolar solutions of cadmium(II), lead(II), and hydrogen ion. The i - t curves observed during the course of the polarographic reduction of these ions were all smooth curves closely

resembling the expected behavior. An example of the i - t curves obtained for cadmium(II) is shown in Figure 14, curve A.

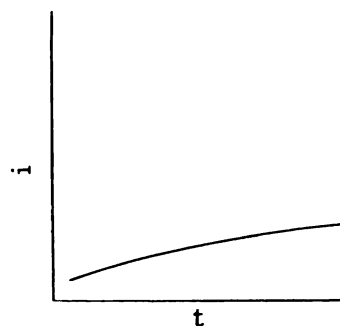
Shown in Figures 14 and 15 are the i - t curves obtained at various potentials with a solution of dysprosium(III) in 0.1 M LiCl plus 0.01% gelatin at a pH of approximately 3. Curve B of Figure 14 shows the i - t curve obtained at a potential on the rising portion of the hydrogen wave, curve C of Figure 14 shows the i - t curve obtained at a potential on the plateau of the hydrogen wave, both of which are quite regular. Curves D of Figure 14 through G of Figure 15 show the i - t curves obtained at potentials on the rising portion of the first wave related to lanthanide ion, and curve H of Figure 15 shows the i - t curve obtained at a potential on the plateau of the first wave related to the lanthanide ion, which is again regular. *curve 3?*

The irregularities seen on curves D through G are reproducible, and are not seen with a solution equivalent to that being observed but without the lanthanide ion.

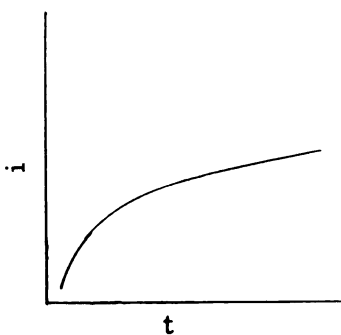
No precedent was found in the literature pertaining to i - t curves of this nature, and an exact interpretation of the phenomena is not possible by this investigator at this time. However, the nature of the irregularity suggests that it is the result of one or more of the following phenomena: an abnormal increase in the size of the drop as a result of a change in surface tension, an abnormal change in the charging rate of the drop as reflected by changes in the double layer capacitance, an abnormal mode of supply of depolarizer to the electrode surface. Any or all of these phenomena might be possible when the tripositive lanthanide ion hydrolyzes and produces a gelatinous solid in the immediate vicinity of the electrode. Further study concerning the conditions at the electrode surface, such as double layer capacitance measurements and measurements of the charging rate, might yield information sufficient to allow an exact interpretation of the processes occurring at the electrode.



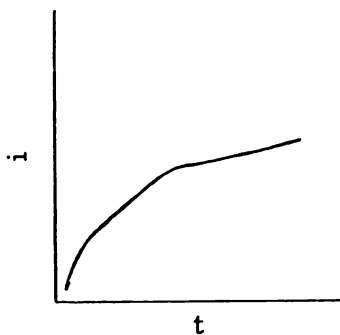
A. Cadmium(II) wave.
 $E_{d.e.} = -1.00 \text{ v. vs. S.C.E.}$



B. Ascending portion of
 hydrogen wave.
 $E_{d.e.} = -1.50 \text{ v. vs. S.C.E.}$

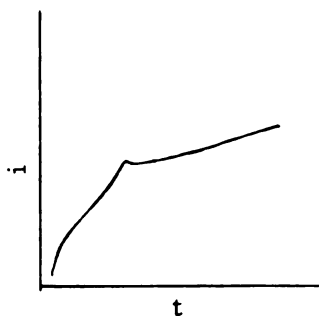


C. Plateau of hydrogen wave.
 $E_{d.e.} = -1.70 \text{ v. vs. S.C.E.}$

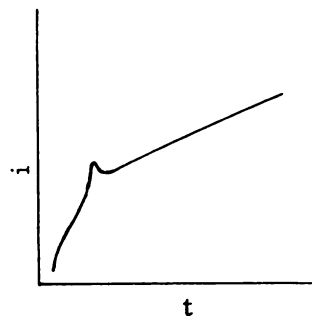


D. Toe portion of the first
 dysprosium(III) wave.
 $E_{d.e.} = -1.78 \text{ v. vs. S.C.E.}$

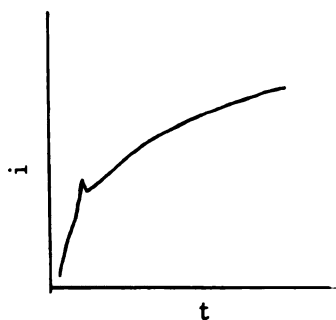
Figure 14. The i - t curves for cadmium(II), hydrogen ion, and the first lanthanide wave in 0.1 M LiCl--0.01% gelatin.



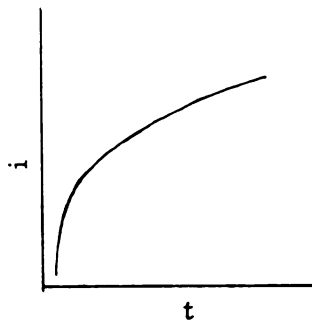
E. Ascending portion of the wave.
 $E_{d.e.} = -1.79 \text{ v. vs. S.C.E.}$



F. Ascending portion of the wave.
 $E_{d.e.} = -1.81 \text{ v. vs. S.C.E.}$



G. Ascending portion of the wave.
 $E_{d.e.} = -1.84 \text{ v. vs. S.C.E.}$



H. Plateau of the wave.
 $E_{d.e.} = -1.89 \text{ v. vs. S.C.E.}$

Figure 15. The i - t curves during the development of the first lanthanide wave in 0.1 M LiCl-0.01% gelatin.

CHARACTERISTICS OF THE SECOND WAVE

General Nature of the Wave

In the measurements related to the second wave, several problems arise which are not encountered with the first wave. The second wave shows no plateau, just a drop in current prior to the final current rise due to discharge of the supporting electrolyte. However, in any attempt to interpret the wave, some reference point for current and potential measurements is necessary, and to this end the midpoint of the oscillation giving the highest current value prior to the fall in current was chosen. The actual significance of the current at this particular point is certainly in doubt, but the fact that it is the highest current value prior to the final current rise and that it can be reproducibly evaluated suggest its use as a reference point. The current between this reference point and the point of measurement of i_d for the first wave was defined as i_r as was shown in Figure 3 and the accompanying discussion in the experimental section. No significance will be attached to the magnitude of this current.

The supporting electrolytes employed in this work begin to be discharged and thus yield an appreciable current during the potential region where the second wave occurs. Thus, the measured i_r values contain current other than that wholly arising from a process which involves the lanthanide ion. Correction of the measured current values by subtraction of the residual current is possible, but this leads to large uncertainties in the resulting values and sometimes tends to complicate the problem rather than simplify it.

Another problem arising in these measurements is that in the potential region under investigation hydrogen bubbles can be seen to accumulate on the tip of the capillary. The result of this accumulation of gas is a disturbance of the drop growth, a shielding of a portion of

the mercury drop, and undoubtedly some stirring of the solution.

All of these factors combined yield an irreproducibility in the wave of such magnitude that accurate measurements of the wave parameters are impossible. Thus, in the discussions to follow, emphasis will be placed on trends suggested by a set of values rather than on the magnitude of the values.

Variation of Wave Parameters with Solution Composition

The variation of i_r with variation of concentration as noted for solutions of dysprosium(III) in 0.1 M LiCl with 0.01% gelatin at a constant pH of 3.00 is shown in Figure 16 and Table VI. As shown in the figure, the current is not linearly proportional to the concentration of dysprosium(III). The current values plotted in Figure 16 and listed in Table VI are not corrected for any residual current contribution to the total current. The actual contribution by residual current to i_r is greater for the higher concentration values than for the lower concentration values, so the plot should actually show a greater curvature.

Table VI. Current-Concentration Relationships of the Second Wave at a Constant pH

Dysprosium(III) in 0.1 M LiCl with 0.01% Gelatin at a pH of 3.00	
Concentration (moles/ml)	i_r (μ amps)
0.2	3.57
0.5	8.64
0.8	9.47
1.0	11.12
2.0	13.66
5.0	17.61

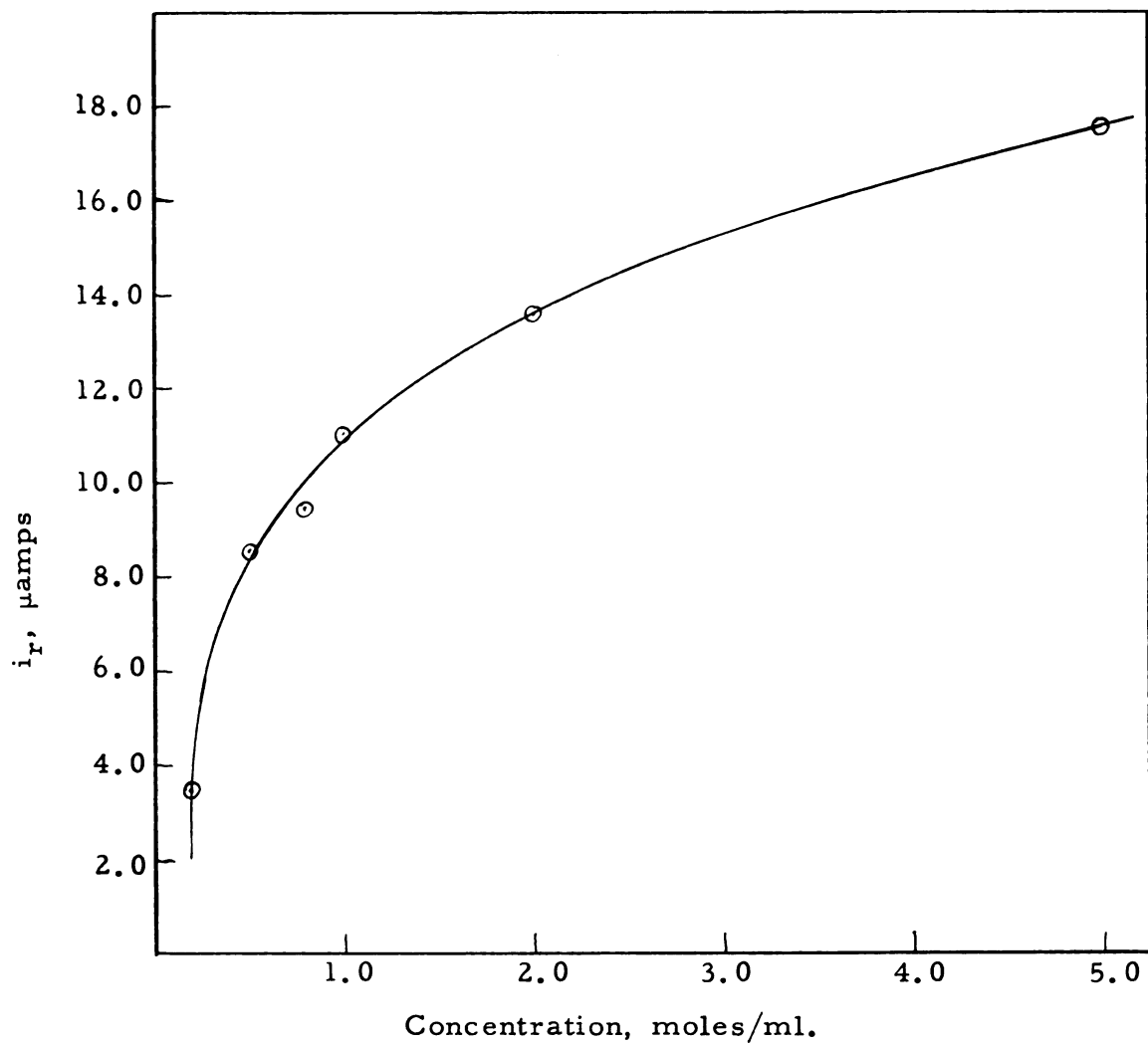


Figure 16. Variation in i_r for the second wave with change in concentration at a constant pH. Dysprosium(III) in 0.1 M LiCl--0.01% gelatin at a pH of 3.00.

When a current does not vary linearly with concentration over the concentration region in question, a current resulting from an adsorption process may be suspected. In the process giving rise to the first wave lanthanide hydrous oxide is produced in the immediate vicinity of the electrode and adsorption of this product could occur. The current resulting from the subsequent reduction process would then be controlled by the degree of coverage of the surface of the mercury drop, and thus would not vary linearly with concentration.

The variation in i_r and E_r with changes in pH are shown in Table VII and Figure 17 for 0.8 mM dysprosium(III) in 0.1 M LiCl with 0.01% gelatin. E_r shows a shift to more negative potentials with a decrease in pH. This shift is expected with this process following another process involving the same species which shows a marked potential shift.

Table VII. Variation of Current-Potential Characteristics of the Second Wave with Changes in pH

0.8 mM Dysprosium(III) in 0.1 M LiCl with 0.01% Gelatin		
pH	E_r (v. vs. S. C. E.)	i_r (μ amps)
2.59	-2.025	0.25
2.78	-2.013	2.48
2.98	-2.009	3.61
3.18	-1.996	3.87
3.53	-1.980	4.60
4.02	-1.967	5.19

The variation in i_r with change in pH as shown in Table VII and Figure 17 is probably somewhat exaggerated. The current values are those obtained after subtraction of the contribution to i_r by discharge of the supporting electrolyte, and the i_r values for lower pH values have a much larger contribution from the discharge of the supporting

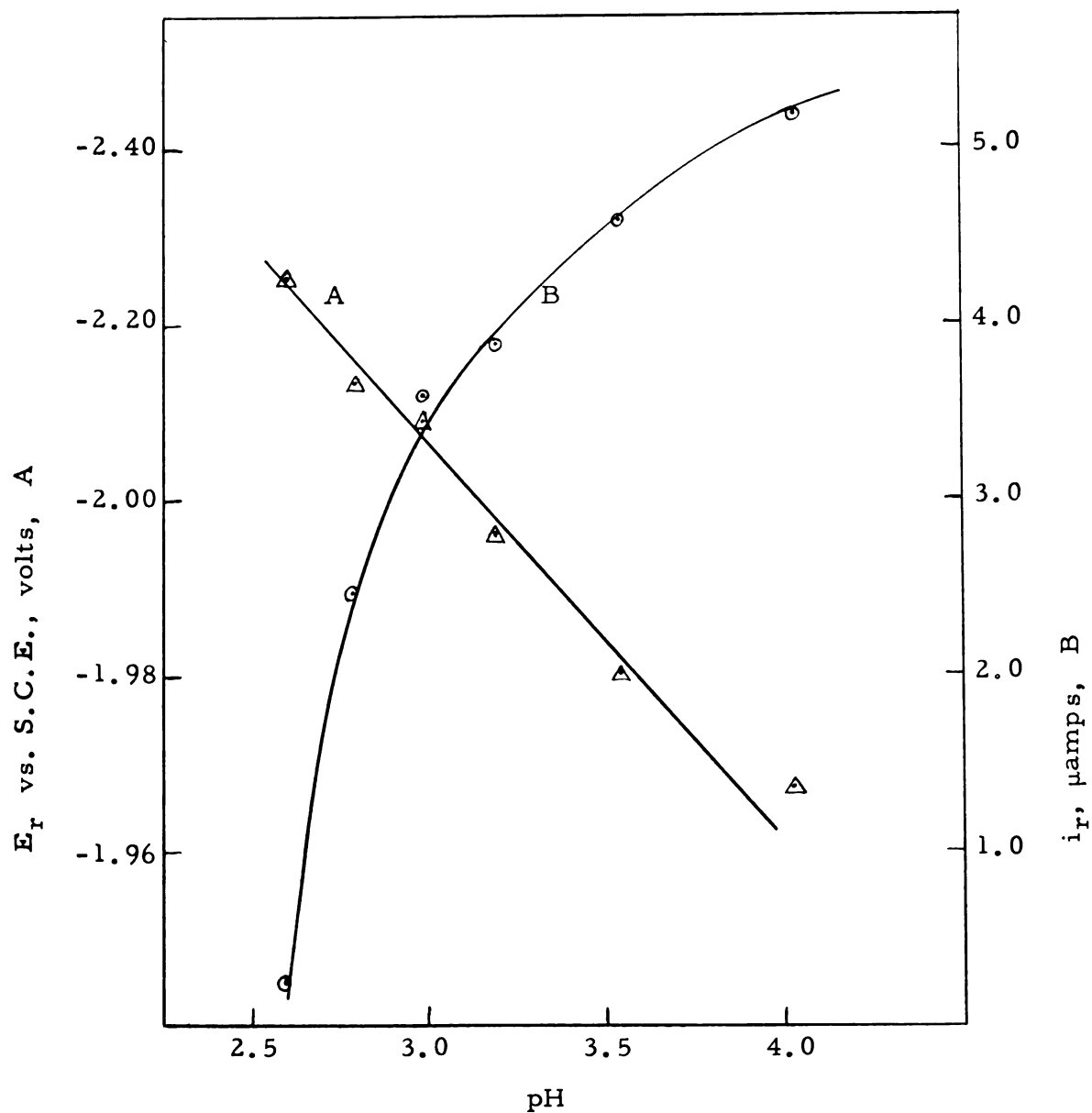


Figure 17. Variation of the wave parameters of the second wave with changes in pH. 0.8 mM dysprosium(III) in 0.1 M LiCl with 0.01% gelatin.

electrolyte than do those at the higher pH values due to the shift of the wave to more negative potentials with a decrease in pH. However, some decrease in the current for the second lanthanide ion process with a decrease in pH would be expected if the process requires the presence of the lanthanide hydrous oxide since the effective hydrogen ion concentration in the reaction layer as determined by the pH in the bulk of the solution would affect the amount of lanthanide hydrous oxide which could persist in the reaction layer.

Figure 18 shows the *i*-*E* curves observed with the successive addition of NaOH to a 1 mM solution of dysprosium(III) in 0.1 M LiCl with 0.01% gelatin. The height of the first wave related to the lanthanide ion is immediately diminished as the pH is increased to a value of 6.60, shows successive decreases in height as additional NaOH is added, and is almost indistinguishable when the pH reaches a value of 7.20. However, the second wave related to the lanthanide ion does not show such a marked decrease in height, and in fact decreases very little even though a precipitate is plainly visible when the pH reaches a value of 7. A suspension of previously precipitated lanthanide hydrous oxide in 0.1 M LiCl also shows *i*-*E* curves of the same nature as curve (E) of Figure 18. Thus the second wave appears to be definitely related to the presence of the lanthanide hydrous oxide.

A greater concentration of hydrogen gas is visible around the electrode in this potential region than at potentials on the plateau of the first lanthanide wave. Thus it appears that the reduction process subsequent to the adsorption of the lanthanide hydrous oxide also involves the reduction of hydrogen ion, with the most likely source of additional hydrogen ion being from water associated with the hydrous oxide.

This second wave related to the lanthanide ion was also observed with solutions employing lithium perchlorate, lithium sulfate, or tetramethylammonium iodide as the supporting electrolyte.

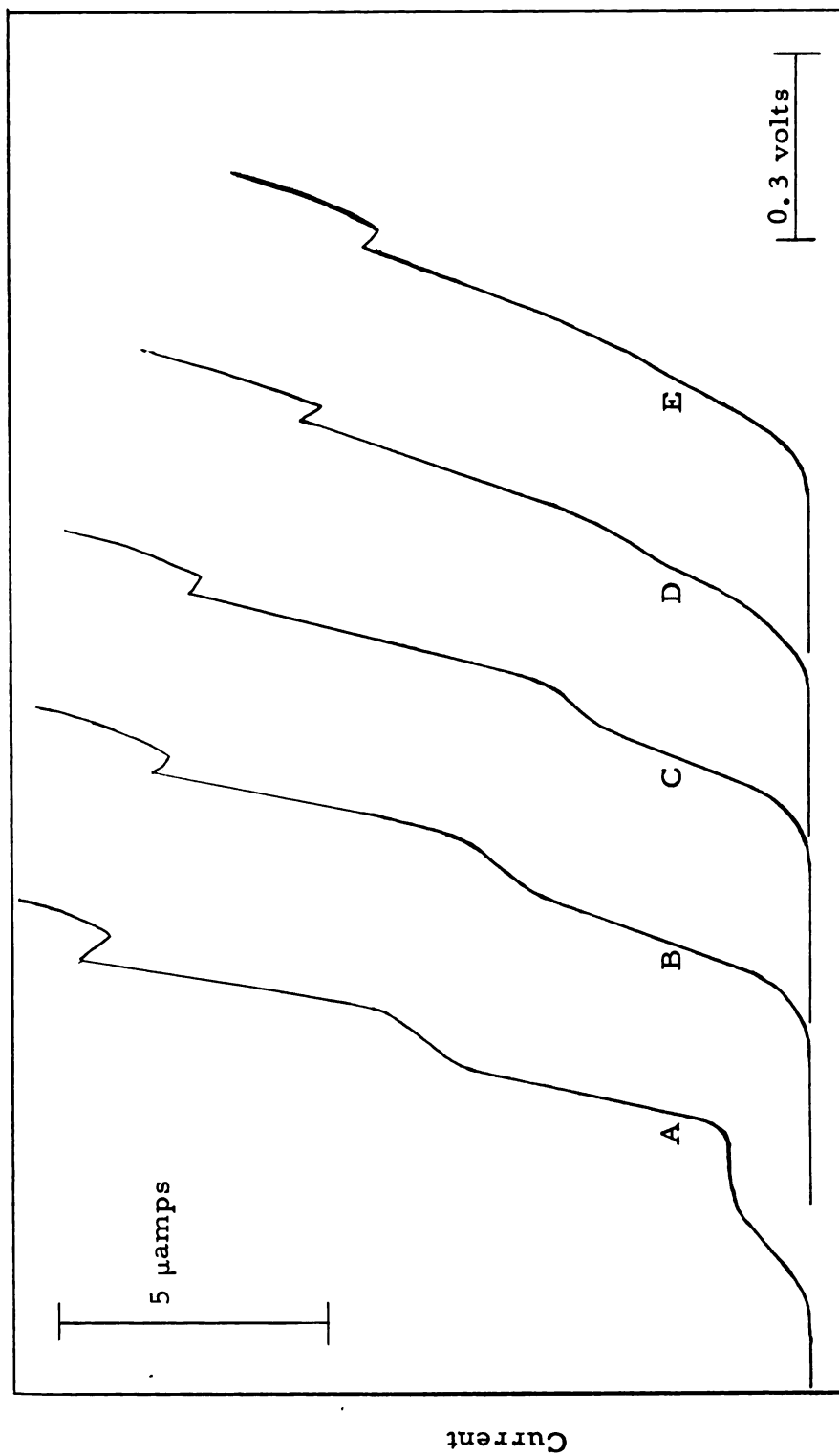


Figure 18. Effect of the addition of base on the i-E curve of 1 mM dysprosium(III) in 0.1 M LiCl-0.01% gelatin, Curve A, pH = 5.65; Curve B, pH = 6.65; Curve C, pH = 6.60; Curve D, pH = 7.20; Curve E, pH = 7.30. All curves start at -1.30 v. vs. S.C.E.

The addition of gelatin or triton X-100 has no noticeable effect on the characteristics of the wave.

As was mentioned earlier in the discussion of the first wave, the second wave was not observed when D_2O was employed as a solvent.

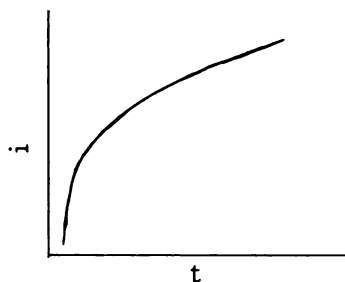
Current-Time Relationships

The i - t curves obtained at various potentials during the development of the second lanthanide wave for a 1 mM solution of dysprosium(III) at pH of 3 in 0.1 M LiCl with 0.01% gelatin are shown in Figure 19. Curve A of Figure 19 shows the i - t curve obtained on the plateau of the first lanthanide wave, curves B, C, and D of Figure 19 shows the i - t curves obtained on the rising portion of the second lanthanide wave, curve E of Figure 19 shows the i - t curve obtained in the region where the current decreases prior to the final current rise, and curve F of Figure 19 shows the i - t curve obtained at a potential sufficient to give the final current rise.

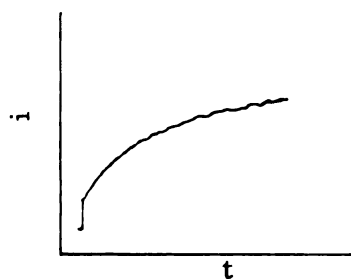
The gross irregularities shown in these figures were quite reproducible and were not observed with a solution of the same composition but without the lanthanide ion.

Again, no precedent was found in the literature to i - t curves of this type, but there can be no doubt that some process is violently disturbing the normal electrode solution interface. With the other evidence at hand, it is quite probable that the process involves the adsorption of the lanthanide hydrous oxide formed by hydrolysis, and subsequent reactions which produce an extreme turbulence at the electrode.

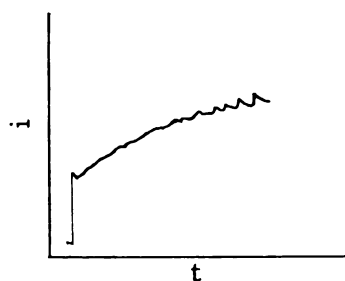
Shown in Figure 20 are electrocapillary curves at an h_{eff} value of 59.6 as obtained in a 0.1 M LiCl solution, a 0.1 M LiCl solution containing 0.01% gelatin, a 0.1 M LiCl solution containing 0.01% gelatin and $HClO_4$ sufficient to give a pH of approximately 3, and a 1 mM solution of dysprosium(III) in 0.1 M LiCl with 0.01% gelatin at a pH of 3.



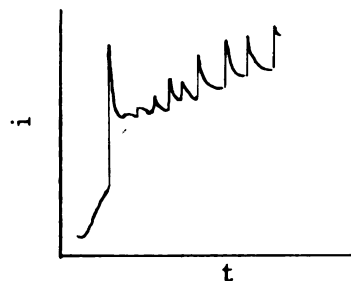
A. Plateau of the first wave.
 $E_{d.e.} = -1.89 \text{ v. vs. S.C.E.}$



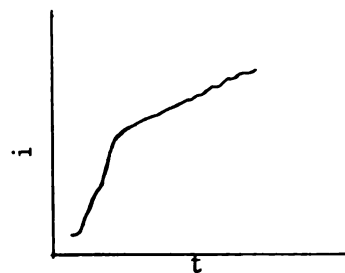
B. Ascending portion of the wave.
 $E_{d.e.} = -1.94 \text{ v. vs. S.C.E.}$



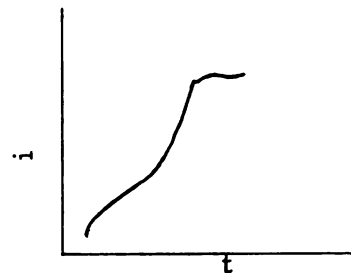
C. Ascending portion of the wave.
 $E_{d.e.} = -1.98 \text{ v. vs. S.C.E.}$



D. Ascending portion of the wave.
 $E_{d.e.} = -2.01 \text{ v. vs. S.C.E.}$



E. Fall in current prior to final rise.
 $E_{d.e.} = -2.05 \text{ v. vs. S.C.E.}$



F. Final current rise.
 $E_{d.e.} = -2.28 \text{ v. vs. S.C.E.}$

Figure 19. The i - t curves during the development of the second lanthanide wave in 0.1 M LiCl--0.01% gelatin.

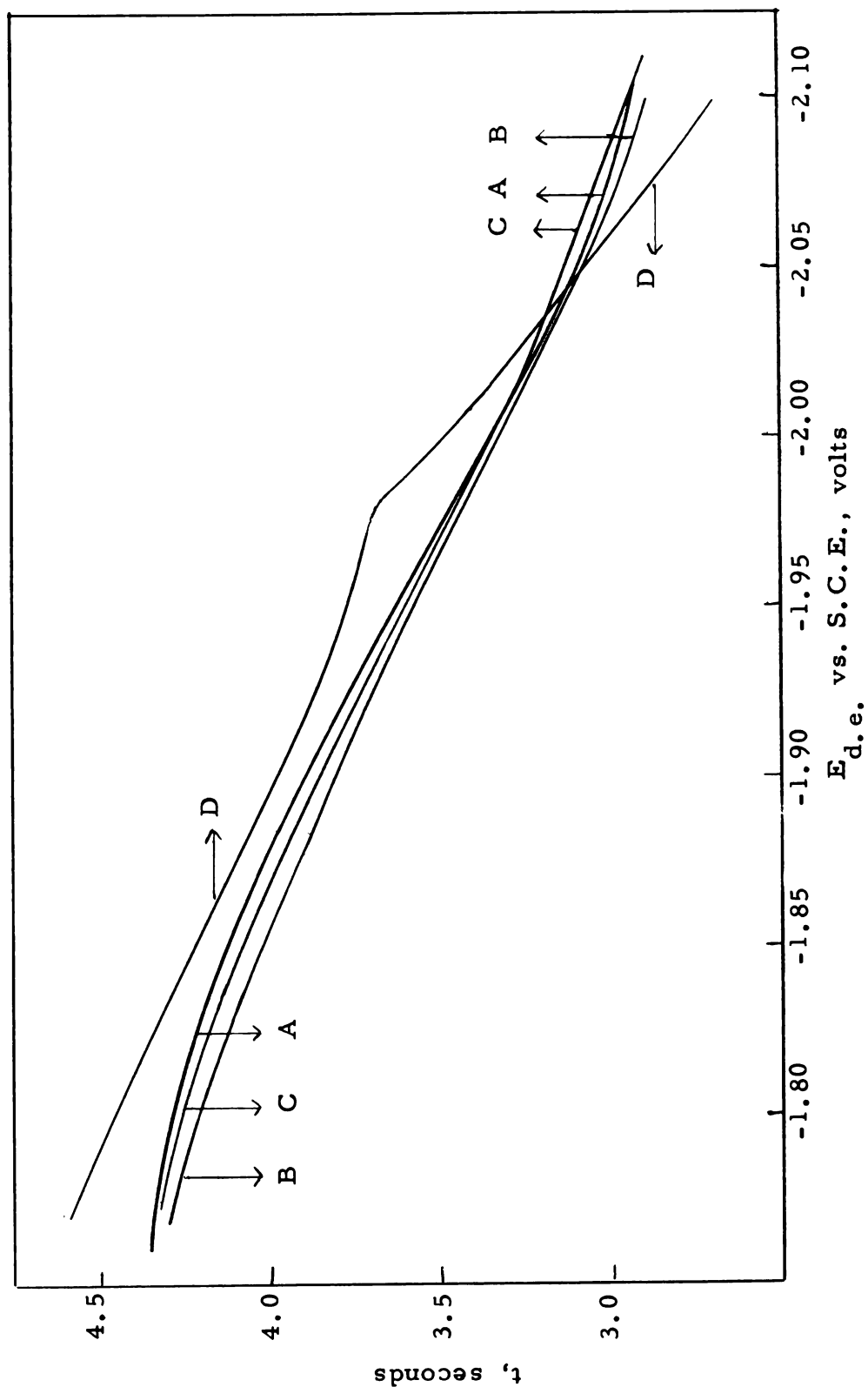


Figure 20. Electrocapillary curves with varying solution conditions. $h = 59.6$ cm. Curve A, 0.1 M LiCl only; Curve B, 0.1 M LiCl-0.01% gelatin; Curve C, HClO_4 at pH of 3 in 0.1 M LiCl--0.01% gelatin; Curve D, dysprosium(III) at pH of 3 in 0.1 M LiCl--0.01% gelatin.

All of the curves are regular except that one for the solution containing dysprosium(III), which shows an irregularity at a potential region corresponding to that in the region of maximum current prior to the fall in current. This irregularity again denotes an abnormal interaction between the mercury drop and the surrounding solution, and adsorption of the lanthanide hydrous oxide would again seem to be the logical explanation for the observed irregularity.

Consideration of Hydride Formation

The suggestion by some workers (29, 42) that the formation of lanthanide hydrides is involved in the electrode processes associated with the lanthanide ions may have some merit, but it seems highly unlikely under polarographic conditions since this involves the reduction of hydrogen ion to the hydride ion and the standard reduction potential for this process has been estimated to be -2.33 v. vs. N.H.E. (11). With the overpotential of the hydrogen ion on mercury taken into account, the potential necessary for the reduction of hydrogen ion to the hydride ion should be much greater than that reached in the course of both of the observed polarographic waves. However, in gross electrolysis, the potentials employed are often quite high and hydride formation might be possible.

COMPARISONS WITH OTHER LANTHANIDE IONS

Shown in Figure 21 is a comparison of the *i*-*E* curves obtained for 1 mM lanthanum(III), 1 mM gadolinium(III), 1 mM lutecium(III), and 1 mM dysprosium(III), all in 0.1 M LiCl with 0.01% gelatin and at the pH values shown. It can be seen from this figure that all of these ions yield *i*-*E* curves of a similar nature to that observed for dysprosium(III). The first wave related to the lanthanide ion in the *i*-*E* curve

for lanthanum(III) is quite difficult to see, at higher pH values, and in fact might be missed if other i - E curves such as those shown in Figure 21 were not available for ready reference. Since both waves for lanthanum(III) occur at more negative potentials than those for dysprosium(III), the second wave might not be noted at lower pH values since the shift in the waves with pH puts this wave into a potential region where it would tend to blend in with the discharge of the supporting electrolyte.

Table VIII compares the $E_{\frac{1}{2}}$ values obtained for the first wave related to the lanthanide ions, lanthanum(III), gadolinium(III), lutecium(III), and dysprosium(III). It can readily be seen that there is a transition to more positive potentials going from lanthanum(III) to gadolinium(III) to lutecium(III), which must reflect the differences in basicity of the three ions. The relative order established by the $E_{\frac{1}{2}}$ values of the ions shown in Table VIII and Figure 21 parallels the order of basicity established by Moeller and Kremers (26).

Table VIII. Comparison of the Half-Wave Potentials of the First Wave for Selected Lanthanide Ions

1 mM in Lanthanide Ion in 0.1 M LiCl with 0.01% Gelatin at the pH Shown		
Ion	pH	$E_{\frac{1}{2}}$ (v. vs. S.C.E.)
Lanthanum(III)	2.80	-1.907
Lanthanum(III)	3.80	-1.849
Gadolinium(III)	2.90	-1.820
Gadolinium(III)	3.85	-1.767
Dysprosium(III)	2.78	-1.807
Dysprosium(III)	3.20	-1.783
Lutecium(III)	2.85	-1.789
Lutecium(III)	3.45	-1.751

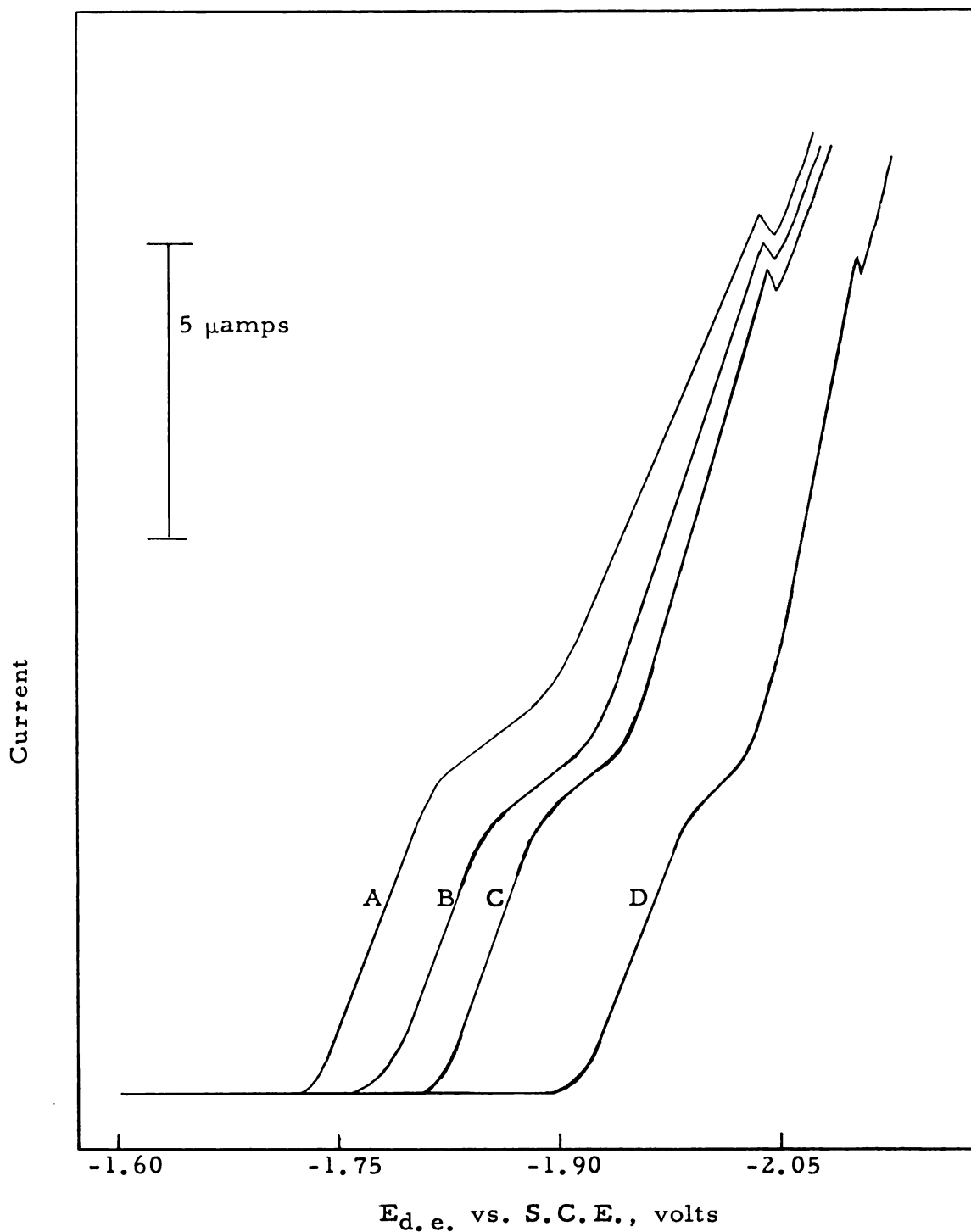


Figure 21. Comparison of the i - E curves obtained for lutecium(III), dysprosium(III), gadolinium(III), and lanthanum(III) in 0.1 M LiCl - 0.01% gelatin. Curve A, 1 mM lutecium(III) at pH = 3.45; Curve B, 1 mM dysprosium(III) at pH = 3.00; Curve C, 1 mM gadolinium(III) at pH = 2.90; Curve D, 1 mM lanthanum(III) at pH = 2.80.

SUMMARY AND CONCLUSIONS

An investigation of the polarographic behavior of the tripositive lanthanide ions having no stable dipositive state in aqueous solution was carried out using the dysprosium(III) ion as a representative of the group. Two waves resulting from the presence of the lanthanide ion were observed.

The first wave related to the lanthanide ion was shown to be irreversible by the curvature and dissymmetry observed, and by the slope of 40 mv. obtained when $E_{d.e.}$ was plotted against $\log i/i_d - i$, and by the high value of +5 mv. per degree of the temperature coefficient of $E_{\frac{1}{2}}$.

The characteristics of the first wave related to the lanthanide ion were quite dependent on the hydrogen ion concentration of the solution. The $E_{\frac{1}{2}}$ of the wave shows a shift to more negative potentials with an increase in hydrogen ion concentration which is of the same order of magnitude as the 90 mv. per unit change in log concentration of the acid observed for a weak acid in unbuffered solutions. The $E_{\frac{1}{2}}$ of the wave was found not to vary significantly with changes in concentration of the lanthanide ion at a constant pH, and was evaluated as -1.791 v. vs. S.C.E. at a pH of 3.20.

The i_d of the first wave related to the lanthanide ion was found to be proportional to the concentration of the lanthanide ion at a constant pH over the concentration range of 0.2 to 5.0 moles per milliliter, but the i_d shows a pH dependence, decreasing as the pH decreases.

The variations in $E_{\frac{1}{2}}$ and i_d of the first wave related to the lanthanide ion with pH suggest that the electrode process involves the reduction of hydrogen ion. This was shown to be true by employing D_2O as a solvent, which resulted in a marked shift in $E_{\frac{1}{2}}$ of the wave to more negative potentials, which would not have occurred if the dysprosium(III) ion were being reduced.

The experimentally determined i_d values were found to be approximately five-sixths of those calculated by the Ilkovic equation assuming an n of 3, which suggests that the electrode process involves the reduction of three hydrogen ions produced by hydrolysis of the lanthanide ion, and that the observed i_d values are less than those calculated by the Ilkovic equation due to some kinetic control of the supply of depolarizer to the electrode surface.

The wave was shown to be partially kinetic controlled by the nature of the plots obtained when i_d is plotted against $(h_{\text{eff}})^{\frac{1}{2}}$. A plot of i_d against $(h_{\text{eff}})^{\frac{1}{2}}$ was shown to vary with the hydrogen ion concentration in the bulk of the solution, with a greater kinetic control of the wave evident at lower pH values. The plot of i_d against $(h_{\text{eff}})^{\frac{1}{2}}$ obtained when D_2O is employed as a solvent shows a somewhat greater kinetic nature than that obtained under similar solution conditions in H_2O .

The characteristics of the first wave related to the lanthanide ion were found not to be dependent on the choice of supporting electrolyte by comparison of the i - E curves obtained employing lithium chloride, lithium perchlorate, lithium sulfate, or tetramethylammonium iodide as supporting electrolytes.

The effect of the concentration of gelatin employed as a maximum suppressor on the first lanthanide wave was found to be primarily a secondary effect related to the need for a maximum suppressor for the preceding wave resulting from the discharge of hydrogen ion, although the wave related to the lanthanide ion shows a slight maximum until the concentration of gelatin approaches 0.01 per cent.

The i - t curves obtained at various potentials during the course of the first wave related to the lanthanide ion show an irregularity which is not seen in the i - t curves obtained at the same potentials with a solution of similar composition except for the presence of the lanthanide ion, and for which no precedent was found in the literature.

The exact nature of the processes giving rise to this irregularity were not explained, and further work will be necessary to elucidate them.

The second wave resulting from the presence of the lanthanide ion was difficult to interpret due to its somewhat irreproducible nature resulting from the discharge of the supporting electrolytes employed and the formation of hydrogen bubbles around the electrode.

The current resulting from the second electrode process related to the lanthanide ion was found not to vary linearly with the concentration of the lanthanide ion, the relative value of the current decreasing as the concentration of the lanthanide ion is increased. Such behavior is indicative of a current controlled by an adsorption process.

The current resulting from the second electrode process related to the lanthanide ion increases with an increase in pH until the pH reaches a value at which hydrolysis of the lanthanide ion occurs in the bulk of the solution, and remains practically constant as the pH is further increased although a precipitate of the lanthanide hydrous oxide is plainly visible. A suspension of previously precipitated lanthanide hydrous oxide yields a current upon electrolysis approximating that observed for a solution, the pH of which was adjusted to 7.20 while in the electrolysis cell. This behavior suggests that the lanthanide hydrous oxide is adsorbed, and the resulting current is controlled by coverage of the surface of the mercury drop.

The i - t curves obtained at potentials during the course of the second wave related to the lanthanide ion were quite irregular, and denote extreme turbulence at the electrode surface. Electrocapillary curves obtained in the presence of the lanthanide ion also show an irregularity in the potential region where the maximum value of the current resulting from the second process related to the lanthanide ion is found. These two phenomena may again be interpreted as indicative of an adsorption process.

Since a high concentration of hydrogen gas is visible around the electrode in this potential region, it appears that the reduction process involves the reduction of hydrogen ion associated somehow with the lanthanide hydrous oxide.

The i - E curves obtained with solutions of lanthanum(III), gadolinium(III), and lutecium(III), were found to be quite similar to those observed with solutions of dysprosium(III). A comparison of the $E_{\frac{1}{2}}$ values for the first wave related to the lanthanide ion shows a potential shift in the waves to more negative potentials with increasing basicity of the lanthanide ion.

From the evidence obtained in this investigation, the polarographic waves observed for aqueous solutions of the dysprosium(III) ion (and thus by inference all the tripositive lanthanide ions exhibiting no stable dipositive state in aqueous solution) are the result of the reduction of hydrogen ions produced by the protolytic dissociation of the hydrated lanthanide ion in the immediate vicinity of the electrode surface, followed by adsorption of the lanthanide hydrous oxide thus produced, and the accompanying reduction of additional hydrogen ions from water associated with the lanthanide hydrous oxide.

SUGGESTIONS FOR FURTHER WORK

Further study concerning the unusual phenomena occurring at the electrode surface during the development of the polarographic waves related to the lanthanide ions as indicated by the i - t curves obtained in this work would be of interest. Measurements of the double layer capacitance at various potentials, and in particular the magnitude of changes in the capacitance with change in potential, could give information leading to a better interpretation of the processes occurring at the electrode surface.

An interesting experiment which might allow a better characterization of the second process associated with the lanthanide ion would be to construct the necessary equipment and carry out polarographic measurements with a capillary which extends upward in the solution rather than downward. With the capillary in this direction, the problems arising from the accumulation of hydrogen gas around the mercury drop might be eliminated, and thus a better definition of the second wave would be obtained.

Solutions of a radioactive isotope of a lanthanide ion could be prepared and electrolyzed at potentials corresponding to those on the polarographic waves of the lanthanide ions and then to look for the presence of lanthanons in the mercury or adsorbed species on the surface of the drop. Adsorption of the lanthanide hydrous oxides from a suspension could also be followed in a similar manner. Special care would have to be given to the development of the technics employed so that any species present in the mercury could be differentiated from adsorbed species. The technics employed would also have to be capable of eliminating any loss of the species prior to the radioactivity measurements.

A study of the polarographic behavior of non-aqueous solutions containing stoichiometric quantities of lanthanide ion and water could yield useful information.

An investigation of the electrochemical properties of the lanthanide ions in fused-salt solvent systems would also yield information which would add to the understanding of processes associated with the reduction of lanthanide ions.

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