THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE CATHODIC REDUCTION OF VANADIUM (V) AT A MERCURY COVERED ELECTRODE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

BY

INEZ MC FALL

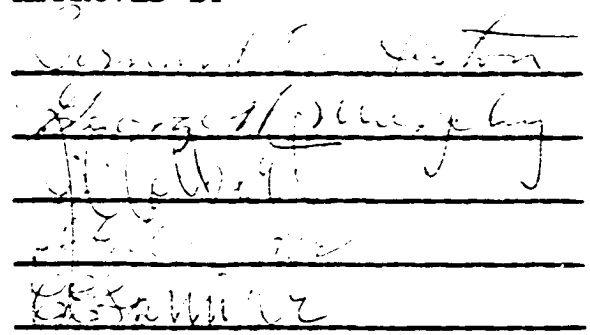
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APPROVED BY



DISSERTATION COMMITTEE

ACKNOWLEDGMENT

The author wished to thank Dr. Bernard O. Heston for suggesting and directing this work.

She also wishes to thank the faculty, staff and fellow students of the Chemistry Department for their friendliness and helpfulness.

U. I. O. G. D.

TABLE OF CONTENTS

Page

LIST OF TABLES..... vi

LIST OF FIGURES..... vii

Chapter

I. INTRODUCTION..... 1

II. EXPERIMENTAL..... 7

III. DISCUSSION..... 26

IV. SUMMARY..... 30

BIBLIOGRAPHY..... 31

LIST OF TABLES

Table		Page
1.	Determination of the Decomposition Potential....	13
2.	Determination of Hydrogen Overvoltage.....	15
3.	Dependence of Current Efficiency on Current Density.....	17
4.	Dependence of Current Efficiency on Initial Concentration.....	19
5.	Dependence of Current Efficiency on Time.....	21
6.	Overvoltage in Vanadium (V) Solution.....	22

LIST OF FIGURES

Figure		Page
1.	Determination of the Decomposition Potential....	14
2.	Hydrogen Overvoltage vs. log Current Density....	16
3.	Current Efficiency vs. Initial Concentration....	18
4.	Current Efficiency vs. Time.....	20
5.	Overvoltage in Vanadium (V) Solution.....	23

THE CATHODIC REDUCTION OF VANADIUM (V) AT A MERCURY COVERED ELECTRODE

CHAPTER I

INTRODUCTION

Many workers have investigated the electrolytic reduction of vanadium compounds in aqueous solution. Foerster and Böttcher (1) used an acid solution and electrodes having low hydrogen overvoltage to determine the emf of the various steps in the reduction. Their experimental apparatus consisted of a compartment cell, a vanadyl sulfate solution in excess sulfuric acid, a platinum gauze anode and various metallic cathodes. They showed that the process V (V)→V (IV)→V (III) can occur at both smooth and platinized platinum cathodes, but that the process V (III)→V (II) cannot occur at the platinized platinum electrode but does take place on the smooth platinum electrode. Their electrolytic reductions of vanadium (V) produced a heavy film adhering to the cathode which resulted in a high polarization for the process V (V)→V (IV). Fischer (2) attempted to produce metallic vanadium by electrolysis of aqueous solutions. He also reviewed thoroughly the researches of Bleecker, Gore, Setterberg,

and Truchot. Gore used platinum electrodes in a sulfuric acid solution saturated with ammonium metavanadate. He reported that the solution changed to an intense blue black color at the cathode and that a jet black powder was deposited on the cathode. Setterberg electrolyzed a concentrated solution of vanadium tetroxide in hydrochloric acid using a compartment cell. A black, brittle deposit, which he said was probably the sesquioxide, formed on the cathode. Bleecker (3) precipitated vanadic acid at the anode in a compartment cell using an alkaline solution. Truchot (4) electrolyzed a hot ammoniacal solution of sodium vanadate causing vanadium to be precipitated as an oxyhydrate on the cathode. Hintz (5) reported the work of Schlucht in which he dissolved vanadium chloride in hydrochloric acid solution and electrolyzed it. No precipitation occurred but the original green color changed to violet. Most acidic solutions of vanadium (II) compounds are violet. Senderoff and Brenner (6) showed that the electrolysis of a basic solution of sodium vanadate at 300° C produced a black crystalline deposit on both anode and cathode. The material did not correspond to any simple oxide and was not completely characterized. Cowper-Coles claimed preparation of metallic vanadium by electrolytic reduction of an aqueous vanadium (V) solution but his work could not be reproduced by Fischer or Borchers (7). In his doctoral thesis de la Breteque (8) described his electrolytic process for the recovery of gal-

lium from alkaline liquors of the Bayer alumina process. A mercury cathode was used, and the electrolysate yielded solids containing about thirty percent vanadium. From ten tons of bauxite approximately 2.5 kilograms of vanadium as the pentoxide could be recovered. Meyers (9) produced reduction but no deposition of vanadium by electrolysis of an acid solution of sodium vanadate using a mercury cathode. Mackay (10) reported that a vanadyl sulfate solution may be electrolyzed in a compartment cell whereupon vanadic anhydride precipitates at the anode and a lower oxide at the cathode. Groves and Russell (11) using a mercury cathode. platinum anode, and a sulfuric acid solution of ammonium metavanadate precipitated vanadium compounds. They found that a cathode of high overvoltage was essential for this deposition. Pokorny and Schneider (12) reported that a thin layer of vanadium could be deposited on an iron or copper base by the electrolysis of alkaline lyes saturated with the oxides or hydroxides of the metal. Britton and Wellford (13) reduced acid solutions of vanadium (V) to vanadium (II) at platinum, lead, and mercury cathodes. They also found that vanadium (IV) solutions could be prepared by shaking an acid solution of vanadium (V) with mercury. Complete reduction required one hour. Stahler and Wirthwein (14) prepared $V_2(SO_4)_3 \cdot H_2SO_4 \cdot 12\ H_2O$ electrolytically and Brierly (15) prepared $V_2O_2(SO_3)_4 + 9H_2O$ by the electrolytic reduction of vanadium pentoxide in dilute sulfuric acid. Continuation

of the electrolysis produced V_2O_2. Chapman and Law (16) studied the reduction of vanadium compounds by electrolysis using various cathodes. They claimed that the hydrogen which was evolved at the electrode acted as the reducing agent. The effect on the reduction when various metals were used as cathode was demonstrated. Electrodes having high hydrogen overvoltage, as zinc, proved most effective. It is of interest that as early as 1831 Berzelius (17) showed the reduction of vanadium (V) with hydrogen.

The processes occurring at the cathode in the course of the reduction in acid solution may be represented by the following equations (18, 19):

$$VO_2^{+} + 1/2\ H_2 + H^{+} = VO^{+2} + H_2O$$

$$VO^{+2} + H^{+} + 1/2\ H_2 = V\ (III) + H_2O$$

$$V\ (III) + 1/2\ H_2 = V(II) + H^{+}$$

Alternatively similar equations may be written without molecular hydrogen.

$$VO_2^{+2} + 2H^{+} + e = VO^{+2} + H_2O$$

$$VO^{+2} + 2H^{+} + e = V\ (III) + H_2O$$

$$V\ (III) + e = V\ (II)$$

In basic solutions the forms of the vanadium (V) and (IV) are not so readily defined since these are dependent on the pH of the solution. Salts of the polyvanadic acids form readily. The reduction of vanadium (V) in alkaline solution as determined by Filipovic (20) and coworkers using polarographic methods was represented by them with the following

equation:

$$H_2VO_4^- + 2H^+ + e = VO(OH)_2 + H_2O$$

However, for a system at a pH lower than 7.5 they give

$$VO^{+2} + 2H^+ + 2e = V\ (II) + H_2O$$

Their experiments showed that at pH 9, HVO_4^{-2} changed to a vanadate ion which required a greater overvoltage for its reduction.

The molecular weight of the vanadium (V) ions increases in a stepwise fashion as the alkalinity decreases, according to Sedgwick (21).

pH	Form
12.0 - 10.6	V_2
9	V_5^4
7	

The colored forms of vanadium (V) have a ratio of alkali metal to vanadium of less than one. This ratio is usually 3:5 or 4:5. The reactions which take place with colorless vanadium compounds are rapid, whereas those with colored species are slow. Ducret (22) represented this phenomenon in the following manner.

$$\text{Colorless ion} + nH^+ \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} \text{Colored ion}$$

The products obtained upon the electrolytic reduction of acid solutions of vanadium (V) are soluble in acid. Vanadate ion in neutral or alkaline solution is not readily reduced (23). Caspari (24) showed that cathodes of high overvoltage were most capable of bringing about the reduction of compounds not readily attacked. This was explained by Potter in the following manner. The electrode of high overvoltage

gives rise to the greater cell voltage required for a certain reduction (25). The products of such reductions of alkaline vanadium (V) solutions are relatively insoluble compared with the products of electrolysis in acid solutions.

A suitable electrolytic process producing insoluble vanadium compounds from ore extracts could prove of commercial importance. Boyer (26) has patented such a continuous process for the recovery of uranium compounds in acid solution at an electrode of high hydrogen overvoltage.

The purpose of this investigation was to find an electrode of high overvoltage at which the cathodic reduction of vanadium in neutral or alkaline solution would occur to produce insoluble vanadium compounds. The electrode should be easy to prepare, use, and clean. A mercury electrode is known to have high hydrogen overvoltage but because it is a liquid it has other undesirable properties. A pool of mercury used as an electrode is hard to stir and clean. The surface tension of mercury is known to change with applied potential. Hoping to overcome these difficulties and yet maintain a high overvoltage the author prepared electrodes which were mercury covered.

CHAPTER II

EXPERIMENTAL

Purification of Vanadium Pentoxide

Technical grade Eimer and Amend (Fisher) vanadium pentoxide was dissolved in sodium hydroxide solution and filtered. The pH of the solution was lowered by the addition of acid to pH 7-8. Ammonium chloride was added which caused ammonium metavandate to precipitate. This was filtered off and ignited to vanadium pentoxide in a muffle furnce at 500^{o} C.

Vanadium pentoxide was also obtained by igniting C. P. Coleman and Bell ammonium metavanadate in a muffle furnace at 500^{o} C.

Preparation of Sodium Amalgam

A sodium amalgam was prepared according to the method of Gilman and Blatt (27). The resulting amalgam was a semi-solid mass and easily liquefied by gentle heating. When not in use the amalgam was stored in a wide mouth ground glass bottle in a vacuum desiccator over calcium chloride. Under a good vacuum an amalgam could be preserved for periods longer than three months. After being used in an

amalgamation, the amalgam was always filtered through a cone-shaped filter paper having a pin hole in the apex. The life of the sodium amalgam could be prolonged by the addition of small amounts of sodium to the old amalgam.

Preparation of Vanadium Solutions Used in the Electrolyses

The first solutions used in this study were prepared according to the instructions given by Foerster and Bottcher (1). Eleven and one-half grams of purified vanadium pentoxide were dissolved with stirring and heating in 3N sulfuric acid and brought to a final volume of 500 ml with sulfuric acid at room temperature. The resulting solution did not reduce permanganate. This showed the absence of any appreciable amount of lower valence state compounds of vanadium.

In later studies an aqueous solution of sodium orthovanadate was used.

In all cases the pH of the solutions was adjusted to the desired value by the addition of either dilute sulfuric acid or sodium hydroxide. Thus all solutions contained some sodium sulfate in addition to the sodium vanadate present in neutral and alkaline solutions. Solutions were all standardized by reducing the vanadium to a known oxidation state and then titrating the mixture with standard potassium permanganate.

Standardization of Potassium Permanganate

Potassium permanganate was standardized against arsenious oxide and stored in a brown glass-stoppered bottle. The solution was restandardized each month.

Titration of Vanadium Solutions

In the first part of this study the vanadium (V) solutions were reduced to vanadium (IV) by saturating the solutions with sulfur dioxide. The color changed from yellow to blue. The excess sulfur dioxide was removed by boiling. The mixture was then titrated with standard permanganate. This titration may be represented by the following equation:

$$10\ VOSO_4 + 2\ KMnO_4 + 2H_2O =$$
$$5(VO_2)_2SO_4 + 2MnSO_4 + 2H_2SO_4 + K_2SO_4.$$

A more rapid method for the determination of vanadium in solution was adapted from that given in Willard and Diehl (28). Vanadium (V) was reduced to vanadium (II) by passing the acidified solution through a zinc reductor. The divalent vanadium is very easily oxidized in air so it was run under suction into a solution of iron (III). This reduced the iron to iron (II) and oxidized the vanadium to vanadium (IV). Both of these species are stable in air for a short time. The mixture was then titrated with potassium permanganate to a rose color. A better end point can be obtained if a few ml of phosphoric acid are added right before the end point is reached. This complexes the iron (III) and the vanadium (V) and so reduces the intensity of

the yellow color. The above reactions may be represented as follows:

$$2HVO_3 + 3Zn + 5H_2SO_4 - 2VSO_4 + 3ZnSO_4 + 6H_2O$$

$$VSO_4 + Fe_2(SO_4)_3 + H_2O - VOSO_4 + 2FeSO_4 + H_2SO_4$$

$$10\ VOSO_4 + 2KMnO_4 + 12H_2O -$$
$$10HVO_3 + 2MnSO_4 + 7H_2SO_4 + K_2SO_4$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 -$$
$$5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4$$

Combination of the last three of these equations gives a net reaction of vanadium (II) and permanganate of:

$$10VSO_4 + 6\ KMnO_4 + 6H_2O -$$
$$10HVO_3 + 6MnSO_4 + 3K_2SO_4 + H_2SO_4$$

With this method more rapid determinations could be made and the results checked well with those obtained using sulfur dioxide as the reducing agent.

The Mercury Covered Electrode

Galvanized iron wire gauze was treated with dilute acid to remove the zinc. Sulfuric acid, about 6N, was found to be the most satisfactory reagent for this. Other methods of cleaning the gauze resulted in the production of electrodes of lower overvoltage. Hydrochloric acid and sodium hydroxide were tried. Anodic cleaning in an acid solution was not at all successful. After the zinc had been removed, the gauze was rinsed several times with distilled water, dried in air and then immersed in the sodium amalgam. Immed-

iate amalgamation occurred if the iron was clean. If not, the gauze was either discarded or cleaned again. The electrodes used in all these studies were formed into the shape of a hollow cylinder. These cylinders had a calculated surface area of 9.7 sq. cm.

Other gauzes which contained elements in addition to iron were used but always gave lower overvoltage values.

Several methods for preserving the electrodes were tried. Storing them under toluene was unsatisfactory. Drying an electrode and storing it in air was usually successful. However, in a few cases the electrode turned black and was unfit for use. The best method found for preserving and cleaning the electrode was polarization of it as a cathode in a dilute acid solution above the decomposition potential of the electrolyte. Hydrogen gas was evolved continuously at the amalgam surface. Electrodes could be preserved indefinitely in this manner.

Apparatus Used

The cell vessel was a 150 or 250 ml beaker. In the beaker was a porous cylinder enclosing the anode and anolyte. The anode in all experiments was smooth platinum. The anolyte consisted of 1N sodium sulfate. The cathode compartment contained the amalgamated iron electrode and the vanadium (V) solution. Either the cathode was rotated or an auxiliary stirrer with a glass shaft and propeller was used. The level of the liquid in the anode compartment was kept

the same as the level outside the compartment.

The house 110v D.C. line was usually used as the current source. On most of the overvoltage determinations, however, a G.M. power supply with 6v D.C. maximum output was used. The current was measured on a Roller-Smith D.C. milliammeter. A Leeds and Northrup type K potentiometer and a Minneapolis Honeywell Electronik null indicator were used to measure the emf of the cathode vs. the reference electrode. It was necessary to make all electrical connections to the null indicator with shielded cable and ground the instrument to an outside ground. Reference electrodes were the saturated calomel and the mercury-mercurous sulfate in 1 molal sulfuric acid solution. When necessary the temperature was kept at 25.0° C by a thermostat.

Procedure for Determining Overvoltage

An electrode was prepared as described previously. Using a dilute sulfuric acid solution, a platinum anode, a reference electrode with a Luggin capillary tip, and a high speed stirrer the applied emf. the current, and the emf of the cathode vs. the reference electrode were measured. The technique of Knobel (29) gave the most nearly reproducible results. This is a direct method of measuring overvoltage, that is, the potential is measured while the current is flowing. The current is adjusted to the appropriate value and the potential read within a minute. Then the current

is increased and another reading made. With Knobel's method emf readings were reproducible to within 0.02v. Knobel Considered readings satisfactory if they were within 0.1v.

The decomposition potential was determined graphically from a plot of current vs. applied emf. Tafel constants were evaluated when a straight line was obtained in a plot of overvoltage vs. log current density. A straight line proves the validity of the Tafel equation $\eta = a + b \log I$ in the range (30). The symbols "a" and "b" represent the Tafel constants; "a" is the overvoltage intercept and "b" is the slope of the line. Typical curves are shown in figures 1 and 2. Data for the figures are shown in the following tables:

TABLE 1

DETERMINATION OF THE DECOMPOSITION POTENTIAL

Applied Emf, v	Current, ma
4.0	29
3.5	17.7
3.0	8.5
2.5	3.7
2.8	5.7
2.0	0.6

FIGURE 1
DECOMPOSITION POTENTIAL - Fe(Hg) CATHODE IN
0.05N H_2SO_4

Current, ma vs. Applied emf, v

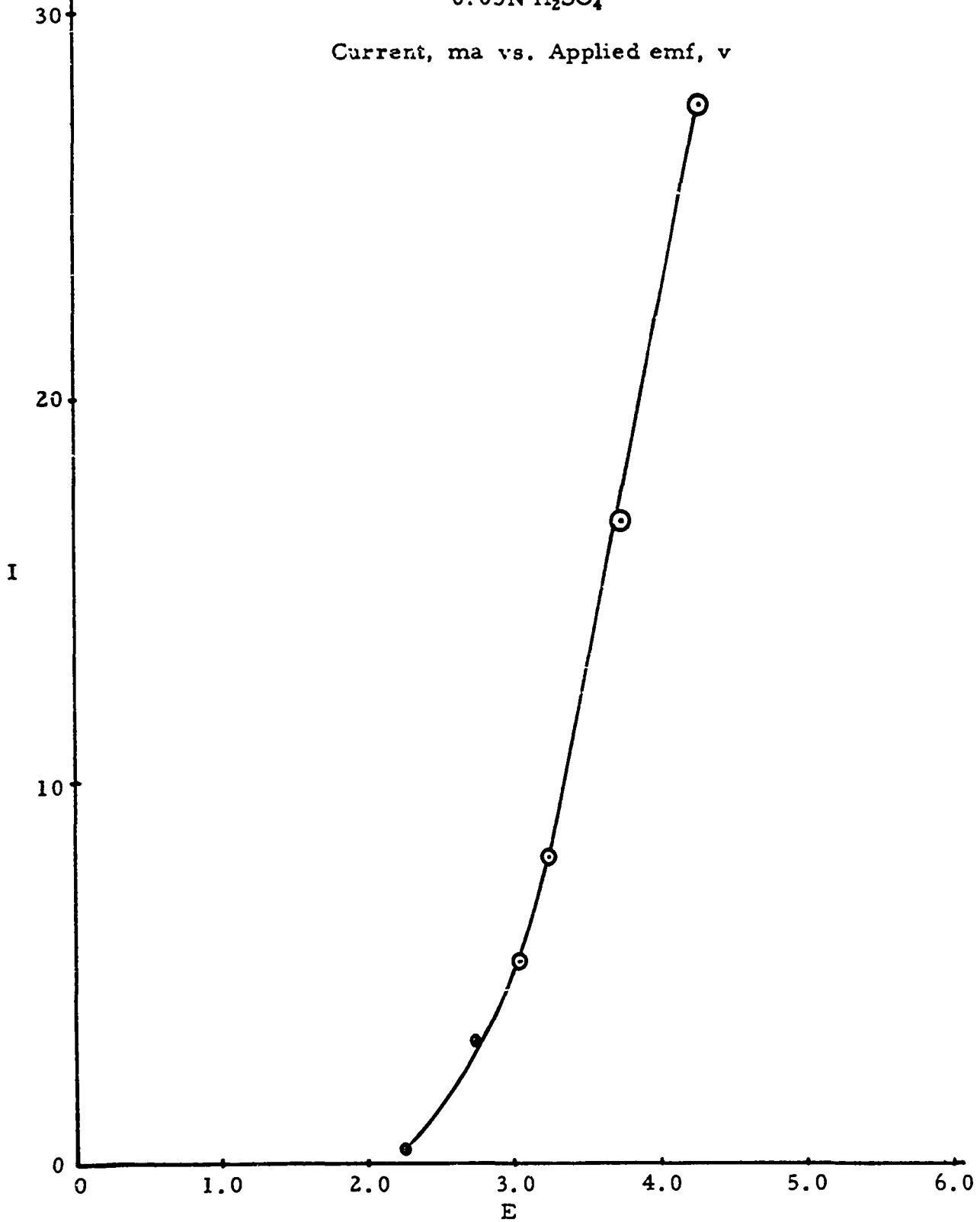


TABLE 2

DETERMINATION OF HYDROGEN OVERVOLTAGE

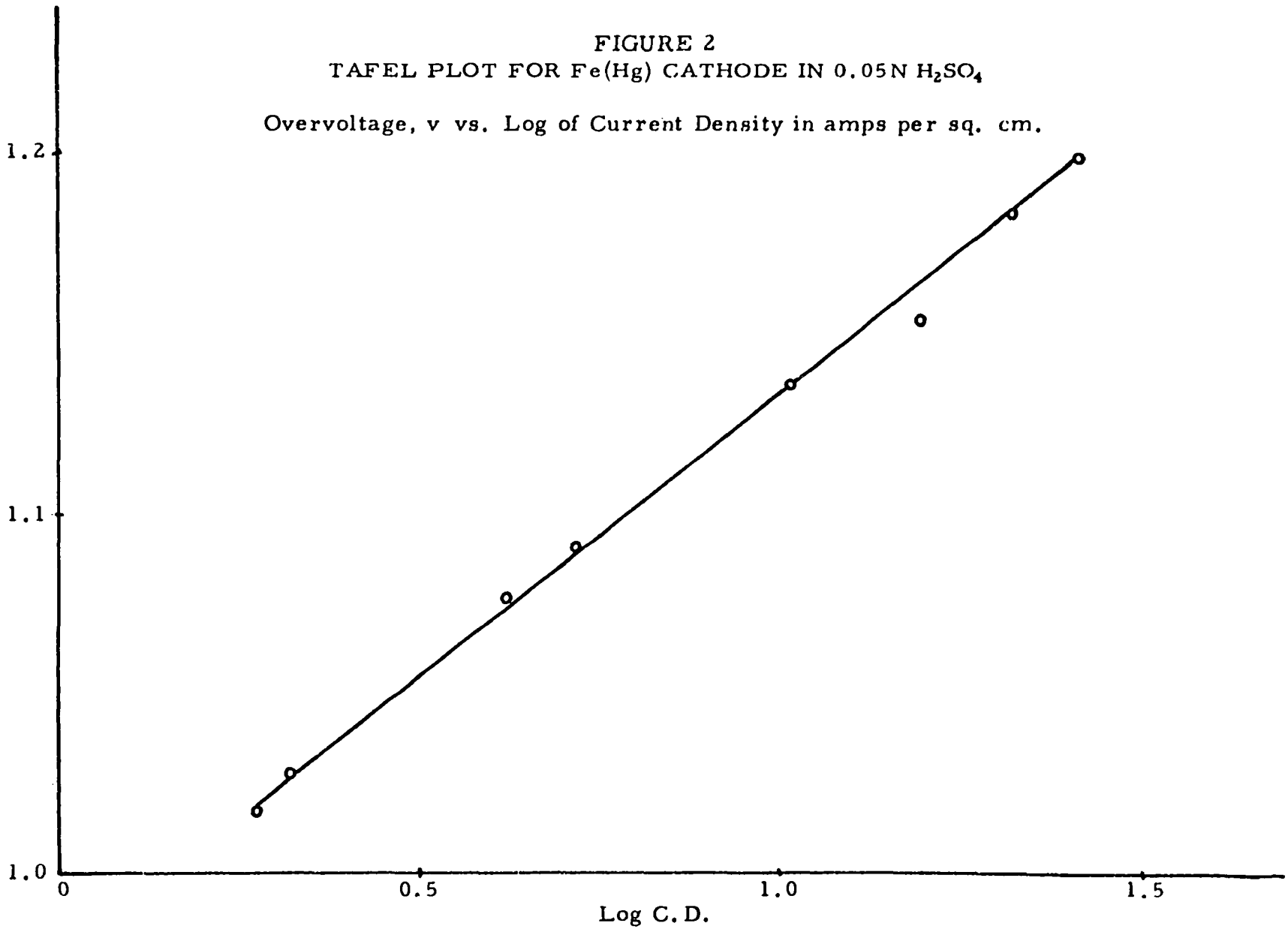
Overvoltage	Current	Current Density	log C. D.
1.017 v	9 ma	1.865 ma/cm^2	0.271
1.027	10	2.08	0.318
1.030	20	4.16	0.618
1.091	25	5.21	0.716
1.136	50	10.4	1.016
1.155	75	15.6	1.19
1.184	100	20.8	1.32
1.201	125	26.1	1.42

Electrolyses of Vanadium (V) Solutions

The selection of the initial pH of the solutions of vanadium (V) to be electrolyzed was determined in a preliminary experiment in which samples of stock vanadyl sulfate were adjusted to various pH values from pH 1 - pH 10 by the addition of sodium hydroxide. The solutions were allowed to stand two days and examined. Only those at pH 6-8 were free from precipitate. Neutral or slightly alkaline solutions were selected for all electrolyses. Qualitative transference experiments showed the vanadium to be the anion in the solutions used. Therefore, it was assumed that the cathodic reduction of the vanadium (V) involves a diffusion process. If this is the case, the current efficiencies

FIGURE 2
TAFEL PLOT FOR Fe(Hg) CATHODE IN 0.05N H_2SO_4

Overvoltage, v vs. Log of Current Density in amps per sq. cm.



should decrease with increase in current density because the adverse potential of the cathode would need to be overcome by the anion before it could be reduced there. Such a relationship was shown to hold. Electrolyses were conducted with the same initial solution, electrodes, temperature, and time.

TABLE 3

DEPENDENCE OF CURRENT EFFICIENCY ON CURRENT DENSITY

Current, amp	Current Density, a/cm^2	Vanadium Removed, wt %	Current Efficiency
0.08	8.24×10^{-3}	4.72	21.4%
0.275	2.82×10^{-2}	27.6	36.7
0.395	4.06×10^{-2}	23.5	21.7
0.64	6.59×10^{-2}	20.9	11.9

Auxiliary evidence in support of a diffusion mechanism is shown by an increase in current efficiency with increase in initial concentration of the solution. Figure 3 gives this relationship for a series of electrolyses each lasting 30 minutes. Data for this series of experiments are given below in Table 4.

FIGURE 3
ELECTROLYSES OF VANADIUM SOLUTIONS

Current Efficiency, % vs. Initial Concentration, me per 50 ml

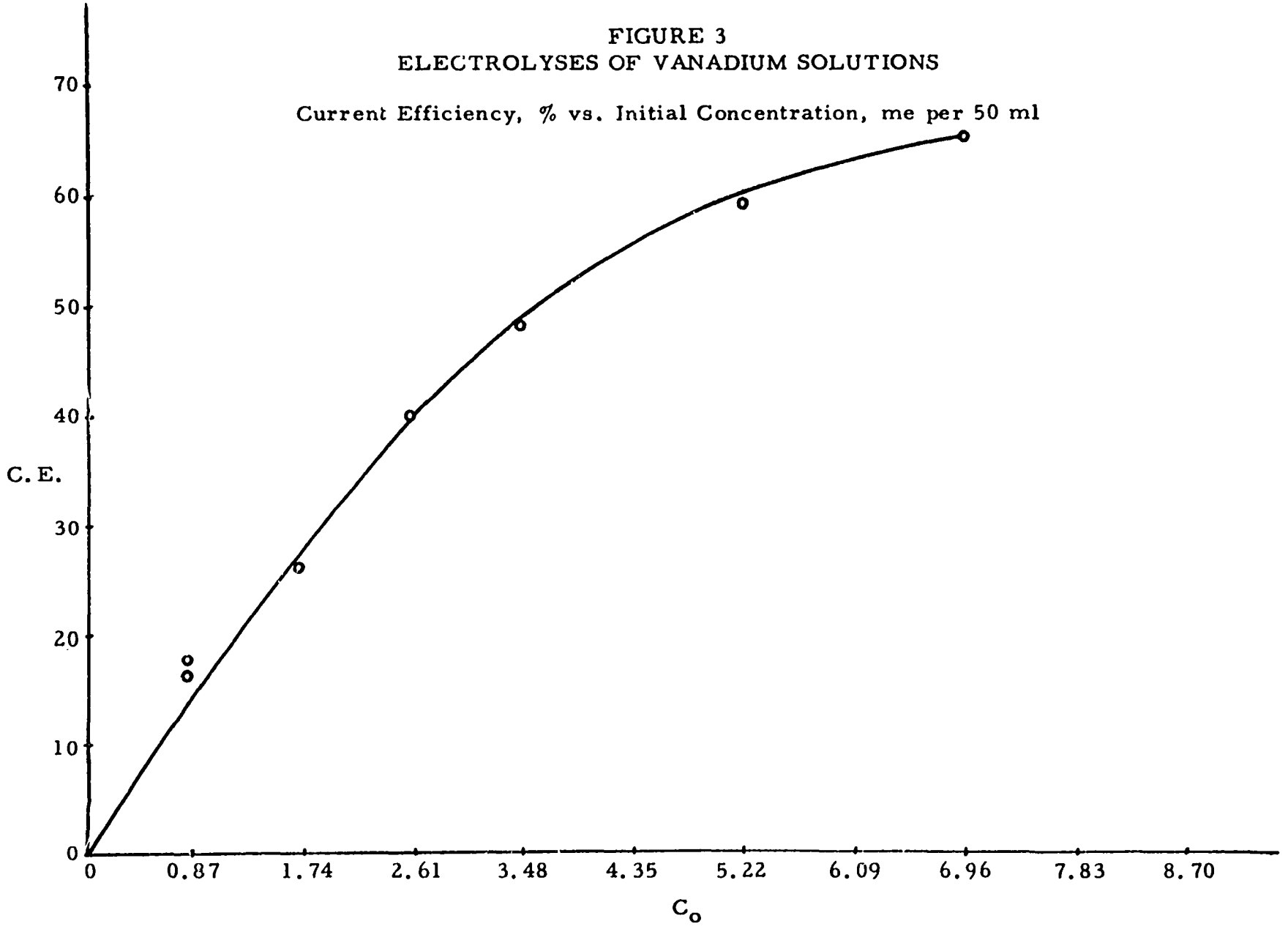


TABLE 4

DEPENDENCE OF CURRENT EFFICIENCY
ON INITIAL CONCENTRATION

Initial Concentration	Vanadium Removed wt %	Current Efficiency
0.868 me/50 ml*	57.6%	17.8%
0.868	52.3	16.3
1.74	42	26.1
2.61**	50	39.8
3.48	38.7	47.9
5.22	37.1	59
6.96	26.2	65

* Based on V(II) $-3e \rightarrow$ V (V).
** Run for thirty-five minutes.

Figure 4 shows the variation of current efficiency with duration of electrolysis. Data are given in the following:

FIGURE 4
ELECTROLYSES OF VANADIUM SOLUTIONS

Current Efficiency, % vs. Time, min

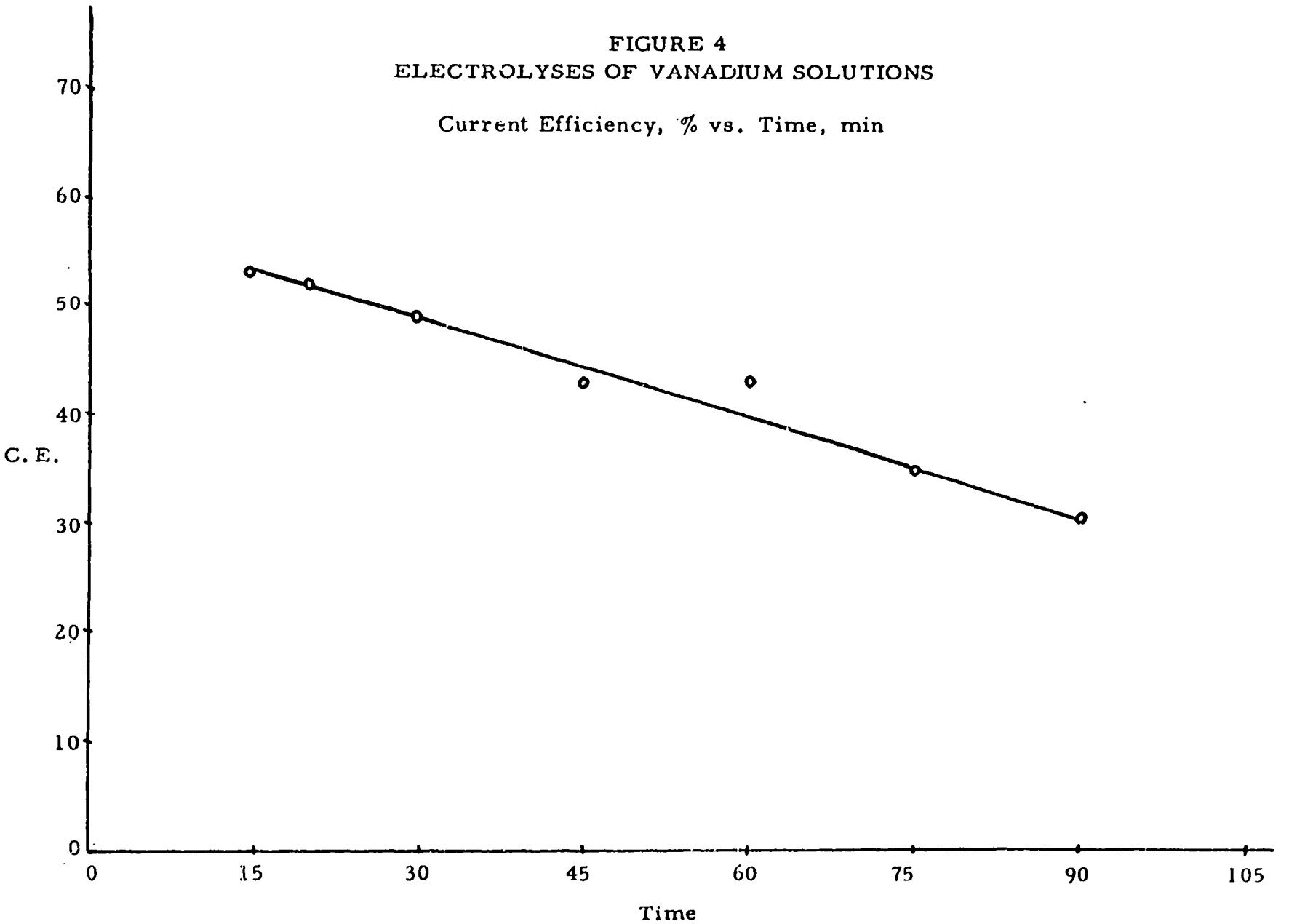


TABLE 5

DEPENDENCE OF CURRENT EFFICIENCY ON TIME

Time, min.	Vanadium Removed wt %	Current Efficiency, wt %
10	14.4	53.5
15	21.4	53.0
20	28.2	52.0
30	39.7	49.3
45	51.7	42.7
60	68.7	42.7
75	70.7	35.0
90	75.4	30.5

Results are as expected since the concentration of the solution lessens with the duration of electrolysis and it has already been shown in this study that current efficiency decreases with decreasing concentration.

Overvoltage measurements were made in a system in which vanadium (V) was being electrolyzed. A vanadyl sulfate solution containing 23g V_2O_5 per liter was brought to a pH 8.2 by the addition of 5 wt % sodium hydroxide. A compartment cell was used with an iron amalgam cathode, a smooth platinum wire anode, and a saturated calomel reference electrode. The results are shown in the following table and in Figure 5.

TABLE 6

OVERVOLTAGE IN VANADIUM (V) SOLUTION

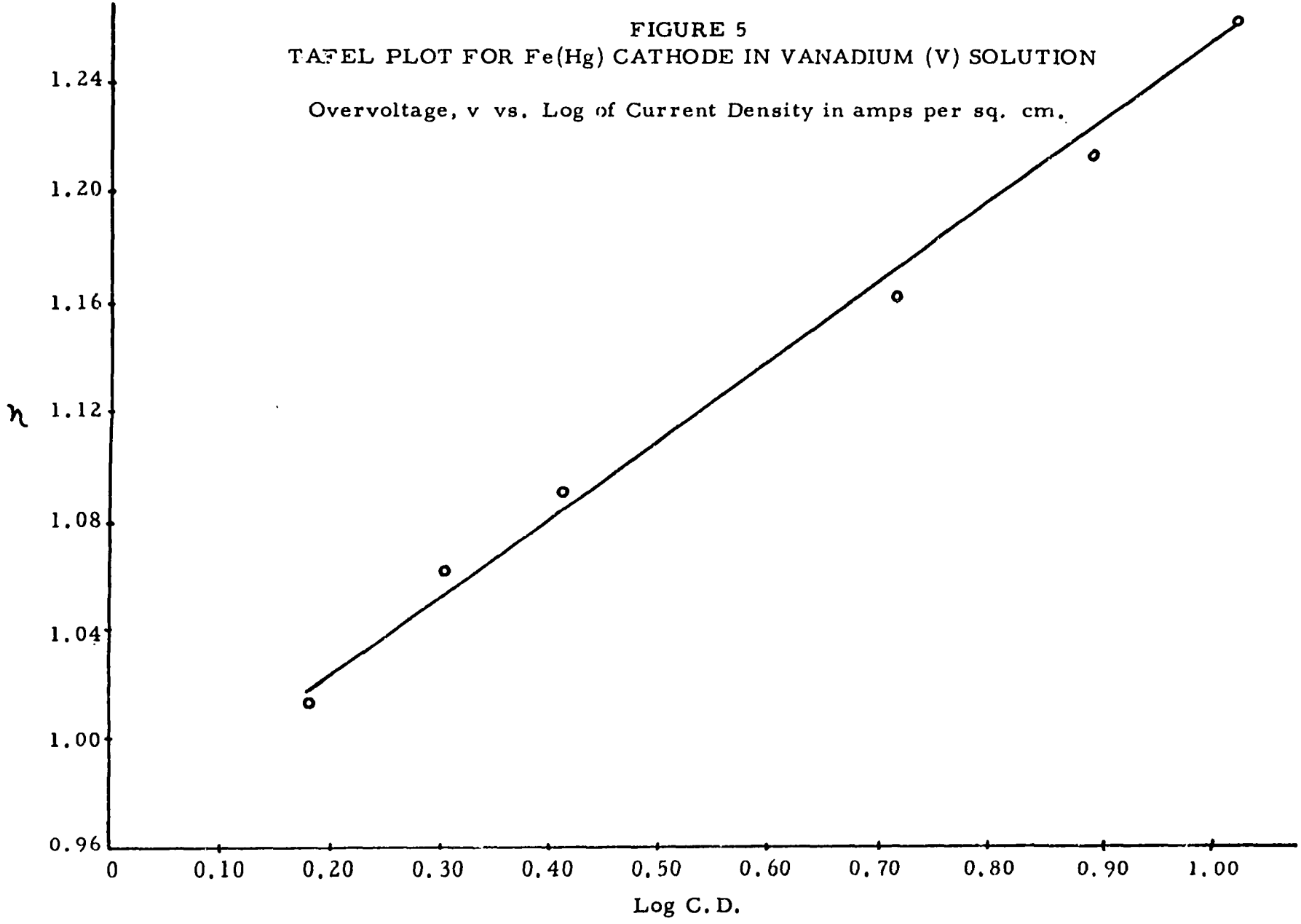
Overvoltage	Current	Current Density	Log C. D.
1.01 v	15 ma	1.54 ma/cm^2	0.189
1.06	20	2.06	0.304
1.09	25	2.58	0.410
1.16	50	5.16	0.712
1.21	75	7.73	0.888
1.26	100	10.3	1.013

In order to demonstrate conclusively that a cathode of high hydrogen overvoltage is necessary for the reduction of vanadium (V) compounds in neutral or basic solution, some reductions were attempted using electrodes of low overvoltage. A solution of sodium metavanadate was brought to pH 6.8 with 1 N sulfuric acid. Bright platinum wires were used as electrodes in a compartment cell. The catholyte changed from yellow to colorless. This is to be expected as the pH rises. There was no apparent reduction of vanadium in the cathode compartment as demonstrated by testing with permanganate. At the anode a red substance precipitated. This could be either a peroxyvanadate formed by anodic oxidation or a hydrated vanadic oxide. During the electrolysis hydrogen was evolved at the cathode. A palladium cathode was also tried. It has a low hydrogen overvoltage and also

FIGURE 5

TAFEL PLOT FOR Fe(Hg) CATHODE IN VANADIUM (V) SOLUTION

Overvoltage, v vs. Log of Current Density in amps per sq. cm.



has the ability to dissolve a large quantity of hydrogen. This electrolysis was conducted in a compartment cell. A bright platinum anode was immersed in a porous cup containing 1N sodium sulfate solution. The catholyte was a solution of sodium orthovanadate at pH 6.8 containing 1.70 me vanadium based on an electron charge of three. A current of 80 ma was run through the cell for a period of nine hours. At the end of this time the catholyte was acidified and permanganate added with no subsequent reduction of the permanganate. These electrolyses were conducted at room temperature. The results show that the evolution of hydrogen alone is not sufficient to bring about the reduction of vanadium (V) in a neutral or alkaline medium, but that the electrode must possess the additional property of high hydrogen overvoltage in order to supply a cell potential high enough to bring about the required reductions.

Characterization of the Products of Electrolysis of Vanadium (V) Solutions

At the end of an electrolysis the electrolysate was filtered through Whatman No. 41 filter paper. The solid material was washed thoroughly with distilled water, and the washings were added to the original filtrate. The solid was then washed with acetone, dried rapidly, transferred to a weighing bottle, and stored in a vacuum desiccator. The filtrate was acidified with dilute sulfuric acid, run through the zinc amalgam reductor and titrated with standard per-

manganate as previously described. A sample of the solid material was weighed to the nearest 0.1 mg. It was then placed in a 500 ml distilling flask. Dilute sulfuric acid solution which had been freed from dissolved oxygen by passing nitrogen gas through it was added to the flask. The flask was closed with a rubber stopper having a nitrogen sparge through it. The side arm of the distilling flask was left open to the atmosphere. The mixture was heated gently and nitrogen passed through it until solution was completed. This method was adapted from one given by Glemser and Schwarzmann (31). The solution, which was then green, was titrated to a rose color with standard permanganate. Then the flask contents were run through the zinc amalgam reductor and titrated again with permanganate. From these results the percent of vanadium and its average valence in the sample were calculated. The solid material was 44 wt % vanadium at an average valence 3. This does not correspond to any simple known oxide of vanadium. Qualitative tests showed the following ions absent in the solid material; Na^{+} by flame test, SO_4^{-2} by test with Ba^{+2}, Fe (II) and (III) by SCN^{-}, Hg (I) and (II) by $Co(SCN)_6^{-3}$ test.

CHAPTER III

DISCUSSION

An iron amalgam electrode which has hydrogen overvoltage high enough to bring about the cathodic reduction of vanadium (V) solutions in neutral and alkaline solutions has been prepared and studied. Assuming the Tafel equation, $\eta = a + b \log C.D.$, valid, the Tafel constants were obtained from Figure 2, and found to be a - 0.99 v and b - 0.16 v. Potter (25) gives a - 1.41 v and b - 0.115 v for a mercury cathode in 0.1 N hydrochloric acid at 20° C and a - 0.67 v, b - 0.116 v for an iron cathode in 2 N sulfuric acid at 20° C. It is interesting to note that "a" for the iron amalgam lies between the values for iron and mercury. The rather high value of "b" for the iron amalgam may be due to some slight impurity in the system. The amalgam electrode has the advantages over a mercury electrode in that it is easy to prepare, stir, and clean.

The efficiency of the amalgam electrodes for the reduction of vanadium could be predicted from the value of the decomposition potential of dilute sulfuric acid. It was learned that when the decomposition potential was 1.9 v or

greater, the electrode could be used successfully. It was therefore customary to determine this decomposition potential with each electrode prepared.

Unsuccessful attempts to bring about the reduction of vanadium (V) at platinum and palladium electrodes, which exhibit low hydrogen overvoltages, support the view that a cathode having a high hydrogen overvoltage is necessary.

Some of the solid product of the reduction adhered to the iron amalgam electrode, but most of it collected in the bottom of the cell vessel. The material was shown to be 44 wt % vanadium at an average valence of three but does not correspond to any simple vanadium compound known. It contains only vanadium, hydrogen, and oxygen. No attempt was made to separate the product into possible components. Examination of the particles with a light microscope showed them to be amorphous in nature. The solid material if left in the air for a time changed from a brown or black color to a blue or a green. Subsequent analysis showed the average valence of vanadium in the new substance to be near four.

The chemical processes taking place at the iron amalgam cathode during the electrolysis are not clearly understood. There is some current efficiency loss due to the production of hydrogen. Thus, current efficiencies are highest at electrodes of high hydrogen overvoltage. The vanadium reductions occur stepwise, the starting material being an anion possibly of a polyvanadic acid. No reliable

solubility data for the lower valence vanadium compounds could be found. The products of electrolysis in an acid solution are soluble even though the solid products of electrolysis in a basic solution are at best difficulty soluble in acid. This indicates that different products are formed in the two cases. The cathodic reductions in alkaline solution may be represented by the following equations according to Filipovic, et al (20).

$$VO_3^- + e + 2H^+ = VO(OH)_2,$$

$$VO(OH)_2 + e + H^+ = V(OH)_3,$$

$$V(OH)_3 + e + H^+ = V(OH)_2 + H_2O$$

Other variations could be written. The experimental work did not determine whether the increase in pH of the catholyte was due only tc the discharge of hydrogen ions.

The color of the catholyte changed during an electrolysis usually in the following sequence: yellow, green, brown, violet, colorless. Corresponding colors in an acid electrolysis are yellow, green, blue, green, and violet. The appearance of the violet color in the electrolysis shows some vanadium (II) formed even though no precautions were taken to exclude oxygen from the system. The low intensity of the violet color indicated only a small amount of soluble vanadium (II) formed. Never more than 90 wt % of the initial charge of vanadium could be removed by the electrolysis regardless of initial concentration and duration of electrolysis.

The chief disadvantage inherent in this process for the recovery of vanadium in solid form from solution is the formation of a film of the solid material on the cathode. This could probably be overcome by a device similar to that used by Boyer in his process for recovering uranium (26). He used a rotating cathode whose mercury surface was constantly renewed by passage through a mercury reservoir during part of its cycle.

The author was successful in reducing uranyl sulfate in sulfuric acid solution at the iron amalgam cathode. Solid product formed without film formation on the electrode. No attempts were made to characterize the product or to determine the current efficiency of the process. The results indicate the possibility of a process for separating both uranium and vanadium from ore extracts using a compartment cell and a cathode of high hydrogen overvoltage. Electrolysis at the initially low pH would cause the uranium to precipitate and fall to the bottom of the vessel where it could be drawn off and further processed. The pH of the cathode compartment would rise as hydrogen ion discharged. At a sufficiently high pH the vanadium compounds would precipitate. Initial experiments with a mixture of vanadium and uranium compounds indicated that careful control of the concentrations and pH would be necessary to insure the success of such a process.

CHAPTER IV

SUMMARY

An electrode having high hydrogen overvoltage was prepared by wetting a clean iron gauze with mercury. This electrode was used as a cathode to reduce vanadium (V) in solutions of high pH causing insoluble vanadium compounds to precipitate. Unsuccessful attempts to reduce the vanadium (V) at high pH using a platinum or palladium cathode demonstrated the need in this process for an electrode of high hydrogen overvoltage. The solid product formed contained 44 wt % vanadium at an average valence of three. A study of the variables current density, concentration, and time indicated that a current efficiency of sixty percent could be obtained for the removal of ninety percent of the vanadium initially persent in the solution.

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