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Electrochemical Studies of the Uranium(VI)–Ethylenediaminetetraacetic Acid Complex

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The electrochemistry of the 1:1 uranium(VI)–EDTA complex has been investigated by cyclic voltammetry, controlled-potential coulometry, and chronopotentiometry at mercury and platinum electrodes. Between pH 5 and 7 the complex is reduced by two irreversible one-electron steps with a chemical step between them (an ECE mechanism) to a stable uranium(IV)–EDTA species. At pH 6.4 and a scan rate of 0.02 V/sec the peak potential for reduction of the complex is −0.87 V *vs.* sce. On the basis of the electrochemical data and pH studies the electroactive species is UO_2YH^- (Y represents the tetraanion of EDTA); its diffusion coefficient at 25° is 5.5×10^{-6} cm²/sec. The electron-transfer kinetic parameters αn_a and $k^\circ_{f,h}$ have values of 0.2 and 2.1×10^{-5}, respectively; mechanisms are proposed for reduction of the complex.

Since the initial observation[1] that some type of interaction occurs between the uranyl ion (UO_2^{2+}) and ethylenediaminetetraacetic acid (H_4Y, EDTA), various workers have concluded that EDTA can react with one or two uranyl ions to form stable complexes.[2–8]

Electrochemical studies of the uranyl ion and many of its complexes have been the subject of numerous investigations, but, surprisingly, work on the EDTA complexes has been limited. The previous literature consists of two polarographic studies;[9,10] apparently the electrochemistry of uranium(VI)–EDTA has appeared so simple (or so complex) that other studies have not been attempted.

The reduction of the 1:1 uranyl–EDTA system has been described as a reversible one-electron transfer,[9,10] but coulometric experiments slightly cathodic of the half-wave potential, $E_{1/2}$, indicate an overall two-electron reduction.[9] The diffusion coefficient for the complex has been reported to be 1.3×10^{-5} cm²/sec, but the diffusion coefficients for the free uranyl ion (6.2×10^{-6} cm²/sec)[11] and its carbonate complex (4.4×10^{-6} cm²/sec)[12] imply that the value is high. In addition, the diffusion currents and half-wave potentials for the complex were found to vary in a nonlinear fashion with pH. Because the time scale for classical polarography is slow, it is a poor method for many mechanistic studies. The limited understanding of the electrochemistry for the uranium(VI)–EDTA complex has prompted additional studies using modern electrochemical techniques.

A series of recent articles provide a basis for the application of cyclic voltammetry (stationary electrode polarography) to the investigation of a wide range of oxidation and reduction mechanisms.[13–16] In addition, several articles have shown chronopotentiometry to be an equally useful electrochemical technique for mechanistic studies.[17–22]

The present work summarizes the results of a detailed study of the electrochemistry of uranium(VI), -(V), and -(IV) complexes with EDTA.

Experimental Section

The electrochemical measurements were made with a combination potentiostat–amperostat (based on solid-state Philbrick operational amplifiers),[23] in principle an upgraded version of the

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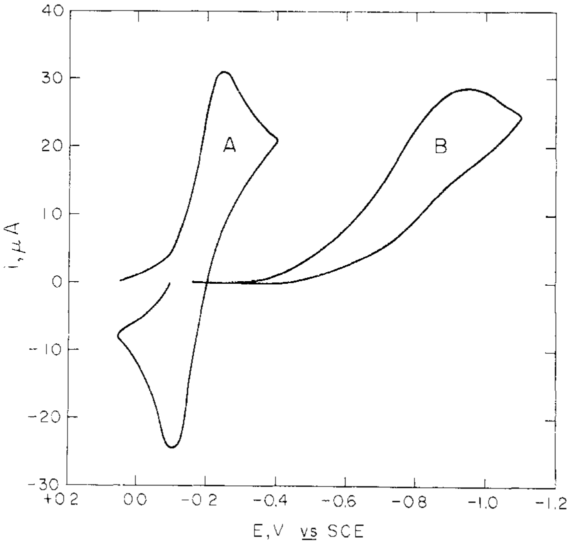

Figure 1.—Typical cyclic voltammetry curves at a mercury electrode: (A) 2.3 × 10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, pH 3.60; (B) 1.93 × 10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, 0.06 *F* Na_2H_2Y, pH 6.40.

"universal" tube-type electrochemical instrument described by DeFord.[24]

Cyclic voltammetric current–potential curves were recorded using a Hewlett-Packard-Mosley X-Y recorder, Model 7030A, for potential scan rates up to 1 V/sec. Faster scan rates were attained by applying a triangular-wave signal from a Hewlett-Packard Model 202A low-frequency function generator to the working electrode circuit of the electrochemical instrument. The resulting voltammetric curves were displayed on a Tektronix Model 564 storage oscilloscope.

Chronopotentiometric potential–time curves were recorded with a Sargent Model SR-2 strip chart recorder or, for shorter times, with the X-Y recorder or the oscilloscope (both of which had calibrated time-base sweep generators which could be connected to the horizontal axis).

The electrochemical experiments were conducted on test solutions contained in a Leeds and Northrup coulometric cell (Kit No. 7961); a three-electrode system was employed for all experiments. The reference electrode was a Leeds and Northrup Ag|AgCl type of miniature reference electrode (part no. 117147) taken from a miniature pH electrode kit (part no. 124138). The concentration of the electrode-filling solution was adjusted to give an electrode potential of 0.000 ± 0.0001 V when referenced to a saturated calomel electrode (sce) at 25°. The auxiliary electrode consisted of a cylinder of platinum gauze isolated from the bulk solution by a glass frit. The working electrode was either a platinum-inlay type (Beckman No. 39273) or a stationary mercury film prepared by amalgamating a platinum-inlay electrode according to the procedure of Moros.[25]

The area of the platinum-inlay electrode was 0.232 cm^2 as determined by chronopotentiometric reduction of potassium ferricyanide in 0.5 *F* KCl solution; the diffusion coefficient was assumed to be 7.67 × 10^{-6} cm^2/sec for the ferricyanide ion.[26] Subsequent experiments using both electrodes indicated an area of 0.215 cm^2 for the mercury-film electrode as compared to the platinum electrode; the geometric area of the latter was 0.208 cm^2.

Coulometric reductions were carried out at a mercury pool to which electrical contact was made with a platinum wire sealed in the bottom of the cell.

Pretreatment of the platinum-inlay and the mercury-film electrodes was necessary to obtain reproducible results. The platinum electrode was treated according to the recommendations of Bard.[22] With the mercury electrode, either washing the electrode with 1 *F* perchloric acid or momentarily anodizing it after each run gave equivalent and reproducible results.

To gain more precision in the measurement of the transition times of chronopotentiograms, the derivative of the normal chronopotentiometric wave was recorded. This was accomplished by inserting a capacitor in series between the potential output jack of the instrument and the input of a solid-state operational amplifier; the output of the latter was connected to the recorder. The other recorder lead was connected to the ground jack of the instrument. Capacitance values between 0.05 and 5.0 μF were used, depending on the system and the applied current.

Initial experiments to test the derivative method were applied to the chronopotentiometric reduction of potassium ferricyanide at a platinum-inlay electrode; the results established the reliability and accuracy of the technique. Subsequent experiments on aqueous solutions of uranyl perchlorate at a mercury-film electrode gave equally reliable results.

Stock solutions of uranium(VI) were prepared from reagent grade uranyl perchlorate hexahydrate (G. Fredrick Smith Chemical Co.). Sodium perchlorate monohydrate (G. Fredrick Smith Chemical Co.) and ammonium perchlorate (Matheson Coleman and Bell) were used as supporting electrolytes. EDTA solutions were prepared from either the disodium salt, $Na_2H_2Y \cdot 2H_2O$, or the tetraacid neutralized with ammonium hydroxide (to exclude sodium ion from solution). Both forms of EDTA were Baker Analyzed reagents (J. T. Baker Chemical Co.) and were used without further purification. All other materials were reagent quality and used as received. Perchlorate salts were used exclusively to minimize complexation of uranium by anions in solution.

The uranium(VI) stock solution was analyzed by the method of Kolthoff and Sandell;[27] its concentration was 0.0485 *F*. Test solutions were prepared by taking aliquots of the stock solution, adding supporting electrolyte and EDTA, and diluting the mixture to a known volume. The adjustment of pH was accomplished with concentrated $HClO_4$ and either saturated NaOH or concentrated NH_4OH.

Oxygen was excluded from the test solutions by bubbling prepurified nitrogen through them for 10 min and then passing nitrogen above the solution surface during electrolysis.

Solutions of uranium(IV)–EDTA were prepared by electrolytically reducing uranyl perchlorate in strong acid at −0.4 V *vs.* sce before adding an excess of EDTA. The pH was adjusted after degassing the solution to prevent reoxidation by dissolved oxygen.

Results

A. Cyclic Voltammetry.—Figure 1 illustrates typical stationary electrode voltammograms for uranium(VI) in the absence of a complexing agent (A) and in the presence of excess EDTA (B). The solution of the free uranyl cation is at sufficiently high pH to prevent the disproportionation of uranium(V).[28–30] Addition of EDTA eliminates any anodic current for the U(VI) cyclic voltammetric curve over the useful potential range of the mercury electrode. This is true for potential scan rates from 0.005 to 25 V/sec and for solutions from pH 4 to 8. These results indicate that the electron-transfer reactions are irreversible for the uranium(VI)–EDTA complex.

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TABLE I

CYCLIC VOLTAMMETRY PARAMETERS FOR 2 m*F* U^{VI}–EDTA IN 0.5 *F* $NaClO_4$ AND 0.06 *F* Na_2H_2Y (pH 6.40) AT A MERCURY ELECTRODE

ν, V/sec	i_p, μA	E_p, V *vs.* sce	$0.95i_p$, μA	$E_{0.95p}$, V *vs.* sce	$i_p/\nu^{1/2}$, μA^2 $sec^{1/2}$ $V^{-1/}$
0.01	22.5	−0.835	21.4	−0.768	225.0
0.02	29.8	−0.870	28.3	−0.795	210.7
0.05	43.9	−0.925	41.7	−0.837	196.3
0.10	56.8	−0.970	54.0	−0.878	179.6
0.20	75.2	−0.985	71.4	−0.916	168.2
0.50	106.2	. . .	100.8	. . .	150.2
1.00	144.0	. . .	136.8	. . .	144.0

Evaluation of the electrochemical data by various diagnostic criteria[13–16] provides additional insight to the reduction mechanism. Table I summarizes the effect of potential scan rate on peak currents, i_p, and peak potentials, E_p, for the reduction of the U^{VI}–EDTA complex. The cathodic peak is unusually broad; for this reason the current and potential at a point 95% up the wave also are included because $0.95E_p$ can be determined more precisely than E_p. A plot of peak potentials *vs.* the logarithm of scan rate gives linear curves with slopes of 0.12 V for $E_{0.95p}$ and 0.14 V for E_p. Assuming an irreversible, diffusion-controlled process these slopes yield values of 0.24 and 0.21, respectively, for αn_a,[13–15] where α is the transfer coefficient and n_a is the number of electrons in the rate-controlling step. Table I also summarizes the effect of varying the scan rate, ν, on the value of $i_p/\nu^{1/2}$. The quantity $i_p/\nu^{1/2}$ should be independent of scan rate for a diffusion-controlled, reversible electron-transfer reaction; a decrease with increasing scan rate indicates kinetic complications.

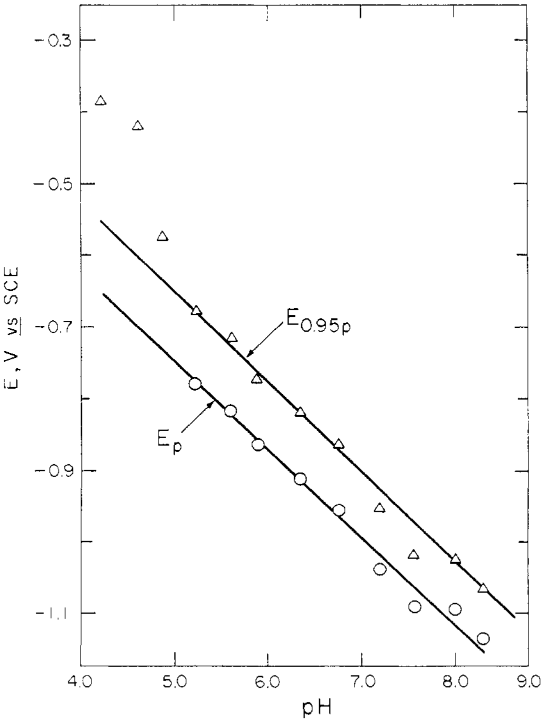

Figure 2.—Variation of E_p and $E_{0.95p}$ with pH at a mercury electrode. Conditions: 1.93 × 10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, 0.06 *F* Na_2H_2Y; scan rate, 0.02 V/sec.

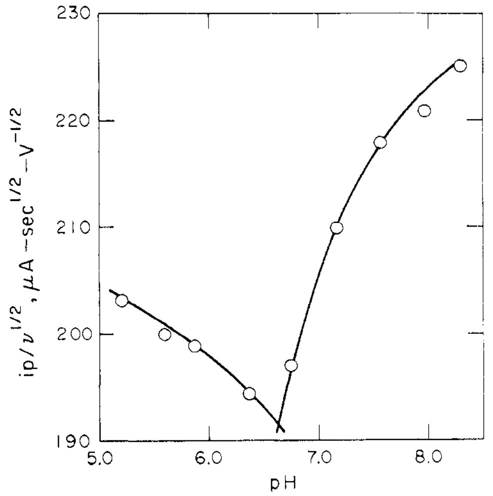

Figure 3.—Variation of $i_p/\nu^{1/2}$ with pH at a mercury electrode. Conditions: 1.93 × 10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, 0.06 *F* Na_2H_2Y; scan rate, 0.02 V/sec.

The peak potential and the quantity $i_p/\nu^{1/2}$ also vary with the pH of the solution. The corresponding functions are plotted *vs.* pH in Figures 2 and 3, respectively. Below pH 5 the cyclic wave is sufficiently broad that peak potentials cannot be measured. For this reason values of $E_{0.95p}$ also are included in Figure 2.

Cyclic potential scans of uranium(IV) solutions containing excess EDTA do not give anodic or cathodic peaks in the potential range covered by platinum-inlay and mercury-film electrodes, a combined range of more than 2 V (from +0.8 to −1.4 V *vs.* sce).

B. Coulometry.—The controlled-potential coulometric reduction of a 2 m*F* uranium(VI) solution containing excess EDTA (0.06 *F*) proceeds rapidly without complications at a potential only slightly cathodic of the peak potential observed in cyclic voltammetry. The electrolysis product at −1.20 V *vs.* sce is U^{IV}–EDTA on the basis of the coulomb integral (*n* value of 2.0 ± 0.1 electrons after 2.5 hr of electrolysis) and a subsequent titration with standard potassium dichromate.[27] By comparison, the reduction at −0.35 V *vs.* sce of a 2 m*F* uranium(VI) solution without EDTA (pH <1) approaches an *n* value of 2 only after extended electrolysis (n = 1.87 after 25 hr). This is due to a slow intermediate step involving the disproportionation of U(V) to give U(IV) and U(VI).[28–35] A significant increase in pH occurs during electrolysis of the EDTA complex (from pH 6.90 to 7.55), which indicates the consumption of protons in the overall reduction process. A comparable electrolysis of an EDTA solution without uranium(VI) gives almost no pH change.

The U^{IV}–EDTA produced by coulometry varies in color, depending on the final pH. Above pH 7.4 the solution is green while at lower pH it appears brown, possibly due to a colloidal suspension of some un-ionized species. With the addition of acid the brown color

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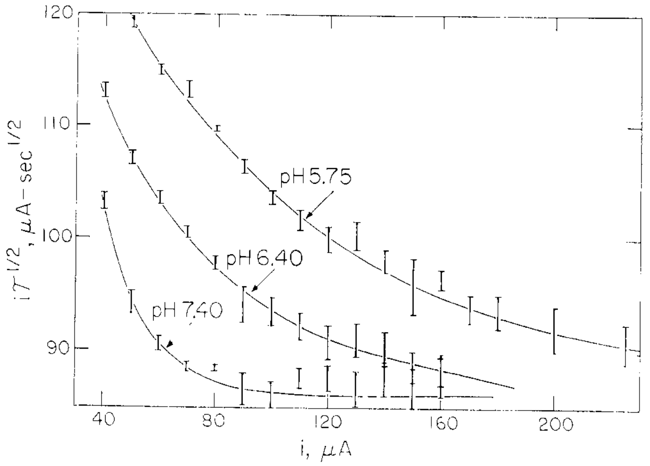

Figure 4.—$i\tau^{1/2}$ *vs.* i for several values of pH at a mercury electrode. Conditions: 1.93×10^{-3} F $UO_2(ClO_4)_2$, 0.5 F $NaClO_4$, 0.06 F Na_2H_2Y.

begins to fade and at pH 3 only a pale green color remains. Below this pH precipitation of free EDTA occurs.

Above pH 3 solutions of U^{IV}-EDTA are unstable to air; the rate of oxidation to U^{VI}-EDTA increases with increasing pH. A solution in air at pH 3.2 does not show a perceptible color change after setting for several hours, but when left overnight a yellow-green precipitate forms which is identical with that given by U^{VI}-EDTA under the same conditions.

Cyclic voltammetry of U^{IV}-EDTA solutions produced by coulometry does not yield anodic or cathodic peaks within the useful potential range of the platinum-inlay and mercury-film electrodes between pH 3.2 and 8.0.

C. Chronopotentiometry.—The reduction of uranium(VI)-EDTA at controlled current is dependent upon the pH of the test solution and upon the magnitude of the applied current i. This dependence is indicated by Figure 4 where $i\tau^{1/2}$ is plotted *vs.* i for a series of pH values; τ is the transition time for the reduction wave. For a diffusion-controlled process the chronopotentiometric constant, $i\tau^{1/2}$, is related to other measurable parameters by the Sand equation[21]

$$i\tau^{1/2} = \frac{\pi^{1/2}}{2} nFAD^{1/2}C \qquad (1)$$

and is independent of the applied current. However, when the electrolysis process includes kinetic complications $i\tau^{1/2}$ may vary with current density and with changes in the actual concentration of the electroactive species.[19] Figure 4 indicates that $i\tau^{1/2}$ is not constant for a given concentration of U^{VI}-EDTA but varies inversely with the applied current; at sufficiently high currents $i\tau^{1/2}$ does approach a constant value. The rising portion of the curves in Figure 5 is shifted toward lower currents as the pH of the solution is increased, but the high-current limit of $i\tau^{1/2}$ appears to be independent of pH.

For the diffusion-controlled irreversible reduction of an electroactive species the potential of the working electrode at any time, t, is given by[21]

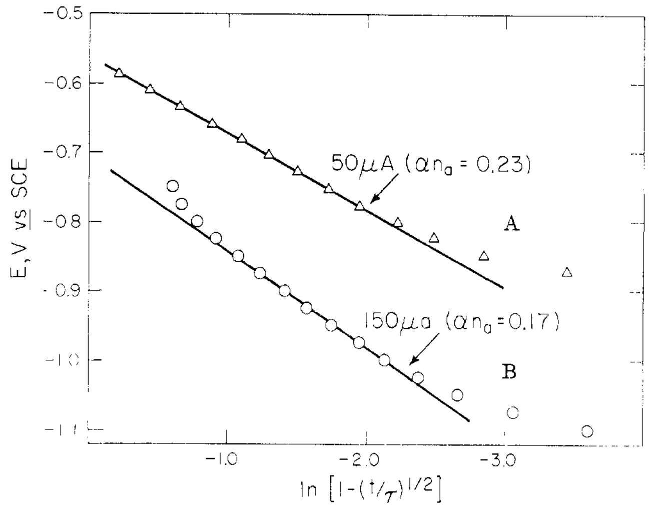

Figure 5.—E *vs.* ln $[1 - (t/\tau)^{1/2}]$ at a mercury electrode. Conditions: 1.93×10^{-3} F $UO_2(ClO_4)_2$, 0.5 F $NaClO_4$, 0.06 F Na_2H_2Y, pH 6.40.

$$E(t) = \frac{RT}{\alpha n_a F} \log \frac{nFAC_0 k^\circ_{f,h}}{i} + \frac{RT}{\alpha n_a F} \log\left[1 - (t/\tau)^{1/2}\right] \qquad (2)$$

where $E(t)$ is the potential *vs.* nhe and $k^\circ_{f,h}$ is the heterogeneous forward rate constant. A graph of $E(t)$ *vs.* log $[1 - (t/\tau)^{1/2}]$ should yield a straight line with a slope of $59/\alpha n_a$ mV and an intercept that gives the value of $k^\circ_{f,h}$. A similar relation to eq 2 applies to reversible chronopotentiometric potential-time curves.[21]

Plots of $E(t)$ *vs.* the corresponding log term for both the reversible and irreversible cases have been made for a series of chronopotentiograms run at various pH values over a wide range of current densities. Graphs for the reversible case typically are S-shaped curves. In contrast, plots for the irreversible case are linear over a large portion of each of the curves (see Figure 5). However, the irreversible log plots at both high and low current densities exhibit some deviation from straight-line behavior at the ends of the curves (near $t = 0$ and near $t = \tau$). Curve A of Figure 5 results from data at low current densities (in the kinetic region indicated by Figure 4) and indicates appreciable deviation from theory as t approaches τ. Curve B results from data in the region of constant $i\tau^{1/2}$ (Figure 4, current-limiting value) and deviates some from linearity for both large and small values of t. The values of αn_a, as calculated from the slopes of the linear portions of the curves, range from 0.17 to 0.24 for all of the graphs plotted at various current density and pH values.

Further information from the chronopotentiometric data has been obtained by evaluating the potential function, $E(t)$, of eq 2 at $t = 0$. For this condition the last term on the right-hand side becomes zero and $E(t = 0)$ can be expressed as a function of concentra-

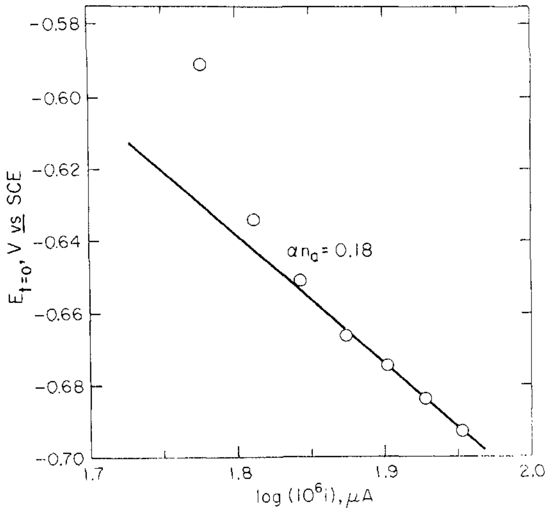

Figure 6.—$E_{t=0}$ *vs.* log ($i \times 10^6$) at a mercury electrode. Conditions: 2.30×10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, 0.06 *F* Na_2H_2Y, pH 5.95.

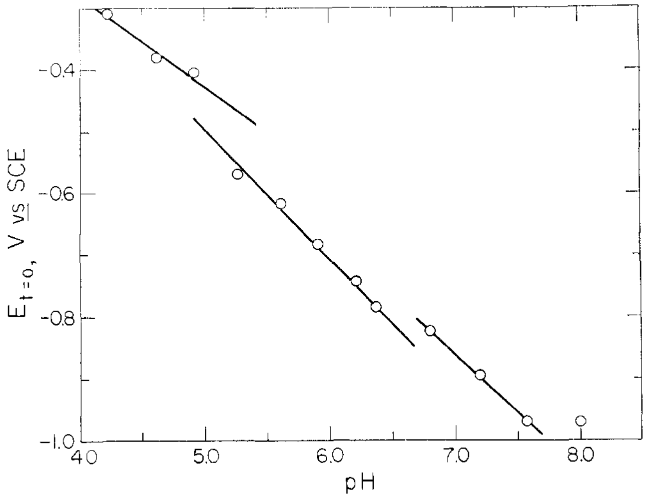

Figure 7.—$E_{t=0}$ *vs.* pH at a mercury electrode: 1.93×10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, 0.06 *F* Na_2H_2Y; i = 50 μA.

tion, current density, and a series of constants. The values of $E(t = 0)$ have been evaluated by extrapolation of the straight-line portion of the $E(t)$ *vs.* log $[1 - (t/\tau)^{1/2}]$ plots to $t = 0$.

At high applied currents where $i\tau^{1/2}$ is constant, $E(t = 0)$ is a linear function of log i, but in the low-current (kinetic) region a systematic deviation from this straight-line behavior is observed (Figure 6). Values for αn_a determined from the slopes of the linear portions of the $E(t = 0)$ *vs.* log i curves range from 0.18 to 0.21. In Figure 7 the variation of $E(t = 0)$ with pH is shown for chronopotentiograms run at constant current; the shift with pH does not appear to be a continuous linear curve.

Current reversal chronopotentiometry has been carried out on solutions of U^{VI}–EDTA at several pH values over a series of current densities. No reverse wave is observed within the useful range of the mercury electrode under these conditions.

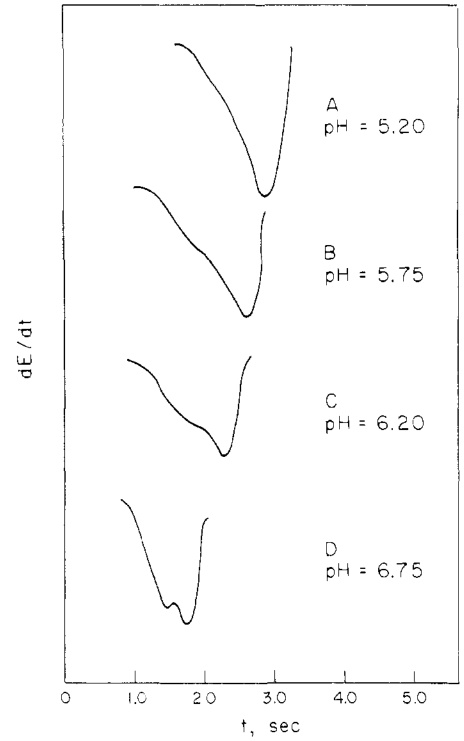

Figure 8.—Derivative chronopotentiometric peaks at several pH values. Conditions: 1.93×10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, 0.06 *F* Na_2H_2Y; i = 70 μA (mercury electrode).

Derivative chronopotentiometry has been used primarily to aid in the measurement of transition times. However, when a series of curves for various pH values are recorded at the same current density, the decrease in the transition time with increasing pH is accompanied by a change in the shape of the derivative peak. Figure 8 illustrates the derivative peaks obtained at a current of 70 μA for several different pH values. As the pH is increased, a shoulder on the left side of the peak becomes more predominant until at pH 6.7 two separate peaks are observed. All transition times measured by the derivative method have been reported as the time to the second peak. Transition times measured to the first peak at several current densities give values for $i\tau^{1/2}$ of about 86–87.5 μA sec$^{1/2}$, which is in excellent agreement with the high-current limit of $i\tau^{1/2}$ shown in Figure 4.

If this limiting value of $i\tau^{1/2}$ corresponds to a one-electron reduction of the U^{VI}–EDTA species, the diffusion coefficient as calculated from eq 1 is $(5.5 \pm 0.2) \times 10^{-6}$ cm²/sec. Such a value appears consistent with the values reported for the uranyl cation[11] and the uranyl carbonate complex.[12]

Discussion and Conclusions

A. General Reduction Mechanism.—The results of the coulometric reduction of uranium(VI)–EDTA establish that the mechanism involves the net transfer of two electrons to yield a stable U^{IV}–EDTA species. A reduction process involving two separate one-electron transfers is indicated by the variation of $i_p/v^{1/2}$ with scan rate (Table I) and by the nonlinear increase of $i\tau^{1/2}$ at lower currents (Figure 4). The behavior in each case implies that the reduction occurs by an ECE mechanism, *i.e.*, with a chemical reaction interposed between the two one-electron transfer steps. The

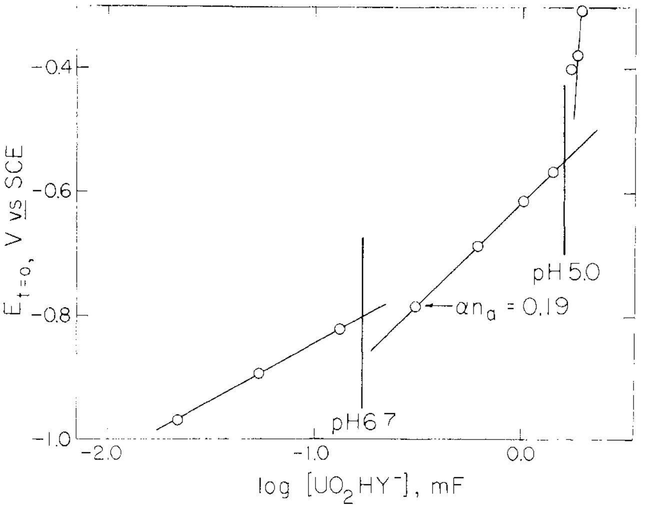

Figure 9.—$E_{t=0}$ *vs.* log [UO_2HY^-] with a mercury electrode. Conditions: 1.93×10^{-3} *F* $UO_2(ClO_4)_2$, 0.5 *F* $NaClO_4$, 0.06 *F* Na_2H_2Y; i = 50 μA. pH values indicate the approximate range where the linear relationship holds (stability range of complex).

intermediate chemical step may also involve a disproportionation reaction with regeneration of the electroactive species.

The possibility of a disproportionation process can be eliminated for several reasons. First, reduction of U^{VI}–EDTA to U^{IV}–EDTA by coulometry proceeds rapidly to completion. In contrast, the coulometric reduction of the free uranyl cation to U(IV), which is known to involve disproportionation of U(V), requires almost 1 day to reach an n value of 2. Second, a voltammetric wave for a disproportionation process should exhibit an anodic shift of about $30/\alpha n_a$ mV per tenfold increase in the potential scan rate;[16] Table I indicates exactly the opposite effect. Assuming an average value of 0.2 for αn_a, the observed cathodic shift is about $28/\alpha n_a$ mV per tenfold increase in ν, characteristic of a straightforward ECE mechanism.[14]

The emergence of a second peak as the pH is increased in the derivative chronopotentiometric study of U^{VI}–EDTA (Figure 8) indicates a unique second step in the reduction mechanism. The reduction of regenerated U^{VI}–EDTA (from a disproportional process) would occur at the same potential as the reactant and cause the transition time to be extended. The presence of the second reduction step does not eliminate the possibility of a disproportionation reaction but it does indicate that a separate second electron transfer also must occur.

In addition to establishing that reduction of U^{VI}–EDTA proceeds by an ECE mechanism, the reversibility of the individual charge transfers is of interest. Because no anodic currents are observed over a wide range of potential scan rates, both reduction steps appear to be irreversible (ICI mechanism).[14] However, the cyclic curve for a two-step reduction following an RCI mechanism would give the same results if the rate of the chemical step were very large relative to the scan rate. In either case the second electron transfer must be irreversible.

B. First Electron Transfer.—To examine the kinetics of the first reduction step in the absence of subsequent complicating processes, experiments must be done on a sufficiently rapid time scale to prevent the intermediate chemical reaction from generating a significant amount of the second electroactive species. Cyclic voltammetry is of little use for such a study of U^{VI}–EDTA because at scan rates above 1 V/sec the cathodic wave is shifted enough to result in interference from solvent reduction. For this reason the first electron transfer has been studied by chronopotentiometry at high current densities.

On the basis of nearly linear plots of $E(t)$ *vs.* log $[1 - (t/\tau)^{1/2}]$ at high currents (Figure 5), the first reduction step appears to be an irreversible electron transfer with an average value for αn_a of 0.2. For an irreversible charge transfer $E(t = 0)$ should shift cathodically by $59/\alpha n_a$ mV for a tenfold increase in the applied current (eq 2). The corresponding equation for a reversible charge transfer[21] requires that $E(t = 0)$ be independent of the applied current. Reference to Figure 6 indicates that $E(t = 0)$ shifts cathodically with increasing current and confirms that the first electron transfer is irreversible. The linear portion of the curve in Figure 6 has a negative slope of 320 mV which corresponds to an αn_a value of 0.19. If the first step is irreversible, then the reduction of U^{VI}–EDTA can be concluded to involve an ICI mechanism (two irreversible electron transfers coupled by a chemical kinetics step).

From eq 2, $E(t = 0)$ should be proportional to the concentration of the electroactive species at a constant current density. However, Figure 7 indicates that the values of $E(t = 0)$ are affected significantly by the solution pH. Thus, the concentration of electroactive species, C, must be dependent on the hydrogen ion concentration. The cathodic shift of $E(t = 0)$ as the pH is increased implies that C is related to C_{H^+} by an equilibrium expression of the general form $A + nH^+ = B$, where B is the electroactive species. From an electrostatic point of view this is reasonable because the species which is more positively charged should be more easily reduced.

The 1:1 uranium(VI)–EDTA complex has been isolated and shown to correspond to the formula $UO_2H_2Y \cdot 2H_2O$,[7] where Y represents the tetraanion of EDTA. The predominant species in solution below pH 5 is the singly charged anion, UO_2HY^-, on the basis of the equilibrium data. The actual species in solution may be $UO_2H_2(OH)Y^-$ which would result from removing the first proton of a coordinated water molecule.

In the pH range from pH 5 to 8 a second proton is removed from the U^{VI}–EDTA complex to yield the dianion UO_2Y^{2-}. The singly and doubly charged species are in equilibrium according to the expression

$$H^+ + UO_2Y^{2-} = UO_2HY^- \qquad (3)$$

with the data of Figure 7 implying that UO_2HY^- is the electroactive species. The equilibrium constant for eq 3 has been evaluated[7,8]

$$K_{\mathrm{eq}} = \frac{k_f}{k_r} = \frac{[\mathrm{UO_2HY^-}]}{[\mathrm{H^+}][\mathrm{UO_2Y^{2-}}]} = 4.17 \times 10^5\ M^{-1} \qquad (4)$$

Using eq 4, the equilibrium concentration of UO_2HY^- has been calculated for pH values corresponding to the data points of Figure 7. The resulting values have been used to plot $E(t = 0)$ as a function of log $[UO_2HY^-]$ (Figure 9). On the basis of eq 2 the plot should be linear with a slope of $59/\alpha n_a$ mV (assuming UO_2HY^- to be the only electroactive species at the observed potential). Reference to Figure 9 indicates that the curve is linear for points calculated from pH 5 up to about pH 6.7 (limits shown on the graph). The straight-line portion of the curve has a slope which corresponds to an αn_a value of 0.19. Thus, $E(t = 0)$ is independent of pH (between pH 5 and 6.7) when C is expressed as the equilibrium concentration of UO_2HY^-. This permits evaluation of the heterogeneous electron-transfer rate constant, $k^\circ_{f,h}$, through the use of eq 2 and the data from the linear portion of the curve in Figure 9. The results give an average value for $k^\circ_{f,h}$ of 2.1×10^{-5} cm/sec.

C. Intermediate Chemical Reaction.—Consideration of the data in Figures 2 and 4 for small currents and scan-rate values permits some qualitative features of the coupled chemical reaction to be deduced. At a constant current density (or scan rate) the value of $i\tau^{1/2}$ (or the peak current function) decreases as the pH of the solution is increased. This indicates that the amount of the electroactive species generated by the chemical reaction is decreased as the hydrogen ion concentration is lowered. On this basis the kinetics step appears to involve protonation of the product of the first electron-transfer reaction

$$\mathrm{UO_2HY^{2-}} + n\mathrm{H^+} = \mathrm{H}_n\mathrm{UO_2HY}^{n-2} \qquad (5)$$

with $H_nUO_2HY^{n-2}$ being the second electroactive species. Other equilibrium expressions are possible but the data require that they involve a hydrogen ion dependent reaction of the first reduction product to yield a species that is further reduced electrochemically.

D. Second Electron Transfer.—Although the reduction of U^V–EDTA to U^{IV}–EDTA has been shown to be irreversible, a more quantitative evaluation of the second charge-transfer step in terms of the kinetic parameters cannot be made because of interferences from the preceding reactions. Such a study would be possible if the U(V) complex could be isolated in a stable form, but as yet this has not been accomplished. However, examination of the derivative chronopotentiograms obtained at varying pH values does reveal an important aspect of the second reduction step.

The resolution of two peaks in the derivative curve is improved as the pH of the solution is increased (Figure 8). At the same time the total value of $i\tau^{1/2}$ is decreasing (Figure 4) which indicates that the peaks are not separating due to an extension of the second transition time. A valid alternative to this reasoning is that the formal reduction potentials become more widely separated as the pH is increased. When the relative values of the formal potentials for the two one-electron transfer steps obey the condition $E_1^{\circ\prime} \leq E_2^{\circ\prime}$, only a single transition will occur for the normal chronopotentiogram and the resulting derivative curve will exhibit a single peak. As $E_2^{\circ\prime}$ shifts cathodic of $E_1^{\circ\prime}$, two transition points will begin to separate on the potential scale. Thus, the derivative curve will achieve its peak value at the first transition point and remain there for increasingly longer periods of time as the potential separation is increased. When $E_2^{\circ\prime}$ is shifted sufficiently cathodic of $E_1^{\circ\prime}$, the two peaks actually will separate; this is observed in Figure 8.

Because $E_1^{\circ\prime}$ for UO_2HY^- has been shown to be independent of pH (section B), the increase in the separation of $E_1^{\circ\prime}$ and $E_2^{\circ\prime}$ must be due to a cathodic shift of $E_2^{\circ\prime}$ with decreasing hydrogen ion concentration. This is consistent with the equilibrium of eq 5 being shifted to the left. The separation of the formal reduction potentials at high pH is sufficiently small and indistinguishable on the normal chronopotentiometric wave that a quantitative measure of the shift of $E_2^{\circ\prime}$ with pH is not possible.

E. Stability of the Uranium(VI)–EDTA Complex.—The UO_2HY^- species tends to dissociate below pH 4.5 to give UO_2^{2+} and HY^{3-}.[7,8] At higher pH values the second proton is lost, yielding the dianion UO_2Y^{2-} (or some equivalent hydrated species). The instability of the complex at low pH values will cause abnormalities in the electrochemical results because any free uranyl ion present will be reduced at a potential anodic of that for reduction of the EDTA complex. Such effects are apparent in Figures 2, 7, and 9 for solution conditions near pH 5.

Similar deviations from the normal curves are observed above pH 6.8. The effect is apparent in Figure 3, where the decrease of the peak current function with increasing pH reverses sharply at pH 6.7 and continues to rise thereafter. This behavior parallels an observed change in the color of the U^{VI}–EDTA solution, going from the normal greenish yellow of the complex to a yellow-gold color which continues to deepen as the pH is increased further.

On the basis of these observations the actual stability range for the U^{VI}–EDTA complex appears to be limited to the region between pH 5 and 7; below pH 5 the complex dissociates to the uranyl cation and free ligand, and above pH 7 it forms either polymeric U^{VI}–EDTA species or polyuranates.

F. Mechanism for the Reduction of the U^{VI}–EDTA Complex.—The fact that the high-current limit of $i\tau^{1/2}$ remains constant at various pH values (Figure 4) indicates that the formation of UO_2HY^- according to eq 3 must be rapid because no kinetic effect on $i\tau_1^{1/2}$ is observed with the current densities used in this study.[19]

There are many possible reactions which are consistent with the observed pH dependence of the intermediate chemical kinetic step. In addition, the exact pH dependence of the second reduction step cannot be established. The most probable series of reactions of the U(V) resulting from the first electron transfer involves protonation and subsequent removal of the uranyl oxygen atoms followed by the second electron transfer to yield a nonoxygenated U^{IV}–EDTA species

$$UO_2HY^{2-} + H^+ \rightleftharpoons UOY^- + H_2O \qquad (6)$$

$$UOY^- + 2H^+ + e^- \longrightarrow UY + H_2O \qquad (7)$$

Additional information on the actual reaction sequence could have been obtained if the intermediate U^V–EDTA species had been isolated. Attempts to generate the U(V) complex by controlled-potential electrolysis at pH 6.5 (where $E_2°'$ lies slightly cathodic of $E_1°'$) were not successful, probably because the two reduction potentials are still not sufficiently separated. The desired intermediate possibly could be prepared by first generating a stable solution of the U(V) cation and then adding EDTA to this. However, U(V) tends to disproportionate to form mixed valence state complexes and makes such a procedure infeasible.

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Proton Nuclear Magnetic Resonance Studies of Uranium(IV)–Ethylenediaminetetraacetic Acid Complexes

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The proton nmr spectrum of a 1:1 paramagnetic uranium(IV)-ethylenediaminetetraacetic acid complex (prepared by dissolving $U^{IV}(EDTA)\cdot 2H_2O$ in aqueous Na_2SO_4 solutions) has been studied as a function of pH and temperature. The magnetic moment of the complex is 3.01 BM as determined from the nmr data. Because of the anisotropy of the U(IV) unpaired electron spin at the ligand protons, the spectra exhibit extensive contact shifts (10–35 ppm). Above 45° the spectrum consists of an AX pattern for the ligand acetate protons plus a singlet for the ethylenic group; the resonances broaden as the temperature is lowered. Below 7° the broadened A resonance splits into two singlets and the X resonance becomes narrower; the ethylenic resonance splits into two singlets. On the basis of the nmr data a plausible solution structure for the complex is proposed as well as an exchange mechanism for the ligand protons. The exchange rates and their energies of activation have been determined. Clear evidence that the nmr spectral displacements are due to pseudocontact shifts is given by the large differences in the chemical shift values for the methylenic protons of the ligand acetate groups.

The complexes of uranium(IV) with the ethylenediaminetetraacetic acid tetraanion (EDTA) have been the subject of a number of investigations.[1–14] There is general agreement that the coordination number of U(IV) is 8,[1] which makes possible a variety of complexes with the sexadentate EDTA ligand. Complexes with metal-to-ligand ratios of 1:1,[2–11] 1:2,[4] 2:1,[5] and 2:3[5] have been reported.

A potentiometric study[5] has indicated that the stable form of the 1:1 complex is $U^{IV}(EDTA)(H_2O)_2$ between pH 0.0 and 3.5 with a formation constant,[8] K_f, of 6×10^{25}. At higher pH values the complex apparently loses a proton to form $U(EDTA)(H_2O)(OH)^-$, which undergoes an olation reaction

$$2U(EDTA)(H_2O)(OH)^- \rightleftharpoons [U(EDTA)(OH)]_2^{2-} + 2H_2O \qquad (1)$$

to form a dimeric hydroxy-bridged species. Previous work has established that the limited solubility of $U(EDTA)(H_2O)_2$ in water (6.45 mM at 25°) can be increased by dissolving the complex in solutions containing ionic complexing agents such as oxalate, carbonate, sulfate, citrate, tartrate, or fluoride ions; apparently these replace one or both of the coordinated waters of the complex.

A dodecahedron or a quasi-dodecahedron with trigonal faces has been suggested for the structure of $U^{IV}(EDTA)(H_2O)_2$ on the basis of its similarity to the Th(IV) complexes.[12] However, a cubic or slightly perturbed cubic symmetry has been proposed as more reasonable because of the low magnetic moment of the complex (2.8 BM);[13] U(IV) complexes with orthorhombic symmetry, such as $U(SO_4)_2\cdot 4H_2O$, have magnetic moments of about 3.6 BM.[13] The structure of U^{IV}(acetylacetonate)$_4$ has been shown to be a square antiprism on the basis of its isomorphism with Th^{IV}-

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