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POLAROGRAPHIC REDUCTION OF URANIUM(VI)
Under Complexing and Noncomplexing Conditions.
Nature of the Sulfate Complex

by

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Polarographic Reduction of Uranium(VI)
Under Complexing and Noncomplexing Conditions.
Nature of the Sulfate Complex

ABSTRACT

Previous studies of the effect of uranium species on the polarographic behavior of certain organic compounds indicated the advisability of further study of uranium itself.

The polarographic reduction of U(VI) to U(V) in acid solution is very sensitive to both type and concentration of anion present. Consequently, the reduction was studied using perchlorate as a non-complexing anion and sulfate as a complexing anion.

In HClO_4 solution, increasing the perchlorate concentration shifted $E_{1/2}$ to more positive potentials, which seem to correspond to junction potential effects. Increasing either HClO_4 or perchlorate concentrations increased the limiting current slightly, which can be attributed to a higher rate of disproportionation of U(V); other factors, e.g., viscosity of the solution, tend to counteract the effect of the disproportionation.

In sulfate media, UO_2^+ is not strongly complexed, the association constant for the U(V)-sulfate complex being 0.15, if UO_2SO_4 is the most stable uranyl sulfate complex present. The effect of acid on the stability of the uranyl sulfate complex confirmed the existence of the complex as an uncharged species. Limiting currents were pseudo diffusion-controlled, e.g., increasing the solution viscosity by increasing the electrolyte content decreased the current; this is due to the maximum disproportionation rate of U(V) having been reached at even the lowest sulfuric acid level investigated; 537 002

increasing the anion concentration consequently slowed down diffusion.

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The polarographic behavior of uranium and of its complexes, particularly those of the higher oxidation states of uranium, have been extensively examined. Study of the polarographic reduction of uranium sulfate complexes has been limited to solutions containing high concentrations of both the electroactive species and gelatin. The usual polarographic analytical procedures for uranium, however, involve solutions containing low concentrations of uranium and either very low concentrations of gelatin or none at all; results obtained in these solutions would be expected to differ from those observed in more concentrated solutions. Consequently, the polarographic behavior of uranyl ion, in the absence of maximum suppressor, was investigated in complexing sulfate media. In order to compare the results to those observed with uncomplexed uranium, polarographic reduction of uranyl ion in perchlorate solution was also studied.

Discussion of Observed Behavior

The U(VI)-U(V) wave appeared over the whole acidity range investigated (0.3 to 5 M H^+); due to the presence of the hydrogen ion discharge wave, reduction waves for U(V) and U(IV) were observed only in solutions of low acidity. The latter waves were ill-defined and, in sulfate media, tended to merge with the hydrogen discharge. Therefore, analysis of the data will be limited to the U(VI)-U(V) wave; this will permit comparison of the effects over the whole range of variations in anion and acid concentrations.

Previous spectrophotometric studies^{1,2} have not been able to detect any perchlorate complex of U(VI), whereas at least one sulfate complex has been identified¹. These findings are supported by the radical difference in the polarographic results obtained in the present study, which indicate the distinctly different nature of the

processes going on in sulfate and in perchlorate media. Consequently the discussion will be divided into two major sections, describing the trends in each type of medium separately. It would be helpful to review first a pertinent aspect of uranium chemistry.

Disproportionation of Uranium(V). An important factor in the polarography of uranium^{3,4} is the disproportionation of U(V):

The rate of this process influences the current of the first uranium wave (reduction of U(VI) to U(V)), which varies between the values expected for 1e and 2e processes. Increasing acid concentration tends to favor the process. The optimum stability of UO_2^+ is in the region of pH 2 to 4.⁵

In perchlorate media (ionic strength, μ , = 0.4 M; UO_2^+ concentration = 10^{-3} to 10^{-5} M) the rate law for the disproportionation is

$$-d[\text{UO}_2^+]/dt = k [\text{H}^+] [\text{UO}_2^+]^2 \quad (2)$$

with k being 130 ± 4 l. moles⁻¹ sec.⁻¹ at 25.0°. ⁶ Below 0.5 M, acid concentration, the probable mechanism is

An increase of k with increasing ionic strength is to be expected for an activated complex such as the $(\text{UO}_2\text{UOOH})^{+3}$ proposed.⁶ A potentiometric study of the U(V) disproportionation kinetics in sulfate media⁷ demonstrated that the probable mechanism is the same as that in perchlorate solution.

Perchlorate Media

In a spectrophotometric study of the complexation of U(VI) by anions,¹ no complexation seemed to occur on varying the HClO_4 concentration from 2 to 6 M.

Variation of $E_{1/2}$. At constant HClO_4 concentration, increasing ionic strength by addition of sodium perchlorate linearly shifts $E_{1/2}$ to more positive potential (Fig. 1B). Twelvefold variation of the acid concentration does not change $E_{1/2}$ or curve shape excessively; the variation in $E_{1/2}$ is almost within experimental error. Plots of $E_{1/2}$ vs. H^+ concentration (Fig. 1C) show increasingly non-linear response to increasing ionic strength. At low acid concentration (0.29 M) i_1 is independent of ionic strength (Fig. 2); at higher acid concentrations, it increases with increasing μ .

Apparently, at lower ionic strength $E_{1/2}$ is independent of acid concentration, but at higher μ becomes sensitive to $[\text{H}^+]$. However, since the electrode reaction, $\text{U(VI)} \rightarrow \text{(V)}$, has been shown to be reversible and not to involve H^+ ,^{8,9} $E_{1/2}$ should be independent of the H^+ concentration. Furthermore, the lowest ionic strength used (Fig. 1C) is quite high (1.5 M) and further increase in it should not have a noticeable effect. (The activity coefficient of H^+ for various HClO_4 concentrations is as follows: 0.77 at $\mu = 0.29$, 0.92 at $\mu = 1.5$ and 1.8 at $\mu = 3.7$.¹⁰ Data for the HClO_4 - NaClO_4 solutions could not be located.)

The results are reminiscent of the similar type of curvature reported for the $E_{1/2}$ - μ plot for cadmium(II),¹¹ which was ascribed to the effects of junction potential and complex formation. However, it is difficult to compare the latter data with the present results since U(VI) and its reduction products are soluble, whereas Cd(II) is reduced to the amalgam.

The Nernst equation for the reversible $U(VI)-U(V)$ reduction indicates that an increase in ionic strength through its effect on the activity coefficients of the two uranium species should shift potentials to more negative values, if at all;³ the actual plot (Fig. 1B) shows the opposite. The linear dependence of $E_{1/2}$ on μ indicates a systematic factor such as a junction potential effect. In 0.29 M $HClO_4$, a difference of 28 mv. was found between the $E_{1/2}$ values obtained in the lowest and highest ionic strength solutions; the difference in pH found for the same $HClO_4$ - $NaClO_4$ solutions with a glass electrode corresponded to a potential difference in the same direction of 38 mv., indicating that most of the $E_{1/2}$ shift is likely due to junction potentials. The acid and salt concentrations used preclude the calculation of - or for that matter, the approximation of - the activity coefficients of the uranium species.

Current Variation. Usually, with a diffusion-controlled process, increasing the ionic strength increases the viscosity of the solution which, in turn, should decrease the rate of diffusion of the electro-active species to the electrode; this would then be reflected in a lower observed i_1 . In the present study, an increase in μ from 0.3 to 5.5 at 0.29 M $HClO_4$ concentration did not change i_1 for the $U(VI)-(V)$ wave (Fig. 2). A fivefold increase in acid concentration raises the current slightly; further addition of sodium perchlorate slightly but linearly increases the current. The slope of the last mentioned relation is greatest at 3.7 M acid.

Since the 0.29 M acid is well outside the optimum stability range of $U(V)$ with respect to disproportionation, almost all $U(V)$ produced at the electrode should immediately disproportionate. Further addition of acid should only slightly more favor the disproportionation and the current should rise only slightly; this is the

case. The increase in slope of the current-anion concentration relation can be similarly interpreted.

At relatively low ionic strength, i.e., 0.4 M , an increase in μ increases the rate constant of the $U(V)$ disproportionation;⁶ the explanation for this was based on the premise that the activated species was sensitive to the ionic atmosphere. In all probability, the same effect causes the rise in i_1 in the present data. The effect at high μ is relatively less, but the disproportionation rate is being increased; the resultant increase in regenerated $U(VI)$ formed per unit time would reveal itself as an increase in i_1 . Therefore, at 0.29 M acid the increase in viscosity caused by the increase in μ is apparently just counteracted by the increase in disproportionation rate and no reduction in wave height is found. At the higher acid concentrations, the increased disproportionation rate not only neutralizes the effect of the decreased diffusion rate, but enhances the current, producing the rising slope in the current-anion concentration relationship.

Sulfate Media

At 0.18 M sulfuric acid, increasing the sodium sulfate concentration shifts $E_{1/2}$ exponentially to more negative potential (Fig. 1A). On increasing the H_2SO_4 concentration, the curvature is eliminated and $E_{1/2}$ becomes slightly but apparently linearly more negative with increasing sulfate concentration, although the slope of the plot decreases considerably.

At constant ionic strength, the plot of $E_{1/2}$ vs. H^+ concentration is exponential (Fig. 1C) and apparently independent of ionic strength since two differing constant μ series gave similarly shaped curves.

The limiting current decreases linearly with increasing sulfate concentration at constant acid concentration (Fig. 2); increasing the latter increased i_1 but did not change the slope of the i_1 -anion concentration relation.

These results are consistent with those expected for complexed species.

Although Heal¹² concluded that UO_2^{++} and its reduction products do not form strong sulfate complexes, both his polarographic data and those of Watters¹³ indicate that the presence of sulfate changes polarographic values considerably beyond the variations expected for experimental error; therefore, uranium sulfate complexes are likely involved. Furthermore, even in very low sulfuric acid concentration i_1 for the first wave is more than that for a $1e$ reduction. Increasing the H_2SO_4 concentration to 0.5 to 1.0 M increases the wave height to about that for a $2e$ reduction.¹³ Since the acid concentration is distinctly below the 6 M level at which the wave approaches a $2e$ height in hydrochloric acid solution,^{8,14,15} the current increase must be due to complexation. If either the U(VI) or U(IV) sulfate complexes are more stable than the U(V) complex, the disproportionation (equation 1) will be favored and the first wave current will increase. Heal¹² based his conclusions on the low stability of sulfate complexes on the constancy of $E_{1/2}$ in both chloride and sulfate media. However, since he used a high uranium concentration (0.01 M) and since the gelatin concentration (0.02%) was sufficient to cause anomalies,^{16,17} $E_{1/2}$ in the two media may be further apart than the results indicate.

Nature of the U(VI)-Sulfate Complex. In a spectrophotometric study¹ of the complexation of U(VI), the species in 2 M H_2SO_4 seemed to have a uranium:sulfate ratio of 1:1 with two major possible forms:

$\text{UO}_2\text{HSO}_4^+$ and UO_2SO_4 . The equilibria involved,

indicate that the bisulfate complex concentration would be relatively independent of small changes in the acid concentration at the 2 M level, whereas the concentration of the neutral sulfate species would be increased by a reduction in the acid concentration. Since decreasing the acid concentration actually increases the concentration of the complexed form, the most likely species is the neutral UO_2SO_4 . The association constant of this complex was determined to be 5.0 ± 0.34 .¹

If the first uranium wave is assumed due to the reduction

$$\text{UO}_2(\text{SO}_4)_p^{-2(p-1)} + e \rightleftharpoons \text{UO}_2(\text{SO}_4)_q^{-(2q-1)} + (p-2)\text{SO}_4^{=}$$

(8)

then the relevant equation for the relation of $E_{1/2}$ to the complexed species at 25° is³

$$E_{1/2} = E^\circ - \frac{0.0591}{a} \log \frac{k_{\text{ox}}}{k_{\text{red}}} - (p-q) \frac{0.0591}{a} \log [\text{ligand}] \quad (9)$$

when $(k_{\text{ox}}/k_{\text{red}}) = (\text{KD}_{\text{ox}}^{1/2}/\text{KD}_{\text{red}}^{1/2})$.

If the diffusion coefficients of U(VI) and U(V) are assumed to be essentially equal, the slope of $E_{1/2} - \log [\text{ligand}]$ plots gives

$$\frac{\Delta E_{1/2}}{\Delta \log [\text{ligand}]} = \frac{-0.0591}{a} (p-q) \quad (10)$$

Since reduction of UO_2^{++} to UO_2^+ involves 1 electron, and since the most stable sulfate complex at the higher H_2SO_4 concentration (2 M) contains one sulfate ion,^{1,2} equation 10 simplifies to

$$\frac{\Delta E_{1/2}}{\Delta \log [\text{ligand}]} = -0.591 (1-q) \quad (11)$$

Plots of $E_{1/2}$ vs. $\log [SO_4^{=}]$ (Fig. 3) can be used to evaluate q . [The error in calculating initial $[SO_4^{=}]$ concentration as being that of the H_2SO_4 added would change the absolute $[SO_4^{=}]$ values, but would not alter appreciably the slope. Furthermore, since the effective complexing species is HSO_4^- , whose concentration is approximately that of the H_2SO_4 added, equating $[SO_4^{=}]$ to the $[H_2SO_4]$ added gives the numerically correct results.]

As the acid concentration is increased, the slope ($\Delta E_{1/2} / \Delta \log [SO_4^{=}]$) decreases, being -0.060 at 0.18 M sulfuric acid, -0.045 at 0.36 M, and -0.019 at 1.0 M. Therefore, at the lowest ionic strength and acid concentration studied, 0.18 M, the U(V) species is not complexed by sulfate but probably exists as an aquated ion. Furthermore, the latter fact plus the decrease in slope with increasing acid concentration indicate that the addition of acid strips the sulfate off the uranium(VI); behavior of this nature supports the contention that the most probable uranium(VI) species is the neutral complex $[UO_2SO_4]$.

$E_{1/2}$ corresponding to $\log [\text{ligand}] = 0.0$ is the standard reduction potential, $(E_{1/2})_c$, of the complex³ and

$$(E_{1/2})_c - (E_{1/2})_s = \frac{0.0591}{a} \log \frac{K_{o.c.}}{K_{r.c.}} \quad (12)$$

where $(E_{1/2})_s$ is the $E_{1/2}$ of the uncomplexed ion, $K_{o.c.}$ is the dissociation constant for the oxidized species, and $K_{r.c.}$ is that for the reduced species.

For the U(VI)-(V) wave, $a = 1$, and $(E_{1/2})_s = -0.180$ v.;⁶ therefore, at 0.18 M sulfuric acid (lowest H_2SO_4 concentration used which gave maximum rate of slope for $E_{1/2}$ vs. $(\log [SO_4^{=}]$),

$$-0.252 - (-0.180) = 0.0591 \log \frac{K_{o.c.}}{K_{r.c.}} \quad (13)$$

The ratio of $K_{o.c.}$ to $K_{r.c.}$ is then 0.06. Since $K_{o.c.}$ has been found to be 0.4 by other techniques,¹ $K_{r.c.}$ would then be approximately 6.7. The association constant for a U(V)-sulfate complex would be 0.15 or, in essence, the dissociation of any U(V)-sulfate complex would be favored.

The variation of $E_{1/2}$ with sulfate concentration (Fig. 1A) is dependent on H_2SO_4 concentration. At the lower acid concentrations, complexation is probably the major factor in the potential shifts. As the acid concentration is increased, however, the increasingly large junction potential seems to diminish the apparent effect of $[SO_4^{=}]$ on $E_{1/2}$. Unfortunately, the effect of activity on the complex cannot be evaluated.

The variation of current with sulfate concentration (Fig. 2) shows a pseudo diffusion-controlled process instead of the catalytic current effect actually present. As the sulfate concentration is increased, the current is lowered. The uranium wave in high acid and sulfate concentrations is affected by the increase in viscosity in the same manner as a diffusion-controlled reaction would be; the maximum rate of disproportionation has been reached and, consequently, further addition of sulfate can only affect the viscosity of the solution and thus decrease the current flow.

Experimental

Reagents. Uranyl perchlorate, prepared by repeated evaporation of uranyl nitrate with perchloric acid, was dissolved to give a 0.1338 M solution. A 0.0640 M uranyl sulfate solution was prepared from the C.P. grade salt (Fisher Scientific Co.). The exact uranium concentration of these solutions was determined by reduction with a Jones reductor, aeration and titration with standard dichromate solution using sodium diphenylaminesulfonate as indicator.

Nitrogen used for deoxygenating solutions was purified and equilibrated by two alkaline pyrogallol scrubs and passage through a portion of the proper background electrolyte solution. All other chemicals were of reagent grade and were used without further purification.

Procedure. Sufficient uranyl solution to produce the desired concentration at final dilution was added to the proper quantities of acid and salt; the solution was brought to volume and mixed; a portion was transferred to a thermostated H-cell¹⁸ kept at $25.0 \pm 0.1^\circ\text{C}$. (Sodium sulfate was used to increase the ionic strength in the sulfuric acid series and sodium perchlorate in the perchloric acid series.) The solution was deoxygenated with nitrogen for 15 min. and polarographed with a Leeds & Northrup Type E Electro-Chemograph. $E_{1/2}$ and i_1 values were determined graphically, using the average of the recorder trace swings. In order to avoid precipitation of potassium perchlorate, the agar salt bridge in the H-cell was made with sodium chloride.

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Ann Arbor, Michigan.

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Figure Captions

Fig. 1. Dependence of $E_{1/2}$ on solution composition.

- (A) $E_{1/2}$ as a function of sulfate concentration at constant sulfuric acid concentration. Sulfuric acid concentration: a, 0.18 M; b, 0.36 M; c, 1.0 M; d, 1.8 M.
- (B) $E_{1/2}$ as a function of the ionic strength at constant acid concentration. Perchloric acid concentration: a, 0.29 M; b, 1.47 M; c, 3.68 M. Sulfuric acid concentration: d, 0.36 M.
- (C) $E_{1/2}$ as a function of acid concentration at constant ionic strength. Ionic strength for perchlorate solutions (solid lines): ●, 1.5 M; ○, 3.7 M; ◐, 5.5 M. Ionic strengths for sulfate solutions (dashed lines): ■, 3.0 M; □, 5.5 M.

Fig. 2. Limiting currents, i_1 , as a function of the total anion concentration at constant acid concentration. Perchloric acid concentration: a, 0.29 M; b, 1.47 M; c, 3.68 M. Sulfuric acid concentration: d, 0.18 M; e, 0.36 M; f, 1.0 M.

Fig. 3. $E_{1/2}$ as a function of the log of the total sulfate concentration at constant acid concentration. Sulfuric acid concentration: a, 0.18 M; b, 0.36 M; c, 1.0 M.

Figure I

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Fig. 3