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HYDROLTIC BEHAVIOR OF METAL IONS I.

THE ACID CONSTANTS OF URANIUM (IV) AND PLUTONIUM (IV)

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The Acid Constants of Uranium (IV) and Plutonium (IV)

Kurt A. Kraus and Frederick Nelson

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HYDROLYTIC BEHAVIOR OF METAL IONS I.

The Acid Constants of Uranium (IV) and Plutonium (IV)

Kurt A. Kraus and Frederick Nelson

Abstract

(1) Through pH measurements of UCl_4 solutions, U^{+4} was established to be the species of uranium (IV) in acidic solutions.

(2) The acid constant of U^{+4} was determined as a function of ionic strength for chloride and perchlorate solutions through a spectrophotometric method. The molarity constants could be fitted approximately to a Debye-Hückel limiting law and the activity constant $K_a = 0.21 \pm 0.02$ was estimated for the equilibrium

$$U^{+4} + 2H_2O \rightleftharpoons UOH^{+3} + H_3O^+$$

(3) The stability constant for the reaction

$$U^{+4} + Cl^- \rightleftharpoons UCl^{+3}$$

was estimated to be $\underline{K}_c$ = ca. 0.63 (μ = 0.5) and K_c' = 7.0 (μ = 0).

(4) The acid constant of Pu^{+4}(K_m = 0.025, μ 0.5) was found to be almost identical with, though slightly smaller than that of U^{+4} (K_m = 0.032, μ = 0.5).

(5) The spectral data, the quantitative hydrolytic data and the observation that the chloride complexes of uranium (IV) and plutonium (IV) are weak, are confirmatory evidence of the hypothesis that these elements are members of a "rare-earth-like" series.

Contribution from the Oak Ridge National Laboratory
Chemistry Division

HYDROLYTIC BEHAVIOR OF METAL IONS I.

The Acid Constants of Uranium (IV) and Plutonium (IV)[1]

Kurt A. Kraus and Frederick Nelson

---

(1) This document is based on work performed under Contract No. W-7405 eng 26 for the Atomic Energy Commission at Oak Ridge National Laboratory. Part of this work has previously been published in the project reports, CN-2289 (November 1944), MonN-370 (September 1947), CNL-37 (April 1948) and AECD-1888 (April 1948). Part of the material was included in a paper presented at the meeting of the American Chemical Society on April 21, 1948.

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1. Introduction

This paper will discuss the spectrophotometric determinations of the equilibrium constants of the first hydrolytic reaction of uranium (IV) and plutonium (IV). This reaction has been identified for both elements as

$$X^{+4} + 2H_2O \rightleftharpoons XOH^{+3} + H_3O^+ \qquad (1)$$

where X indicates either element.

Both uranium (IV) and plutonium (IV) undergo further hydrolytic reactions yielding eventually polymeric solutions with composition approaching that of the hydroxide. As mentioned earlier these polymeric reactions greatly affect the chemistry of uranium (IV) and plutonium (IV) systems[2][3][4] and they will be considered in

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(2) K. A. Kraus, F. Nelson and G. L. Johnson, J. Am. Chem. Soc. 71.2510(1949).

(3) K. A. Kraus and F. Nelson, J. Am. Chem. Soc. 71.2517 (1949).

(4) For a summary of some observations on polymeric plutonium (IV) see:

(a) K. A. Kraus, Report MDDC-814 (March 1947).
(b) K. A. Kraus and F. Nelson, Report AECD-1888 (April 1948).

some detail in later papers.

Some confirmatory results will be included, pertaining to the identification of the species U^{+4} for uranium (IV) in acidic solutions, using pH measurements of solutions of uranium tetrachloride. These experiments appeared necessary since the spectral data alone yield information only on changes in a system. Although evalution of the hydrolytic constants is intrinsically possible through such experiments the available salt (UCl_4) did not appear sufficiently pure to warrant its use for more than confirmatory evidence. Unfortunately, due to unavailability of a similar plutonium salt, parallel experiments could not be carried out.

2. Experimental

2.1 Materials

(a) Uranium. Uranium (IV) stock solutions of known acidity were prepared by dissolution of uranium tetrachloride in acids of known strength or by reduction of uranium (VI) solutions with known amounts of zinc or by electrolytic reduction. The uranium (VI) solutions in chloride and perchlorate were prepared from uranyl nitrate hexahydrate of high purity through ammonia precipitations. The purity of the solutions was checked spectroscopically[5]. The stock solutions were stored in oxygen-free

(5) We are indebted to Mr. C. Feldman of the Chemistry Division of Oak Ridge National Laboratory for the spectrographic analyses.

nitrogen, which was prepared by passing tank nitrogen over copper shavings at ca. 500°C.

Before use the solutions were analyzed for uranium (IV) either polarographically or by cerate oxidimetry.

(b) Plutonium. All experiments were carried out with the isotope Pu^{239} (α-emitter, $T_{1/2}$ = 24110 y[6]) and its concentration determined by standard radio-

(6) J. W. Stout and W. M. Jones, Phys. Rev. 71.582(1947).

chemical techniques. Plutonium (IV) chloride solutions were prepared by dissolution of the hydroxide in hydrochloric acid followed by heating at a hydrochloric acid concentration larger than 6 M to remove possible small concentrations of polymeric plutonium (IV).

Purity of the solutions with respect to other oxidation states was checked spectrophotometrically, taking advantage of the fact that each oxidation state has a very characteristic spectrum.

2.2 Equipment.

The spectrophotometric data were collected with a Beckman Model DU quartz spectrophotometer.

The pH measurements were carried out with the vibrating reed electrometer assembly previously described[3][7]. The electrode system (glass vs. calomel)

(7) K. A. Kraus, R. W. Holmberg and C. J. Borkowski, Report ORNL-383(September 1949).

was carefully standardized with acids of known strength and of the same ionic strength as the solutions investigated.

All experiments were carried out in a thermostated room at 25 ± 1°C. In a number of experiments the temperature of the solutions was measured before and after the experiments and was found to be 25 ± .2°C.

2.3 Procedure.

The stock solutions were diluted with potassium chloride, sodium chloride or sodium perchlorate solutions of known ionic strength and known acidity (HCl or $HClO_4$). Spectral data were collected as soon as possible after mixing (ca. 0.5 to 1 minutes) and if necessary extrapolated to zero time. The final acidity of the solutions was determined by direct pH measurements or by calculation taking into consideration the acid liberated on hydrolysis. All experiments with uranium were carried out under nitrogen with careful exclusion of oxygen.

The technique of the acidity measurements of solutions of uranium tetrachloride was similar to that described for uranium pentachloride(3).

3. Results and Discussion

3.1 Uranium (IV).

(a) Acidity of UCl_4 Solutions - Identification of the Species U^{+4}. Although many data, including e.g., entropy calculations(8) suggest that the formula of

(8) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Report BC-82 (April 1947).

uranium (IV) in acidic solutions is the hydrated U^{+4} ion(9) most observations on

(9) This hydrated ion could be written $X(H_2O)_8^{+4}$, the choice of the coordination number eight resting primarily on the fact that the dioxides have a fluoride structure (W. H. Zachariasen Report MDDC-67(June 1946)) in which each metal ion is surrounded by eight equidistant oxygen ions.

Using this symbolism equation (1) can be written

$$X(H_2O)_8^{+4} + H_2O \rightleftharpoons X(H_2O)_7(OH)^{+3} + H_3O^+ \qquad (1a)$$

Since the more detailed description is very cumbersome it will not generally be used here. However, the choice of the term "acid constant" instead of "hydrolysis constant" for describing equilibrium (1) is predicated on this symbolism which demonstrates that the ions are acids in the Brønsted meaning of the term.

the chemistry of uranium (IV) neither prove nor disprove the existence of this ion. In this class are particularly the potential determinations of uranium couples. Thus the practical invariance of the potential of the uranium (III)/(IV) couple with acidity[10][11] can equally well be interpreted by assuming that both uranium

(10) I. M. Kolthoff and W. E. Harris, J. Am. Chem. Soc., 67.1484(1945).

(11) H. G. Heal, Trans. Far. Soc. 45.1(1949)

(III) and uranium (IV) are hydrolyzed to the same extent [10][11] or by assuming that both species are the non-hydrolyzed U^{+3} and U^{+4}. Conclusions from the potentials of the uranium (IV)/(VI) couple as a function of acidity are somewhat more decisive, since the species UO_2^{++} for U(VI) is reasonably well established. It was found[3][12]

(12) F. Nelson and K. A. Kraus, Report ORNL-286 (September 1949).

that the potentials of this couple in chloride and perchlorate solutions between pH 1 and 3 are consistent with the assumption of the species U^{+4}, UOH^{+3} and UO_2^{++} and of equilibrium (1).

Confirmation of the assignment U^{+4} was attempted through measurement of the acidity of solutions of uranium tetrachloride. Since the experiments could best be carried out in an acidity range where the spectral data suggest a hydrolytic reaction of the initial species, verification of the assumed reaction was attempted by determining the hydroxyl number "n" of uranium (number of hydroxide ions/uranium ion) in this hydrolysis range. If the starting species is U^{+4}, the hydroxyl number should be between zero and one.

The amount of acid liberated on dissolution of uranium tetrachloride in a solution of known initial acidity was determined by measuring the change in the potential (ΔV) of a glass electrode-calomel assembly. The ionic strength of the solutions was made high enough ($\mu = 0.5$) compared with the concentration of uranium (ca. 10^{-3} M) to permit the assumption that the liquid junction potentials and the activity coefficients of the oxonium ions do not change and that therefore the approximation can be made

$$\Delta V = S \log \frac{m_2}{m_1} \qquad (2)$$

where m_1 and m_2 are the initial and final molarities of acid respectively and where S is the slope of the V vs. log m plot. The "Nernst" slope S is ideally 0.05915 volts at 25°C, but in practice it is somewhat smaller for most glass electrodes and dependent on the acidity of the solutions and thus must be determined experimentally. If M is the concentration of uranium (IV) the hydroxyl number n is given by

$$n = \frac{m_2 - m_1}{M} \qquad (3)$$

Since the uranium tetrachloride samples contained a small amount of uranium (VI) in unknown initial form (concentration determined polarographically[2]) an uncertainty of ca. 10 to 20% is introduced in the value of n. Within this error it was found that n is less than unity and of the order of magnitude expected from the numerical value of the spectrophotometrically determined acid constants (Tables 2 and 3) at final acidities of the order of 10^{-2} M. This agreement is close enough to appear to constitute positive proof of the existence of U^{+4} in acidic solutions.

(b) The Acid Constant of U^{+4} - Estimation of the Activity Constant. The absorption spectrum of uranium (IV) in acidic solutions is characterized by a number of sharp bands in the visible region[13] as shown in Fig. 1 and Table 1.

---

(13) The sharpness of these bands is reminiscent of rare earth spectra. It is tempting to use this characteristic as confirmatory evidence that uranium (IV) contains two 5 f electrons, although the extinction coefficients of uranium (IV) as well as those of similar "actinides" are at least an order of magnitude larger than those of the rare earths. If less than two "f" electrons were present, rare earth-like spectra would not be expected. (See e.g. S. Freed Phys. Rev. 38.2122(1931), S. Freed and R. J. Mesirow, J. Chem. Phys. 5.22 (1937) and J. H. van Vleck, J. Phys. Chem. 41.67(1937)). This conclusion is also corroborated by the absence of sharp absorption bands in uranium (V) and neptunium (VI) both of which could have only one "f" electron and by the presence of such sharp bands in each one of the members of the isoelectronic sequence U(IV), Np(V), Pu(VI). This series, incidentally, appears to have in common an infared transition whose wavelength decreases with increasing atomic number (U(IV):1075 mμ, Np(V): 985 mμ, Pu(VI): 831 mμ).

The spectrum shown was obtained from data for a 1 M $HClO_4$-1M $NaClO_4$ solution through correction for a small amount of hydrolysis using the acid constant given in Table 2. The spectrum in perchlorate solutions is practically invariant with acidity above 1 M H_3O^+. Those in chloride solutions differ only in minor details up to ca. 2 M [14].

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(14) These observations are in confirmation of the data of A. R. Nichols and C. Gropp, Report RL-4.6.927(August 1945).

The absorption spectrum changes appreciably with decreasing acidity (below 1 M H_3O^+) for both media. These changes occur practically instantaneously on adjustment of the acidity. At very low acidities the rapid changes are followed by slow progressive changes. As mentioned earlier these "slow" changes are probably due to polymeric reactions. Whenever investigation was carried out in the region

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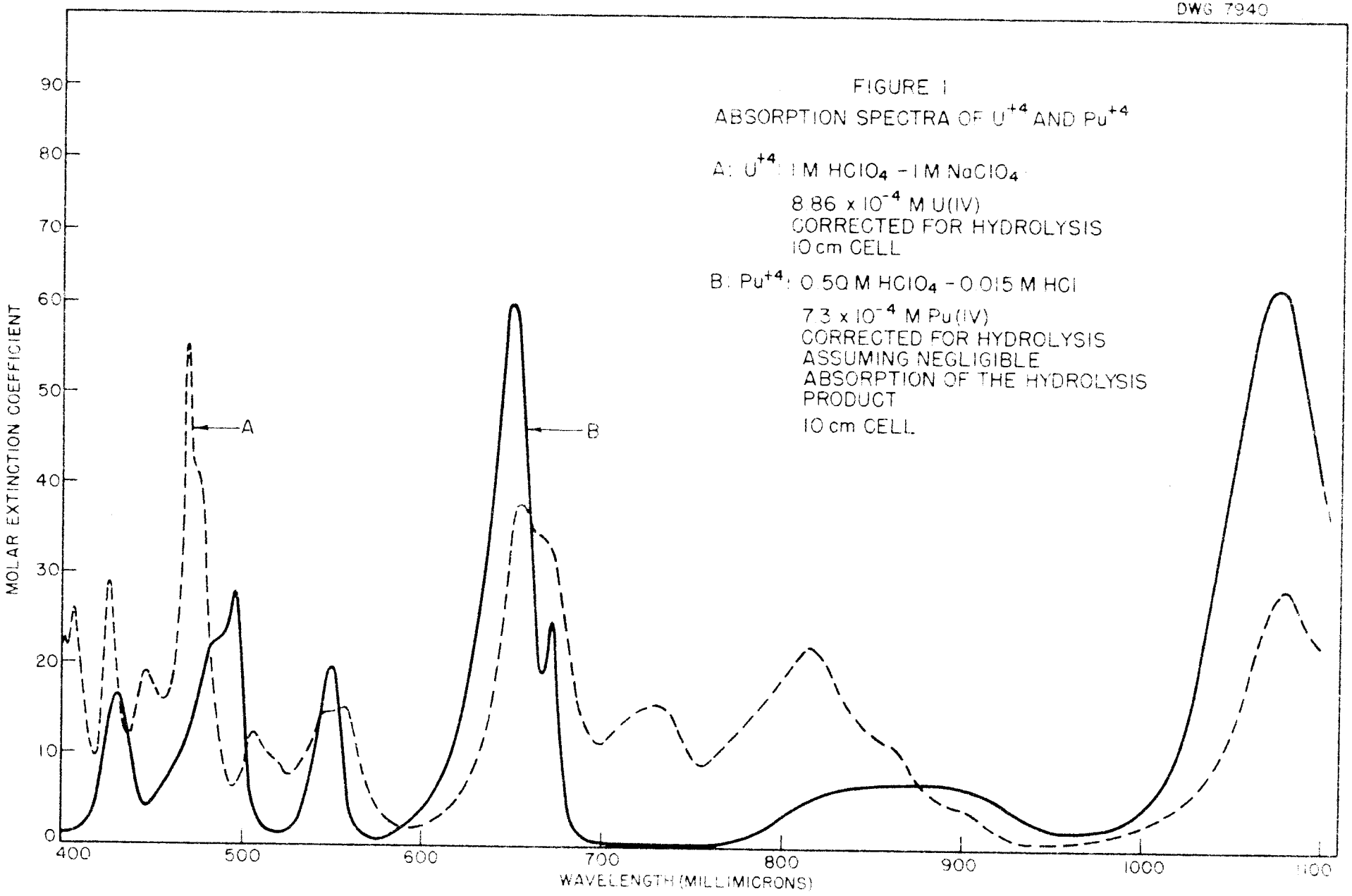


FIGURE 1
ABSORPTION SPECTRA OF U^{+4} AND Pu^{+4}

A: U^{+4}: 1 M $HClO_4$ - 1 M $NaClO_4$
8.86×10^{-4} M U(IV)
CORRECTED FOR HYDROLYSIS
10 cm CELL

B: Pu^{+4}: 0.50 M $HClO_4$ - 0.015 M HCl
7.3×10^{-4} M Pu(IV)
CORRECTED FOR HYDROLYSIS
ASSUMING NEGLIGIBLE
ABSORPTION OF THE HYDROLYSIS
PRODUCT
10 cm CELL

of "polymerization", the data given here represent "zero time" values obtained by extrapolation to the time of mixing.

Table 1

Minima and Maxima in the Absorption Spectrum of U^{+4}

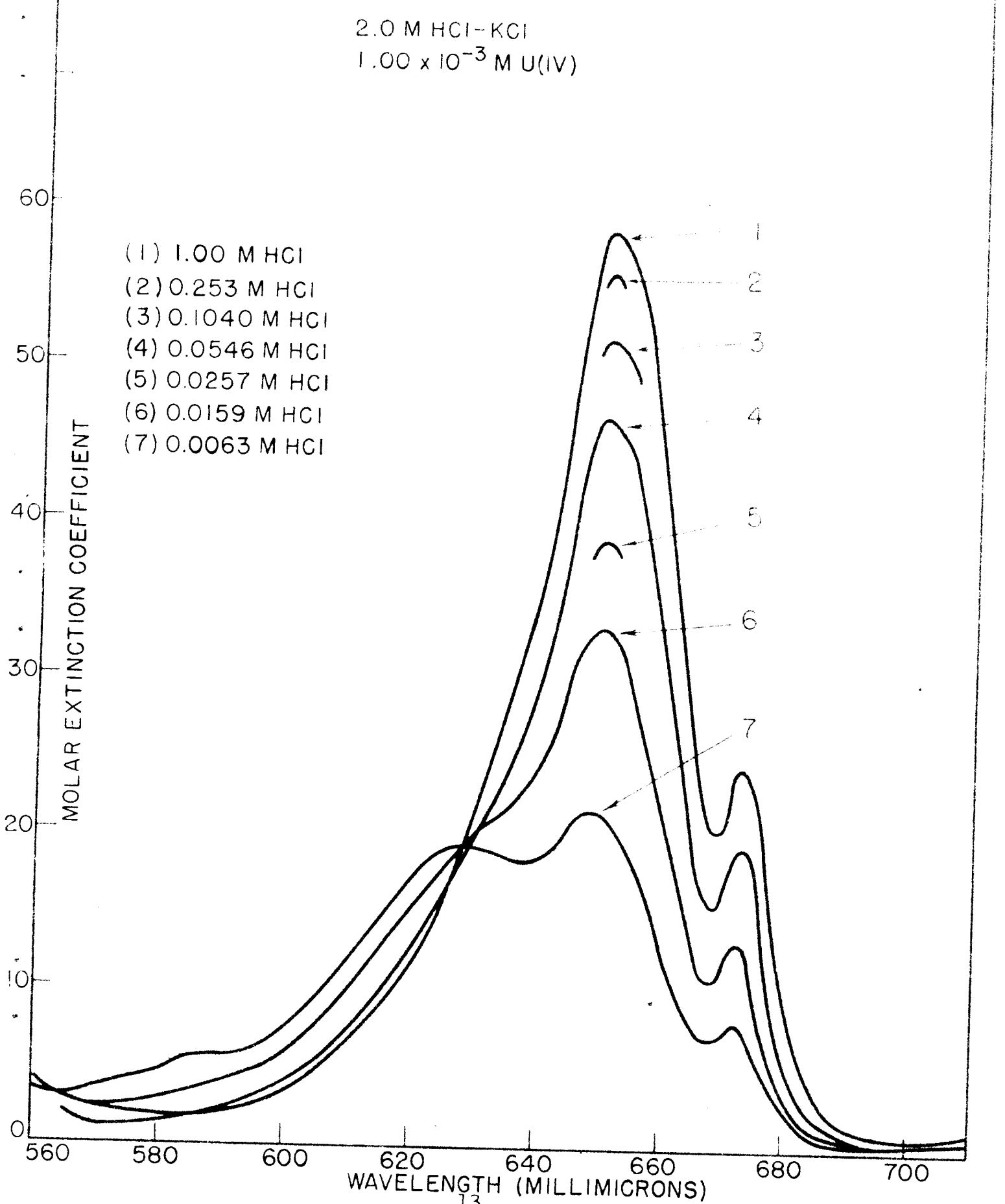
Wave length (mμ)	E_1 (a)	Wave length (mμ)	E_1 (a)
400	1.0	429	16.6
447	3.9	485	22.5
		496	28.1
520	1.2	549	19.6
575	0.9	648	60.0
667	19.0	671	24.8
730	0.4	870	7.2
970	2.1	1075	62.0

(a) Extinction coefficient obtained from data for 8.86×10^{-4} M U(IV) solution in 1 M $HClO_4$ - 1 M $NaClO_4$ after correction for a small amount of hydrolysis. (10 cm cell length, slit-width ca. 0.04 mm except in infrared where minimal slit-widths were used).

Analytically most useful appeared the absorption band located near 648 mμ whose extinction coefficient ($E_0(648)$) decreases with decreasing acidity as shown in Fig. 2. A plot of $E_0(648)$ vs. log m_2 (Fig. 3) has the characteristic "S" shape of a simple hydrolytic reaction.

The absorption in the region 600-680 mμ does not disappear completely with decreasing acidity. The product of the hydrolytic reaction also has absorption bands in this spectral range with a maximum located near 625 mμ and an extinction coefficient $E_2(625)$ of approximately 20. The absorption curve of this hydrolysis product (apparently UOH^{+3}) is shown in Fig. 4. It was obtained from the data at low acidity by correcting them for the contribution of U^{+4}, using the appropriate

FIG. 2
CHANGE IN ABSORPTION NEAR 650 mu WITH ACIDITY



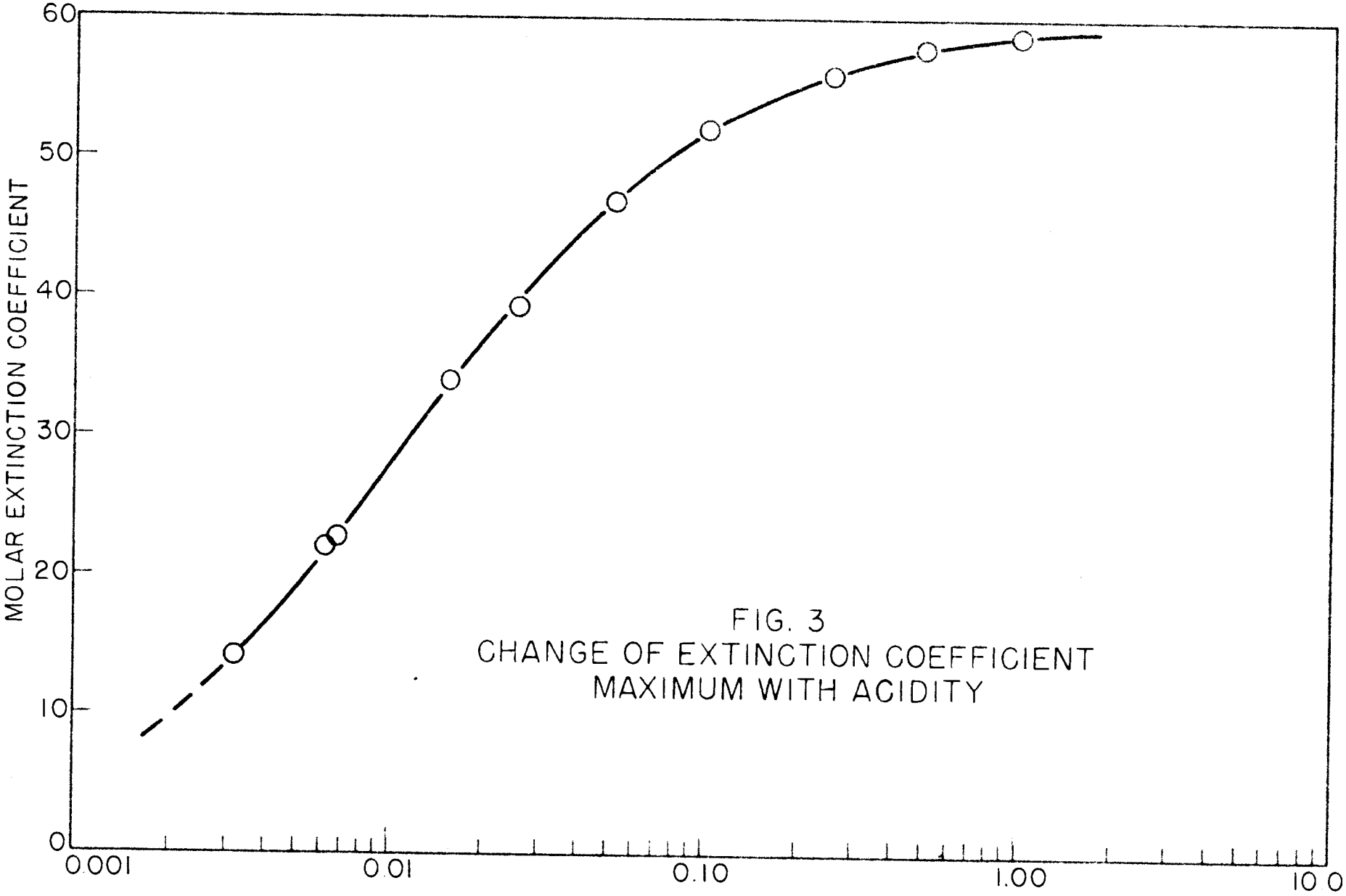
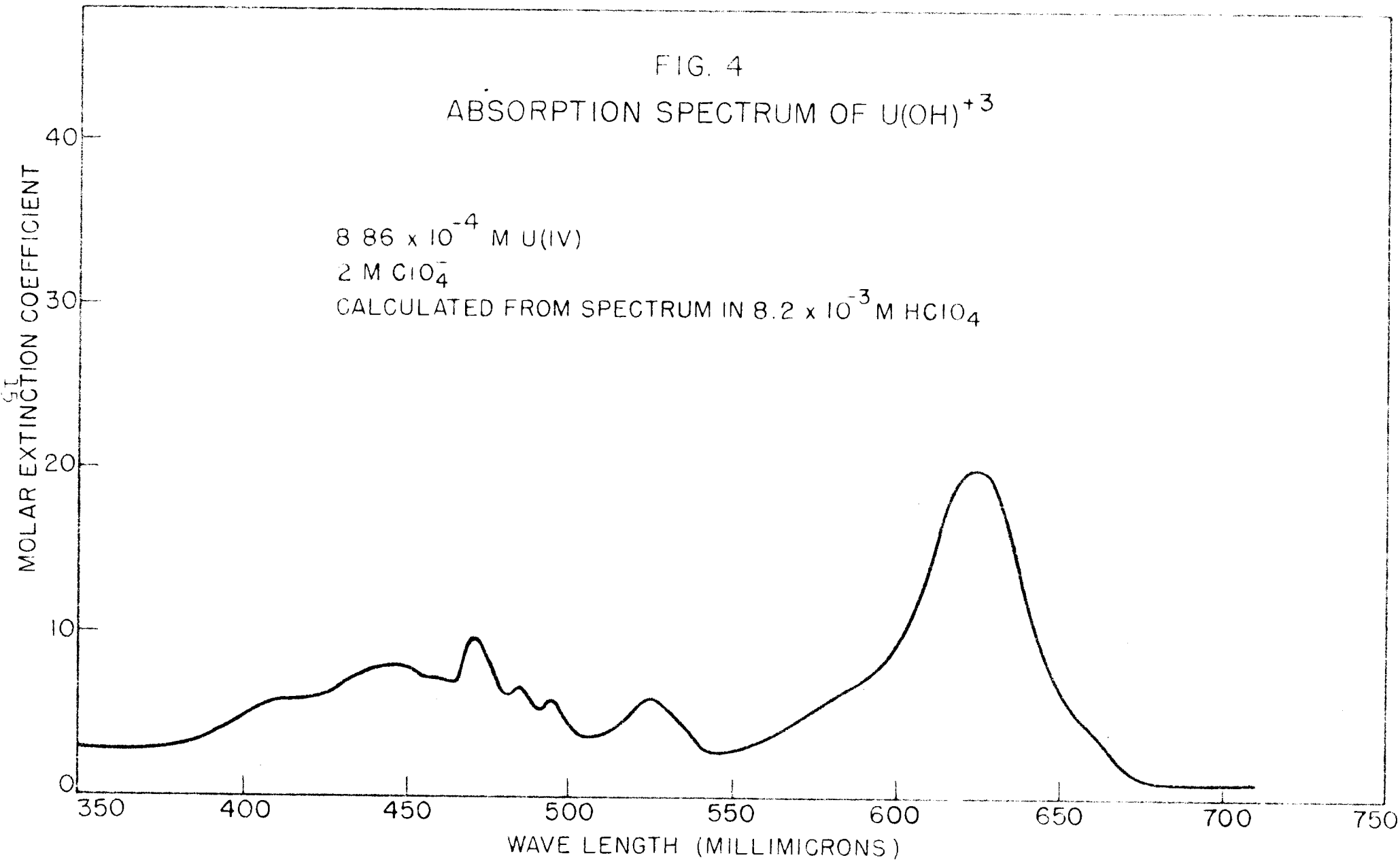


FIG. 3
CHANGE OF EXTINCTION COEFFICIENT
MAXIMUM WITH ACIDITY

FIG. 4

ABSORPTION SPECTRUM OF $U(OH)^{+3}$



acid constant. Actually both the acid constants and the absorption curves of U^{+4} and UOH^{+3} were obtained through successive approximations. This procedure is quite rapid since the extinction coefficient of U^{+4} ($\underline{E}_1(648) = 60$ for perchlorate solutions) is very much larger than the extinction coefficient of UOH^{+3} ($\underline{E}_2(648) = 6$).

In strong chloride solutions the maximum is shifted slightly towards longer wave lengths (from ca. 648 to ca. 650 mμ) and the extinction coefficient at the maximum is somewhat lower. Thus best fit of the chloride data was obtained by assuming an extinction coefficient maximum of 59 for 2 $\underline{M}$ Cl^- solutions and proportionately higher values at lower chloride concentration (see also section C).

It was found that in the pertinent concentration range (using minimal slit-widths) the absorption bands of U^{+4} obeyed Beer's law. Since the bands of UOH^{+3} probably also obey this law, it can be assumed that the observed extinction coefficients ($\underline{E}_o$) are a linear function of the concentrations of U^{+4} and UOH^{+3}, i.e.,

$$\underline{E}_o = \frac{\underline{M}_1}{\underline{M}} \underline{E}_1 + \frac{\underline{M}_2}{\underline{M}} \underline{E}_2 \qquad (4)$$

where $\underline{E}_1$ and $\underline{E}_2$ are the extinction coefficients of the pure species X^{+4} and UOH^{+3} and $\underline{M}_1$ and $\underline{M}_2$ their respective molarities.

The results of the experiments are shown in Tables 2 and 3 where the ionic strengths (μ), the molarities of uranium (IV)($\underline{M}$), the final acidities ($\underline{m}_2$, determined by calculation or potentiometric measurements), the observed extinction coefficients of the maximum located near 648 mμ ($\underline{E}_o(648)$), the percentages of UOH^{+3} (calculated according to equations (1) and (4)) and the calculated acid constants $\underline{K}_m$ (molarity constants) are listed. K_m is defined by the equation

$$\underline{K}_m = \frac{[H_3O^+][XOH^{+3}]}{[X^{+4}]} \qquad (5)$$

where brackets represent concentrations in moles per liter.

Table 2

Acid Constant of U(IV) in Perchlorate Solutions

μ	M U(IV) x 10^3	Remarks	Final $[H_3O^+]$	$E_o(648)$	$\%UOH^{+3}$	K x 10^2
2.004	.886	1,4,5	.0082	20.4	73.6	2.28
		4	.0175	29.2	57.3	2.34
		4	.0325	37.5	41.9	2.34
		4	.0568	44.5	28.9	2.31
		3	.105	49.5	19.5	2.54
						av.2.36
1.014	.886	2,4,5	.0320	35.3	46.0	2.73
		4	.0560	42.0	33.5	2.82
						av.2.78
.503	.183	2,3,6	.0107	19.1	76.0	3.4
		3	.0201	28.4	58.8	2.9
		3	.0390	37.2	42.5	2.9
		3	.0769	44.4	29.1	3.2
		3	.153	52.5	14.0	2.5
		3	.304	56.1	7.2	2.5
						av.2.9
.520	.725	2,3,5	.0047	14.3	85.1	(2.68)
		3	.0143	23.2	68.4	3.10
		3	.0234	29.2	57.3	3.14
		3	.0422	37.0	42.8	3.16
		3	.0800	44.8	28.3	3.16
		3	.155	50.7	17.3	3.24
		3	.305	55.3	8.8	2.94
						av.3.12
.519	.886	1,4,5	.0096	17.1	79.9	(3.73)
		4	.0204	27.0	61.4	3.24
		4	.0323	32.8	50.6	3.33
		4	.0680	43.1	31.5	3.12
		3	.128	49.5	19.5	3.10
		3	.250	54.0	11.2	3.16
						av.3.19
.55	3.55	2,3,7	.025	27.0	61.4	3.98
		3	.043	34.2	48.4	3.99
		3	.061	40.0	37.3	3.62
		3	.106	46.0	26.1	3.75
		3	.133	49.8	19.0	3.12
		3	.170	51.8	15.3	3.07
		3	.240	53.5	12.1	3.35
						av.3.55

Table 2 (Cont.)

Acid Constant of U(IV) in Perchlorate Solutions

μ	M U(IV) x 10^3	Remarks	Final $[H_3O^+]$	$E_o(648)$	%UOH^{+3}	K x 10^2
.272	.886	1,4,5	.0146	19.3	75.7	4.55
		4	.0208	23.6	67.7	4.36
		4	.0395	31.6	52.9	4.43
		4	.0708	39.7	37.9	4.32
		3	.131	47.5	23.3	3.98
						av.4.33
.116	1.228	1,4,8	.0555	34.3	47.8	5.26
		4	.105	42.1	33.4	5.08
						av.5.17
.115	1.222	1,4,8	.0190	19.4	75.5	5.85
.112	.662	2,3,5	.0047	9.8	93.6	(6.85)
		3	.0110	14.5	84.6	6.05
		3	.0204	19.6	75.1	6.15
		3	.0360	26.7	62.0	5.88
		3	.0674	35.1	46.0	5.85
		3	.0900	38.1	40.8	6.20
						av.6.03
.108	.616	1,4,8	.0160	18.7	76.8	5.30
.0634	.890	2,4,5	.0469	26.1	61.0	7.2
.0452	.890	1,4,5	.0288	20.4	73.6	7.9
.0349	.890	2,4,5	.019	14.5	84.6	10.
.0328	.616	1,4,8	.0285	19.7	75.0	8.6
.0173	.616	1,4,8	.0134	11.7	89.9	12.

(1) Temperature 25±.2°C.
(2) Temperature ca. 25°C.
(3) Acidity calculated.
(4) Acidity measured potentiometrically.
(5) Contains ca. 3.5×10^{-3} M Zn^{++}.
(6) Contains ca. 8.6×10^{-4} M Zn^{++}.
(7) Contains 1.65×10^{-2} M Zn^{++}.
(8) From UCl_4, i.e., Cl^- = 4 M U(IV).

Table 3

Acid Constant of U(IV) in Chloride Solutions

μ	M U(IV) x 10^3	Remarks	Final $[H_3O^+]$	$E_o(648)$	%UOH^{+3}	K x 10^2
2.004	1.00	1,4,5	.0032	14.4	84.1	1.69
		4	.0063	22.0	69.7	1.45
		4	.0069	22.8	68.3	1.49
		4	.0159	34.0	47.1	1.42
		4	.0257	39.2	37.3	1.53
		4	.0546	46.9	22.8	1.61
		4	.1040	52.2	12.8	1.53
		3	.253	56.0	5.7	1.53
						av.1.53
1.014	.948	1,4,5	.0065	18.8	76.1	2.07
		4	.0113	26.0	62.5	1.87
		4	.0162	30.5	54.1	1.92
		4	.0310	39.8	36.7	1.80
		4	.0555	46.5	23.9	1.74
		3	.129	52.9	12.0	1.76
		3	.250	55.4	7.3	1.97
						av.1.88
.67	9.23	2,3,9	.0535	42.4	32.0	2.52
		3	.130	50.4	17.0	2.66
						av.2.59
.519	.932	1,4,5	.0064	15.8	81.9	2.90
		4	.0163	26.9	61.0	2.55
		4	.0260	33.4	48.9	2.49
		4	.0550	42.7	31.4	2.52
						av.2.62
.529	1.34	2,3,10	.0139	22.1	70.0	(3.24)
		3	.0181	28.7	57.7	2.47
		3	.0283	35.1	45.7	2.38
		3	.0483	42.9	31.1	2.18
		3	.109	50.2	17.4	2.30
						av.2.33
.506	.679	2,3,11	.0057	16.5	80.6	2.37
		3	.0166	25.7	63.2	2.85
		3	.0216	30.6	54.1	2.54
		3	.0365	38.0	40.3	2.45
		3	.0765	46.1	25.0	2.55
		3	.201	53.3	11.6	2.64
						av.2.57

Table 3 (Cont.)

Acid Constant of U(IV) in Chloride Solutions

μ	M U(IV) x 10^3	Remarks	Final $[H_3O^+]$	$E_o(648)$	$\%UOH^{+3}$	K x 10^2
.272	.932	1,4,5	.0113	20.1	73.9	3.20
		4	.0162	24.0	66.5	3.21
		4	.0312	31.9	51.8	3.35
		4	.0561	40.1	36.5	3.22
						av.3.25
.123	.932	1,4,5	.0165	20.1	74.0	4.70
		4	.0261	25.2	64.5	4.74
		4	.0550	36.4	43.6	4.25
		4	.104	45.4	26.8	3.81
						av.4.38
.115	1.222	1,4,8	.0160	20.9	72.5	4.22
		4	.0160	20.2	73.9	4.53
	1.228	4,11	.0257	25.5	63.9	4.55
		4	.0266	25.7	63.5	4.63
		4	.0460	35.4	45.5	3.84
		4	.105	44.2	29.1	4.31
		4	.106	42.5	32.2	4.99
						av.4.44
.108	1.222	1,4,8	.0431	32.3	51.4	4.56
.0654	1.228	1,4,11	.055	31.8	52.5	6.1
.0449	1.228	1,4,11	.0352	24.8	65.8	6.8
.0395	1.222	1,4,8	.0305	21.2	72.1	7.9
.0345	1.228	1,4,11	.0253	19.8	74.8	7.5
.0327	.616	1,4,8	.0282	21.3	72.2	7.3
.0250	1.228	1,4,11	.0163	14.1	85.4	9.6
.0235	.616	1,4,8	.0155	13.6	86.3	9.8

(1) to (8): See footnotes Table 2.
(9) Contains ca. 5.7 x 10^{-2} M Zn^{++}.
(10) Contains ca. 8.2 x 10^{-3} M Zn^{++}.
(11) Prepared by electrolytic reduction.

The reasonable constancy of K_m, calculated over a considerable hydrolysis range, suggests that the hydrolytic reaction studied involves one oxonium ion as indicated in equations (1) and (5). The values for K_m tend to be high in the neighborhood of 80% hydrolysis suggesting that further hydrolytic reactions assume prominence. However, since in this region the observed extinction coefficients approach E_2 and the extrapolations to zero time become less accurate, the experimental precision is sufficiently lowered to preclude a final decision at this time. Further work to elucidate this point is in progress.

According to equation (5), K_m should be practically independent of the uranium (IV) concentration at constant μ. This was found to be essentially the case (see Tables 2 and 3). The small increase of K_m with concentration which seems to be occurring may still be within experimental error or it could be caused by increasing importance of polymeric hydrolytic reactions at the higher uranium (IV) concentrations. The trend is too small, however, to be compatible with the assumption that the first hydrolysis product is dimeric or of higher degree of aggregation.

It can be seen from Tables 2 and 3 that K_m is strongly dependent on ionic strength and decreases continuously with increasing μ for both chloride and perchlorate solutions. An attempt was made to evaluate the activity constant K_a for reaction (1) from these data. The relationship between K_a and K_m is

$$K_a = K_m \quad \frac{\gamma_{H_3O^+}\ \gamma_{UOH^{+3}}}{\gamma_{U^{+4}}} \qquad (6)$$

where γ is the activity coefficient of the ion indicated as subscript. It was assumed that the activity coefficients of the ions in equation (6) follow a

Debye-Hückel limiting law of the form

$$\log \gamma_i = -0.509\, Z_i^2 \frac{\mu^{1/2}}{1 + 0.3286\, \mathring{a}_i\, \mu^{1/2}} \qquad (7)$$

where Z_i is the charge of the ion and $\mathring{a}_i$ the "mean distance of approach"(15)(16)(17).

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(15) R. A. Robinson and H. S. Harned, Chem. Rev. 28.419(1941).

(16) Equation (7) differes from the Debye limiting law in that γ_i has been substituted for f_i, the activity coefficient on a mol fraction basis, (see ref. (15)), and Z_i^2 for Z_iZ_j, the product of the charges of the positive and negative ions. In view of the limited precision of the data no distinction will be made between f_i, γ_i, and y_i, the activity coefficients on a mole fraction, molality and molarity basis since the error introduced is small (less than 10% even at an ionic strength of 2). For the relationship between f_i, γ_i and y_i, see ref. (15).

(17) For values of the constants in equation (7) see G. G. Manov et al. J. Am. Chem. Soc. 65.1765(1943).

Assuming that an average value $\mathring{a}$ can be used instead of the different values $\mathring{a}_i$ for the three different ions of equation (6), substitution of equation (7) into equation (6) yields

$$\log K_a = \log K_m - 0.509\, \Delta Z_i^2 \frac{\mu^{1/2}}{1 + 0.3286\, \mathring{a}\, \mu^{1/2}} \qquad (8)$$

where $\Delta\left(Z_i^2\right) = -6$.

Using $\mathring{a} = 7.5\ \mathring{A}$ the perchlorate data can be fitted to equation (8) within the rather wide limits of experimental error (ca. $\pm$ 10%) up to $\mu = 2$. The agreement is illustrated in Fig. 5 where $\log K_m$ has been plotted as a function of $\mu^{1/2}/(1+2.465\ \mu^{1/2})$. The solid line in Fig. 5 has been drawn with the theoretical slope -6. Extrapolating the data to $\mu = 0$, $K_a = 0.21 \pm 0.02$ was found.

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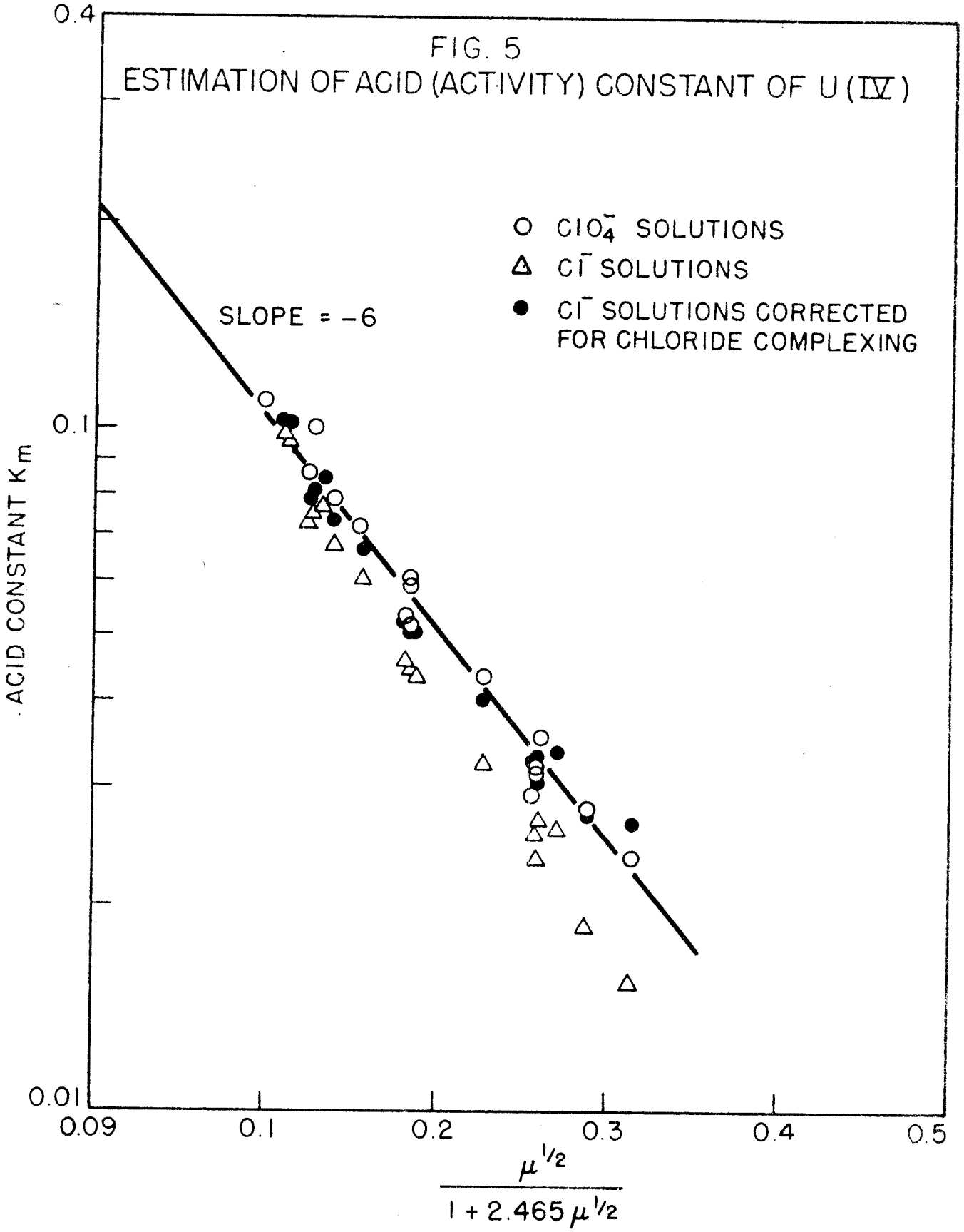

The choice of $\mathring{a}$ = 7.5 Å appears reasonable since even for 2-1 electrolytes (i.e., for electrolytes of considerably lower valence type than occur here) values of $\mathring{a}$ = 6 Å have been used[15]. Similarly, it was found that $\mathring{a}$ = 7.5 Å permits a reasonable fit of the data for 3-1 electrolytes at low molarity.

Using equation (8) (with $\mathring{a}$ = 7.5) the activity coefficient ratios of equation (6) were calculated as a function of μ (see Table 4). In the same table are given estimates of the activity coefficient ratios $\gamma_{UOH^{+3}}/\gamma_{U^{+4}}$ (calculated assuming $\gamma_{H_3O^+} = \gamma_{\pm HCl}$) and of $\gamma_{UOHX_3}/\gamma_{UX_4}$, where X denotes ClO_4^- or other non-complexing anions (calculated assuming $\gamma_{\pm HCl} = \gamma_{\pm HClO_4}$). The values $\gamma_{\pm HCl}$ given by Harned and Hamer[18] for 0.01 M HCl solutions in KCl were used. If a suitable assumption

(18) H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. 55,2194(1933).

is made for the activity coefficients of γ_{UOHX_3}, the data in Table 4 should permit an estimation of γ_{UX_4}. Since $UOHX_3$ can be considered a 3-1 electrolyte and since the activity coefficients of most 3-1 electrolytes differ only by a few percent for values of μ = 1 and appear to obey the Debye limiting law for $\mathring{a}$ = 7.5, γ_{UOHX_3} was correspondingly calculated. The results have been included in Table 4 as well as the calculated values of $\gamma_{\pm UX_4}$.

c) Estimate of the Stability Constant of the Uranium (IV)-Chloride Complex. The values of K_m for the chloride solutions are generally lower than for the perchlorate solutions, which is probably due to chloride complexing of uranium (IV) according to the equation

$$U^{+4} + Cl^- \rightleftharpoons UCl^{+3} \qquad (9)$$

Table 4

Activity Coefficients in the U^{+4} - UOH^{+3} System

μ	$\frac{\gamma_{H_3O^+}\gamma_{UOH^{+3}}}{\gamma_{U^{+4}}}$ (a)	$\gamma_{\pm HCl}$ (b)	$\gamma_{UOH^{+3}}/\gamma_{U^{+4}}$ (c)	$\gamma^4_{UOHX_3}/\gamma^5_{UX_4}$ (d)	$\gamma_{\pm UOHX_3}$ (e)	$\gamma_{\pm UX_4}$ (f)
.01	1.79	.904	1.98	.683	.75	.68
.02	2.09	.873	2.39	.613	.69	.61
.04	2.56	.836	3.14	.559	.63	.53
.06	2.93	.815	3.59	.515	.58	.48
.10	3.49	.790	4.42	.460	.54	.43
.20	4.46	.752	5.93	.396	.47	.38
.50	6.13	.706	8.67	.327	.41	.29
1.00	7.61	.719	10.58	.253	.36	.26

(a) Calculated using equation (7).

(b) From Harned and Hamer, ref. (18). It will be assumed that $\gamma_{\pm HCl}=\gamma_{\pm HClO_4}$.

(c) Calculated from column (2) assuming $\gamma_{H_3O^+}=\gamma_{\pm HCl}$.

(d) Calculated from column (2) by dividing by $\gamma^2_{\pm HCl}$. "X" indicates a non-complexing negative ion, particularly ClO_4^-.

(e) Calculated from $\log \gamma_{\pm} = -0.509\, \underline{Z}_i \underline{Z}_j \frac{\mu^{1/2}}{1 + 0.3286\, \underline{\mathring{a}}\, \mu^{1/2}}$, using $\underline{\mathring{a}} = 7.5$.

(f) Calculated from columns (5) and (6).

To evaluate the stability constant $\underline{K}_c$ for this reaction ($\underline{K}_c'$ at $\mu = 0$) it was assumed that equation (8) is applicable. It should be noticed that for this equilibrium, however, $\Delta(Z_i^2) = -8$. Through trial and error $\underline{K}_c' = 7.0$ was found to correct the apparent acid constants adequately and to bring them in line with the values $\underline{K}_m$ for the perchlorate solutions (see Fig. 5). The data are not sufficiently accurate to permit more than an estimate of $\underline{K}_c'$ and it is questionable that the value given is better than $\pm$ 30%. The best values for $\underline{K}_c$ at $\mu = 0.5$ and 1.0 are 0.62 and 0.47 respectively suggesting that U^{+4} is 24 and 32% complexed in these solutions. Complexing in 2M HCl can be estimated to be ca. 42%. It is surprising that this large amount of complexing hardly affects the absorption spectrum.

3.2 Plutonium.

(a) Assignment of the Species Pu^{+4}(19). The evidence for the assignment of

(19) For a more detailed discussion regarding the evidence for this assignment see ref. 4a.

the formula Pu^{+4} for plutonium (IV) is similar to that for uranium (IV). Thus the potential of the plutonium (III)/(IV) couple was found to be practically independent of acidity(20) (from 0.2-1 M H_3O^+) and the acid dependence of the plutonium (IV)/(VI)

(20) J. C. Hindman, Report CN-2289 (November 1944).

couple is in fairly close agreement with the assignment of the species Pu^{+4} and PuO_2^{++}.(4a)

In addition, Pu(III) was found to hydrolyze near pH 7 as predicted by analogy with the rare earths(4b)(21). Since during this hydrolysis more than two hydroxide

(21) K. A. Kraus and J. R. Dam, Report CN-2832 (August 1946).

ions are picked up, the assignment Pu^{+3} for acidic solutions can be made with fair certainty and hence the assignment Pu^{+4}.

(b) The Acid Constant of Pu^{+4}. The general technique and the calculations for the evaluation of the acid constant K_m (molarity constant) of Pu^{+4} were very similar to those used for uranium (IV) and thus will not be discussed in detail. Since plutonium (IV) polymerizes more readily than uranium (IV) and since it undergoes disproportionation into plutonium (III) and plutonium (VI) (with rate increasing with decreasing acidity) extrapolation of the data to "zero-time" is considerably more important for plutonium (IV) than for uranium (IV). For the same reasons it is difficult to obtain data on the monomeric reactions under conditions where more than ca. 50% of the Pu^{+4} are hydrolyzed.

The absorption spectrum of unhydrolyzed Pu^{+4} is shown as curve B in Fig. 1. A listing of the extinction coefficients of the various maxima and minima can be found in Table 5. The striking similarity of the absorption curves for U^{+4} and Pu^{+4} is of interest particularly since the similarity extends apparently to a number of details.

For analysis theprominent absorption band located near 470 mμ was chosen ($E_1(470) = 55$). Deviations from Beer's law of this maximum was negligible in the concentration range of interest if the slitwidth used is small (ca. 0.04 mm).

There was no indication for an absorption maximum of the hydrolysis product in the wavelength range studied (ca. 450-500 mμ) although absorption due to it is by no means negligible ($E_2(470)$ = ca. 17).

Table 5

Minima and Maxima in the Absorption Spectrum of Pu^{+4}

Wavelength (mμ)	E_1 (a)	Wavelength (mμ)	E_1 (a)
		402	21.6
404	20.8	407	24.6
420	9.2	426	27.2
438	11.2	447	18.0
456	15.0	470	53.2
		475	38.8
495	6.1	506	11.8
527	7.3	556	14.4
595	2.0	655	35.6
		667	32.4
700	10.8	730	14.8
755	8.6	815	21.0
950	0.6	1080	27.0

(a) Observed extinction coefficients of plutonium (IV) in 0.5 M $HClO_4$-0.015 M HCl not corrected for partial hydrolysis. 10 cm cell length; 7.20×10^{-4} M Pu(IV).

The results of two series of experiments for perchlorate and chloride solutions are summarized in Table 6. In addition a few experiments were carried out which confirmed the concentration independence of K_m (range covered: 3.6×10^{-4} to 2.9×10^{-3} M Pu(IV)) within the rather wide limits of experimental accuracy.

Thus, apparently the same (rapid) hydrolytic reaction (equation (1)) applies for plutonium (IV) and uranium (IV) and in addition, the two elements behave quantitatively very similarly. The observed constants for uranium (IV) (K_m=0.032 μ=0.5) and plutonium (IV) (K_m=0.025,μ=0.5) show that uranium (IV) is more acidic. The difference is barely outside the experimental error and thus appears to be significant. On the basis of simple "coulombic" arguments the reverse would be expected since uranium (IV) is larger than plutonium (IV) as indicated by the metal

oxygen distances of the dioxides (U-O:2.363Å, Pu-O:2.332Å)[22].

(22) W. H. Zachariasen, Report MDDC-67 (June 1946).

Table 6

Acid Constant of Plutonium (IV) in Perchlorate and Chloride Solutions

(ionic strength μ = 0.5)

Perchlorate					Chloride				
M Pu(IV) x 10^3	Final $[H_3O^+]$	$E_o(470)$	%$Pu(OH)^{+3}$	K x 10^2	M Pu(IV) x 10^3	Final $[H_3O^+]$	$E_o(470)$	%$Pu(OH)^{+3}$	K x 10^3
.72	.011	25.8	76.8	(3.64)	.72	.011	25.3	78.0	(3.9)
	.021	33.4	56.8	2.76		.031	38.9	42.3	2.27
	.031	38.0	44.5	2.49		.051	43.4	30.3	2.22
	.051	42.7	32.2	2.42		.091	47.3	20.2	2.30
	.091	46.9	21.2	2.45		.131	49.8	13.6	2.06
	.131	48.8	16.1	2.51		.500	53.3	4.5	2.35
	.211	51.3	9.6	2.24					av. 2.24
	.500	53.2	4.7	2.47					
				av. 2.49					

Although the data are not sufficiently accurate to warrant calculation of the stability constant K_c for the chloride complex of plutonium (IV) (see equation 9) as was done for uranium (IV), the slightly smaller value of K_m for chloride solutions as compared with perchlorate solutions indicates that weak chloride complexing occurs.

3.3 Conclusions Regarding a Second "Rare-earth" Series.

Although uranium and plutonium are now generally agreed to be members of a "rare-earth-like" series (actinide, thoride or uranide) it might be pointed out that

the experiments reported here lend further confirmation to this hypothesis. The salient points are:

(1) The quantitative similarity of the hydrolytic properties of these elements is typical of the persistence of properties with changing atomic number which is a characteristic attribute of rare earths of the same oxidation number.

(2) The elements form very weak chloride complexes. If they were transition elements strong chloride complexes would be expected.

(3) The absorption spectra of uranium (IV) and plutonium (IV) are reminiscent of those of the rare earths, and very similar with respect to each other. (see footnote 13).

4. Summary

(1) Through pH measurements of UCl_4 solutions, U^{+4} was established to be the species of uranium (IV) in acidic solutions.

(2) The acid constant of U^{+4} was determined as a function of ionic strength for chloride and perchlorate solutions through a spectrophotometric method. The molarity constants could be fitted approximately to a Debye-Hückel limiting law and the activity constant $K_a = 0.21 \pm 0.02$ was estimated for the equilibrium

$$U^{+4} + 2H_2O \rightleftharpoons UOH^{+3} + H_3O^+$$

(3) The stability constant for the reaction

$$U^{+4} + Cl^- \rightleftharpoons UCl^{+3}$$

was estimated to be $\underline{K}_c$ = ca. 0.63 (μ = 0.5) and K_c' = 7.0 (μ = 0).

(4) The acid constant of Pu^{+4} ($K_m = 0.025$, $\mu = 0.5$) was found to be almost identical with, though slightly smaller than that of U^{+4} ($K_m = 0.032$, $\mu = 0.5$).

(5) The spectral data, the quantitative hydrolytic data and the observation that the chloride complexes of uranium (IV) and plutonium (IV) are weak, are confirmatory evidence of the hypothesis that these elements are members of a "rare-earth-like" series.

Acknowledgement

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