

Variation of Stability Constants of Thorium and Uranium Oxalate Complexes with Ionic Strength

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Abstract

The extraction of Th(IV) and UO_2^{2+} by a solution of TTA and HDEHP, respectively in toluene has been used to obtain stability constants of their oxalate complexes at 298 K in 1, 3, 5, 7 and 9 M ionic strength (NaClO_4) solutions. The complexes formed were the MOx , MHOx , MOx_2 and $\text{M}(\text{HOx})_2$ ($\text{M} = \text{Th}, \text{UO}_2$) species. The values were analyzed by the Specific Interaction Theory and agreed to $I \leq 3$ M but required an additional term for fitting at $I > 3$ M.

Introduction

The use of nuclear energy requires an ability to dispose safely of the resulting nuclear wastes. The solution chemistry of the actinides in connection with nuclear fuel reprocessing cycles as well as with their behavior in the environment associated with geological repositories is of major interest presently. The hydrolysis of actinide cations in natural waters can limit their solubility, lead to precipitation or sorption, and reduce complexation by other ligands in the waters. For modeling requirements, stability constant values are necessary for the ligands of interest in natural waters as well as hydrolysis constants. Normal titration techniques to determine such constants require relatively high metal ion concentrations which may be prevented by hydrolysis. Furthermore, such concentrations can lead to radiolysis which can complicate the measurements and perturb the results. These difficulties can be avoided by using solvent extraction techniques with tracer concentrations of the metal ions [1–4].

In this study, the stability constants of thorium and uranium oxalate complexes were measured over a range of ionic strengths.

The distribution coefficient, D , is defined for the extraction system as:

$$D = \Sigma[\text{M}]_o / \Sigma[\text{M}]_a \quad (1)$$

Assuming only a single organic phase species, MA_n , and the various species in the aqueous phase, equation (1) can be expressed by:

$$D = [\text{MA}_n]_o / ([\text{M}]_a + [\text{ML}]_a + [\text{MHL}]_a + [\text{ML}_2]_a + [\text{M}(\text{HL})_2]_a + \dots) \quad (2)$$

where L is a complexing anion in the aqueous phase. This equation can be written, with the conventional symbols for stability constants, [5] as,

$$D = [\text{MA}_n]_o / [\text{M}]_a (1 + (\beta_{101} + \beta_{111}[\text{H}])[\text{L}] + (\beta_{102} + \beta_{122}[\text{H}]^2)[\text{L}]^2 + \dots) \quad (3)$$

We define “apparent” stability constants as:

$$\beta_1^{\text{app}} \equiv \beta_{101} + \beta_{111}[\text{H}] \quad (4)$$

$$\beta_2^{\text{app}} \equiv \beta_{102} + \beta_{122}[\text{H}]^2 \quad (5)$$

The constant in the absence of complexation is:

$$D_o \equiv [\text{MA}_n]_o / [\text{M}]_a \quad (6)$$

This allows restating equation (3) as:

$$D_o/D = 1 + \beta_1^{\text{app}}[\text{L}] + \beta_2^{\text{app}}[\text{L}]^2 + \dots \quad (7)$$

A plot of β_1^{app} vs. $[\text{H}]$ should give a straight line with an intercept equal to β_{101} and a slope of β_{111} while a plot of β_2^{app} vs. $[\text{H}]^2$ should be linear with an intercept of β_{102} and a slope of β_{122} .

Experimental

Reagents and solutions

All reagents were analytical grade. A stock solution of 0.0010 M sodium oxalate (Aldrich) was prepared. Thenoyltrifluoroacetone, TTA, was purified by sublimation. A 0.01 M stock solution of TTA in toluene was stored in the dark. Di-(2-ethylhexyl) phosphoric acid, HDEHP, (Pfaltz and Bauer Co.) was purified by precipitation as $\text{Cu}(\text{DEHP})_2$ using the procedure of McDowell *et al.* [6]. The purified HDEHP was dissolved in toluene and standardized with standard NaOH solution. Sodium perchlorate (anhydrous, Mallinckrodt) was used for ionic strength adjustment without further purification.

^{230}Th tracer (from Oak Ridge National Laboratory) was prepared in a solution of pH 2 (HClO_4) such that 10 μl contained ca. 4.5×10^4 cpm. ^{233}U tracer (Oak Ridge National Laboratory) was evaporated to dryness and dissolved in a pH 3 (HClO_4) solution such that 10 μl of the solution had a count rate of 3.5×10^4 cpm. These count rates were obtained with the same efficiency as for the samples from the solvent extraction

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measurements. All solutions used in the experiments were filtered with a 0.45 μm microfiltration system. Contamination from airborne particles was reduced by performing the experimental manipulations in a laminar flow hood (Environmental Air Control, Inc.).

Silanizing

To minimize the sorption of the uranyl and thorium radiotracers on extraction vials, the latter were silanized according to the process in reference [3]. The 20 ml standard borosilicate scintillation vials were washed with 1 M NaOH, soaked in 3 M HCl, rinsed and dried at 100 °C. The precleaned vials and their caps were silanized by shaking for 4–6 hours in a solution containing 5% trimethylchlorosilane and 5% hexamethyldisilazane in toluene. The vials were dried overnight at 120 °C.

pH Measurements

A research pH meter (Accumet 950, Fischer Scientific) was used with a combination glass electrode. The KCl solution in the salt bridge was replaced with NaCl solution, as the low solubility of KClO_4 at high ionic strengths causes erratic readings. The electrode was calibrated with 4.01 ± 0.01 and 7.00 ± 0.01 pH buffer standards. The pH readings were converted to hydrogen ion concentration (pH) using calibration curves obtained by a series of HClO_4 dilutions in 1 to 9 M NaClO_4 solutions.

Radioactive tracer

The radioactive tracers used were checked for radioactive purity by alpha and gamma ray spectrometry. The alpha radioactivity in aliquots from the experiments was counted on a Packard Instrument Tri-Carb 4000 (Hewlett Packard Instruments) liquid scintillation counter using an emulsion scintillation cocktail (Ecolume, ICN Biomedicals Co.) for both aqueous and organic phases.

Experimental procedure

Determination of the dissociation constants of oxalic acid

The pK_a values of oxalic acid were determined at 3, 5, 7, and 9 M ionic strengths by potentiometric (NaClO_4) titration. The titrations were carried out using 40 ml solutions in a 150 ml vessel. A water bath maintained at 25 ± 0.2 °C was used for circulating water in the jacket of the titration vessel. The Gran method was used for calibrating the glass electrode at each ionic strength [7, 8]. A standardized solution of 0.1 M HClO_4 (in NaClO_4 of a certain ionic strength) was titrated against a volume V_0 of NaClO_4 of the same ionic

Table 1. Dissociation constants of oxalic acid at different ionic strengths (NaClO_4) and $T = 298$ K

I (M)	pK_{a1}	pK_{a2}
1	1.04 ± 0.04 [10]	3.56 ± 0.02 [10]
3	1.3 [10] 1.0 ± 0.3 (p.w.)	3.81 [10] 3.85 ± 0.1 (p.w.)
5	2.19 ± 0.04	4.47 ± 0.01
7	2.61 ± 0.04	4.91 ± 0.01
9	2.26 ± 0.08	5.20 ± 0.01

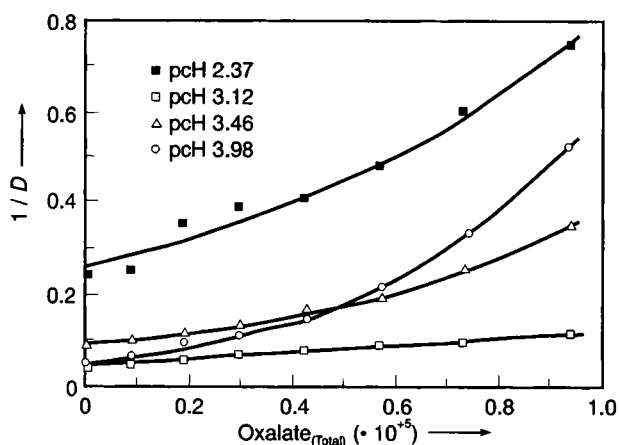


Fig. 1. The variation of $1/D$ for Th(IV) as a function of total oxalate concentration at an ionic strength of 5 M NaClO_4 .

strength as that of HClO_4 . The exact concentration of the titrant (HClO_4 in NaClO_4) was determined by titrating a known amount of Na_2CO_3 using bromocresol green as indicator. The titration used constant amounts of titrant for each addition. The data analysis of pK_a determination was done by using the Fortran program HNFITMQ [9].

Solvent extraction procedure

For each extraction experiment, 5.0 ml of pre-equilibrated aqueous solution adjusted to the appropriate pH were placed in silanized vials. Aliquots of oxalate stock solution were added to each vial followed by 5 ml of TTA and HEDHP in toluene. The concentration of the organic extractant was adjusted according to the ionic strength and pH of the solutions used. After addition of 10 μl of either ^{230}Th or ^{233}U , the vials were shaken for 2–3 hours at room temperature. Kinetic measurements indicated that equilibrium was attained in these experiments in about 10 min (Th) and 1 h (U). The vials were centrifuged and duplicate aliquots from both phases were taken for counting and pH measurement.

Results

Dissociation constants of oxalic acid

The experimental acid dissociation constants of oxalic acid are given in Table 1. pK_a values up to 3 M ionic

Table 2. Apparent stability constants of Th+Ox complexes ($T = 298$ K). $\log \beta_1^{\text{app}}$

pH	Ionic strength				
	1 M	3 M	5 M	7 M	9 M
1.29	7.92±0.06	8.02±0.04	8.96±0.02	9.57±0.02	8.92±0.02
1.40	7.90±0.01	7.99±0.01			
1.50	7.88±0.02		8.68±0.02		
1.58		7.94±0.03	8.66±0.05		
1.67	7.79±0.05				
1.84	7.70±0.02	7.78±0.04	8.37±0.06	8.99±0.05	8.79±0.07
1.90	7.62±0.03				
1.94	7.58±0.04				
2.17	7.37±0.01				
2.30	7.44±0.06				
2.37	7.19±0.04		7.68±0.07	8.40±0.07	8.53±0.04
2.41		7.31±0.04			
3.08				7.23±0.09	7.27±0.04
3.12	6.76±0.02	6.78±0.05	6.76±0.04		7.18±0.04
3.32				7.15±0.05	7.08±0.01
3.46	6.50±0.04	6.47±0.01	6.45±0.01	6.91±0.05	7.14±0.05
3.98	6.00±0.08	6.09±0.17	6.29±0.07	6.75±0.08	7.06±0.10

Table 3. Apparent stability constants of Th+Ox complexes ($T = 298$ K). $\log \beta_2^{\text{app}}$

pH	Ionic strength				
	1 M	3 M	5 M	7 M	9 M
1.29	13.34±0.31	14.26±0.34	16.31±0.45	18.16±0.17	17.49±0.14
1.40	13.62±0.14	13.94±0.35			
1.50	13.62±0.13				
1.67	13.78±0.02				
1.84	13.71±0.01	13.66±0.16	15.90±0.02	16.81±0.42	16.23±0.76
1.90	13.61±0.05				
2.17	13.44±0.03				
2.37	13.00±0.02				15.98±0.03
3.12	12.79±0.03	12.76±0.07	12.44±0.04	13.63±0.03	14.31±0.03
3.46	12.16±0.02	12.18±0.03	12.47±0.02	13.30±0.05	13.13±0.31
3.98	12.99±0.04	12.06±0.02	12.23±0.05	13.77±0.02	13.17±0.14

strength are reported in the literature [10]. The pK_{a1} values have somewhat larger errors than those of pK_{a2} , reflecting the increased difficulty in determining the values for pK_{a1} .

The thorium oxalate complexes

Speciation calculations of the oxalate ligand indicate that in the pH range of these studies the predominant species is the protonated anion HOx^- .

Metal oxalate complexation

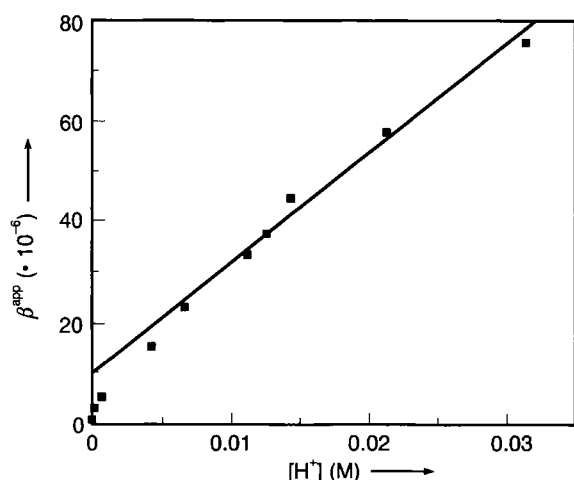
A series of experiments covering pH's from 1.3 to 4.0 were conducted at ionic strengths of 1, 3, 5, 7, and 9 M NaClO_4 . The concentration of oxalate anion in each vial was calculated from the measured pH, the total oxalate and the pK_a values of oxalic acid.

Typical curves showing the variation of $1/D$ with oxalate anion concentration at different pH values are

shown in Figure 1. The data were analyzed with Eq. (7) when nonlinear curves were obtained over higher oxalate ranges as this indicates the presence of both 1:1 and 1:2 complexes. From analysis of the curves, the apparent stability constants β_1^{app} and β_2^{app} were obtained as listed in Tables 2, 3, and 4. These values represent results of at least two determinations. The relationship of these apparent stability constants to the β_{101} , β_{111} , β_{102} , and β_{122} stability constants are given by Equations (4) and (5). Figure 2 is a plot of the apparent β_1^{app} as a function of hydrogen ion concentration. The intercept and slope of the linear least squares fit correspond to β_{101} and β_{111} , respectively. This technique where by the perturbation of complexing by oxalate due to competitive hydrolysis can be used only where hydrolysis has not proceeded too far. The deviation from linearity at low $[\text{H}^+]$ in Figure 2 reflects this problem which is also observed by a poor mass balance due to sorption and/or precipitation of the neutral hydroxide. The slope at higher $[\text{H}^+]$ values becomes unreliable due to small degree of complexation

Table 4. Apparent stability constants of the $\text{UO}_2^{2+} + \text{Ox}$ complexes ($T = 298 \text{ K}$). $\log \beta_1^{\text{app}}$ and $\log \beta_2^{\text{app}}$

pcH	Ionic strength			
	3 M	5 M	7 M	9 M
1.61	6.20 ± 0.02			
1.89	6.13 ± 0.01			
2.19	6.07 ± 0.02			
2.23				7.96 ± 0.03
2.27		7.16 ± 0.02		
2.32	6.12 ± 0.02			
2.49		6.70 ± 0.02		
2.79		6.80 ± 0.05		
2.84			7.60 ± 0.06	
3.03		6.92 ± 0.01 (12.92 ± 0.01)		
3.07			7.50 ± 0.05 (14.43 ± 0.21)	
3.11				7.54 ± 0.04 (14.14 ± 0.09)
3.22	6.05 ± 0.06 (11.07 ± 0.20)			
3.34				7.43 ± 0.04 (14.09 ± 0.10)
3.42	5.97 ± 0.06 (11.09 ± 0.10)			
3.52		6.84 ± 0.04 (12.40 ± 0.11)		
3.54			7.04 ± 0.06 (13.18 ± 0.19)	

**Fig. 2.** Variation of the apparent stability constant, β_1^{app} , for thorium plus oxalate complexes as a function of hydrogen ion concentration at 1 M ionic strength.

and the values at pcH 1.29 and 1.40 have not been included in Figure 2. The β_{101} , β_{102} , β_{111} , and β_{122} values are given in Tables 5 (a) and (b) where the errors indicated represent 1σ .

Discussion

The bonding of Th(IV) to inorganic and organic ligands in complexes can be described by an ionic model. As a result the number of ligands as well as their geometric arrangement about the thorium cation are

determined primarily by electrostatic and steric factors. The hydrolysis of Th(IV) can be extensive even in relatively acidic solutions ($\text{pH} \geq 1$). Since most organic ligands involving carboxylate groups (e.g., oxalate) require pH values of 3 or higher in order to provide enough ionization of the ligand for interaction, studies of thorium complexation are limited due to hydrolytic competition. Only a single study exists in the literature of the stability constants β_{101} and β_{102} of thorium-oxalate complexes in perchlorate solution [11] obtained from solubility measurements. Our values are not in agreement with these data.

Uranyl ion, UO_2^{2+} , does not hydrolyze as readily and has been studied more extensively than thorium. Stability constants for the UO_2^{2+} -oxalate system are available in the literature for 4 M ionic strength [11, 12, 13] and below. In the present work, we obtained a $\log \beta_{101}$ of 6.00 ± 0.05 which compares well with that reported at 4 M [13].

The Nuclear Energy Agency has recommended [14] the use of Specific Ion Interaction Theory (SIT) in the analysis of stability constants measured at different ionic strengths up to ca. 3 m. In the SIT approach, the value of the stability constant at zero ionic strength, β^0 , is related to the value β^I at ionic strength I (in molality) by:

$$\log \beta^I = \log \beta^0 \pm \Delta Z^2 \cdot D - \Delta \epsilon \cdot I. \quad (8)$$

Here,

$$\Delta Z^2 = (Z_{\text{ML}})^2 - Z_{\text{M}}^2 - Z_{\text{L}}^2 \quad (9)$$

and

Table 5. (a) Stability constants of Th + Ox complexes

<i>I</i> (M)	$\log \beta_{101}$	$\log \beta_{111}$	$\log \beta_{102}$	$\log \beta_{122}$
1	6.93±0.03	9.47±0.01	13.13±0.17	17.01±0.04
3	7.06±0.09	9.52±0.12	13.16±0.05	16.95±0.03
5	7.12±0.08	10.24±0.05	13.19±0.17	19.29±0.01
7	7.37±0.04	10.84±0.01	13.76±0.06	20.21±0.01
9	6.74±0.12	10.63±0.01	13.03±0.18	19.79±0.01

(b) Stability constants of UO_2^{2+} + Ox complexes

<i>I</i> (M)	$\log \beta_{101}$	$\log \beta_{111}$	$\log \beta_{102}$	$\log \beta_{122}$
1	5.99 ¹¹			
3	6.00±0.05	7.57±0.06	11.21±0.18	
5	6.55±0.28	9.22±0.17	12.28±0.11	18.86±0.15
7	6.55±0.33	10.43±0.07	12.94±0.40	20.04±0.42
9	7.37±0.05	10.06±0.02	14.08±0.11	19.48±0.59

Table 6. Results of the extended SIT analysis

Species	$\log \beta^0$	$\Delta \epsilon$	$\Delta \delta$
HOx^-	4.33	0.26	-0.0062
UO_2HOx^+	5.60	1.03	-0.044
UO_2Ox	5.60	0.45	-0.019
ThHOx^{3+}	11.0	0.51	-0.020
ThOx^{2+}	9.8	0.42	-0.022
$\text{Th}(\text{HOx})_2^{2+}$	18.13	1.42	-0.061
ThOx_2	17.5	0.56	-0.028

$$D = 0.509I^{1/2}/1 + 1.5I^{1/2} \quad (10)$$

$$\Delta \epsilon = \epsilon_{\text{ML}} - \epsilon_{\text{M}} - \epsilon_{\text{L}} \quad (11)$$

where *Z* is the charge on the designated species and ϵ is an interaction coefficient for the cation and anion pair. Values of $\log \beta$ predicted by the SIT agree well with the experimental values from 0 to ca. 3 M ionic strength. Above *I* = 3 M there is usually a growing difference between the experimental data and the SIT calculation.

Recently an extension of the SIT treatment has been proposed [15] to cover higher ionic strengths by including a quadratic term of the interaction, $+\Delta \delta \cdot I^2$, in Equation (8). The results of extended SIT analysis of our data are given in Table 6 which Figure 3 illustrates the extended SIT fitting of the ThOx^{2+} complex stability constant. This extension of the S.I.T. treatment to higher ionic strengths is empirical and, generally, analyses at such ionic strengths have used the Pitzer formalism [16]. We have not used this latter approach in this study due to insufficient data to obtain the Pitzer parameters.

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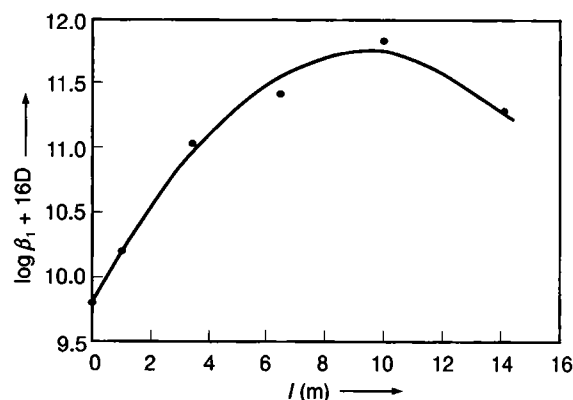


Fig. 3. The "extended" SIT treatment of the β_{101} values for Th + Ox as a function of the ionic strength (in molality).

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