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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 in 1, 3, 5, 7 and 9 M ionic strength ($NaClO_4$) solutions. The complexes formed were the MOx, MHOx, MOx_2 and $M(HOx)_2$ (M = Th, 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 solution chemistry of actinides is relevant to radioactive waste management. The behavior of actinide elements in the natural environments associated with geologic repositories is of particular interest. 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. Modeling of chemical behavior requires values for hydrolysis constants and stability constants with ligands present in natural waters. Normal titration techniques to determine such constants require relatively high metal ion concentrations, which may not be attainable for some systems due to hydrolysis. Furthermore, high concentrations increase the effects of 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:

$$D = \Sigma[M]_o/\Sigma[M]_a \tag{1}$$

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

$$D = [MA_n]_o/([M]_a + [ML]_a + [MHL]_a + [ML_2]_a + [M(HL)_2]_a + \ldots) \tag{2}$$

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

$$D = [MA_n]_o/[M]_a(1+(\beta_{101}+\beta_{111}[H])[L]+(\beta_{102}+\beta_{122}[H]^2)[L]^2+\ldots) \qquad (3)$$

We define "apparent" stability constants as:

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

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

The constant in the absence of complexation is:

$$D_o \equiv [MA_n]_o/[M]_a \qquad (6)$$

This allows restating equation (3) as:

$$D_o/D = 1 + \beta_1^{app}[L] + \beta_2^{app}[L]^2 + \ldots.. \qquad (7)$$

A plot of β_1^{app} vs. [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. $[H]^2$ 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. Thenoyltrifluroacetone, 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 $Cu(DEHP)_2$ using the procedure of McDowell et al.[1] 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 and ^{233}U tracers were obtained from Oak Ridge National Laboratory. A ^{230}Th tracer solution of approximately 4.5×10^3 cpm/μL was prepared in perchloric acid with pH 2. The ^{233}U solution of approximately 3.5×10^3 cpm/μL was prepared by evaporating the stock U solution to dryness, and dissolving in perchloric acid with pH 3. All solutions used in the experiments were filtered with a 0.45 μm microfiltration system. All experimental manipulations were performed in a laminar flow hood (Environmental Air Control, Inc.) to reduce contamination from airborne particles.

Silanizing

To minimize sorption of the uranyl and thorium radiotracers on extraction vials, the vials were silanized according to the process in ref. [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.

pcH 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 because the low solubility of $KClO_4$ at high ionic strengths can cause 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 (pcH) 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 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 hr. (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 I. pK_a values up to 3 M ionic 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 pcH range of these studies the predominant species is the protonated anion HOx^-.

Metal Oxalate Complexation

A series of experiments covering pH's from 1.5 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 pcH, 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 pcH 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_{101}^{app} and β_{102}^{app} were obtained as listed in Tables II and III. 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_{101}^{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. The experimental points deviate from a straight line at low hydrogen ion concentrations due to hydrolysis of the Th(IV) cation. The β_{101}, β_{102}, β_{111}, and β_{122} values are given in Tables IV (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 ($pH \geq 1$). 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]. This measurement, based on solubility studies which are not a very reliable technique for such measurements and the reported constants do not agree with our values.

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 β_{101} of 6.00 ± 0.05 which compares well with that reported at 4M [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. 3m. In the SIT approach, the value of the stability constant at zero ionic strength, β_o, is related to the value β, at ionic strength I (in molality) by:

$$\log \beta = \log \beta_o - \Delta Z^2 . D - \Delta \epsilon . I \qquad (8)$$

Here,

$$\Delta Z^2 = (Z_{ML})^2 - Z_M^{\,2} - Z_L^{\,2} \qquad (9)$$

and

$$D = 0.509I^{1/2}/1+1.51^{1/2} \qquad (10)$$

$$\Delta\epsilon = \epsilon_{ML} - \epsilon_M - \epsilon_L \qquad (11)$$

Where Z is the charge on the designated species and ϵ is an interaction coefficient. Values of log β 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 theory has been proposed [15] to cover higher ionic strengths by including a quadratic term of the interaction, $-\Delta\delta . I^2$, in equation (8). The results of extended SIT analysis of our data are given in Table V and while Figure 3 illustrates the extended SIT fitting of the $ThOx^{2+}$ complex stability constant.

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REFERENCES

1. F.I.Khalili, G.R.Choppin and E.N.Rizkalla, Inorg.Chim.Acta 143, 131 (1988).

2. M.S.Caceci and G.R.Choppin, Radiochim. Acta 33, 101 (1983).

3. M.S.Caceci and G.R.Choppin, Radiochim. Acta 33, 207 (1983).

4. G.R.Choppin and J.N.Manthur, Radiochim. Acta 52/53 (1991).

5. L.G.Sillen and A.E.Martell, Spec.Pub.Chem. Soc.No 17 (1964).

6. McDowell, W. J.; Perdue, P. T.; Case, G. N. J. Inorg. Nucl. Chem. **1976**, 38, 2127-2129.

7. G. Gran, Acta Chem. Scand. **1950**, 4, 559-577.

8. G. Gran, Analyst, **1952**, 77, 661-671.

9. R. A. Torres, private communication, Lawrence Livermore National Laboratory.

10. Martell, A. E.; Smith, R. M. In Critical Stability Constants; Plenum: New York, 1989; Vol. 6 (Second Supplement), p. 325.

11. A.I.Moskvin and L.N.Essen, Russian J.Inorg.Chem. 12, 630 (1967).

12. Miyake, C.; Nurnberg, H. W. J. Inorg. Nucl. Chem. **1967**, 29, 2411-2429.

13. Havel, J. Coll. Czech. Chem. Commun. **1969**, 34, 3248-3265.

14. I.Grenthe, J.Fuger, R.Lemire, A.Muller, C.N.T-Gegu, H.Wanner, Chemical Thermodynamics of Uranium, NEA-TDB, OECD, France (1991).

15. M.Du, Chemistry Department, Florida State University Tallahassee, Private Communication (1993).

16. Martell, A. E.; Smith, R. M. In Critical Stability Constants; Plenum: New York, 1989; Vol. 6 (Second Supplement), p. 325.

TABLE I

Dissociation Constants of Oxalic Acid at Different Ionic Strengths ($NaClO_4$) and T = 298K.

I(M)	pK_{a1}		pK_{a2}	
	Reference 10	present work	Reference 10	present work
1	1.04 ± 0.04		3.56 ± 0.02	
3	1.3	1.0 ± 0.3	3.81	3.85 ± 0.1
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

TABLE II

Apparent Stability Constants β_{101}^{app}, β_{102}^{app} of Th+Ox Complexes.

T = 298 K.

	Ionic Strength				
pcH	1M	3M	5M	7M	9M
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 III

Apparent Stability Constants, log β_1^{app} and log β_2^{app} of UO_2^{2+} + Ox Complexes.

T = 298 K.

	Ionic Strength			
pcH	3M	5M	7M	9M
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	

TABLE IV

(a) Stability Constants of Th+Ox Complexes

I(M)	log β_{101}	log β_{111}	log β_{102}	log β_{112}
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(M)	log β_{101}	log β_{111}	log β_{102}	log β_{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 V

Results of the Extended SIT Analysis

Species	Log β°	$\Delta\epsilon$	$\Delta\delta$
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
$Th(HOx)_2^{2+}$	18.13	1.42	-0.061
$ThOx_2$	17.5	0.56	-0.028

TABLE VI

Hydrolysis Constants of Th at Different Ionic Strengths ($NaClO_4$)

T = 298 K.

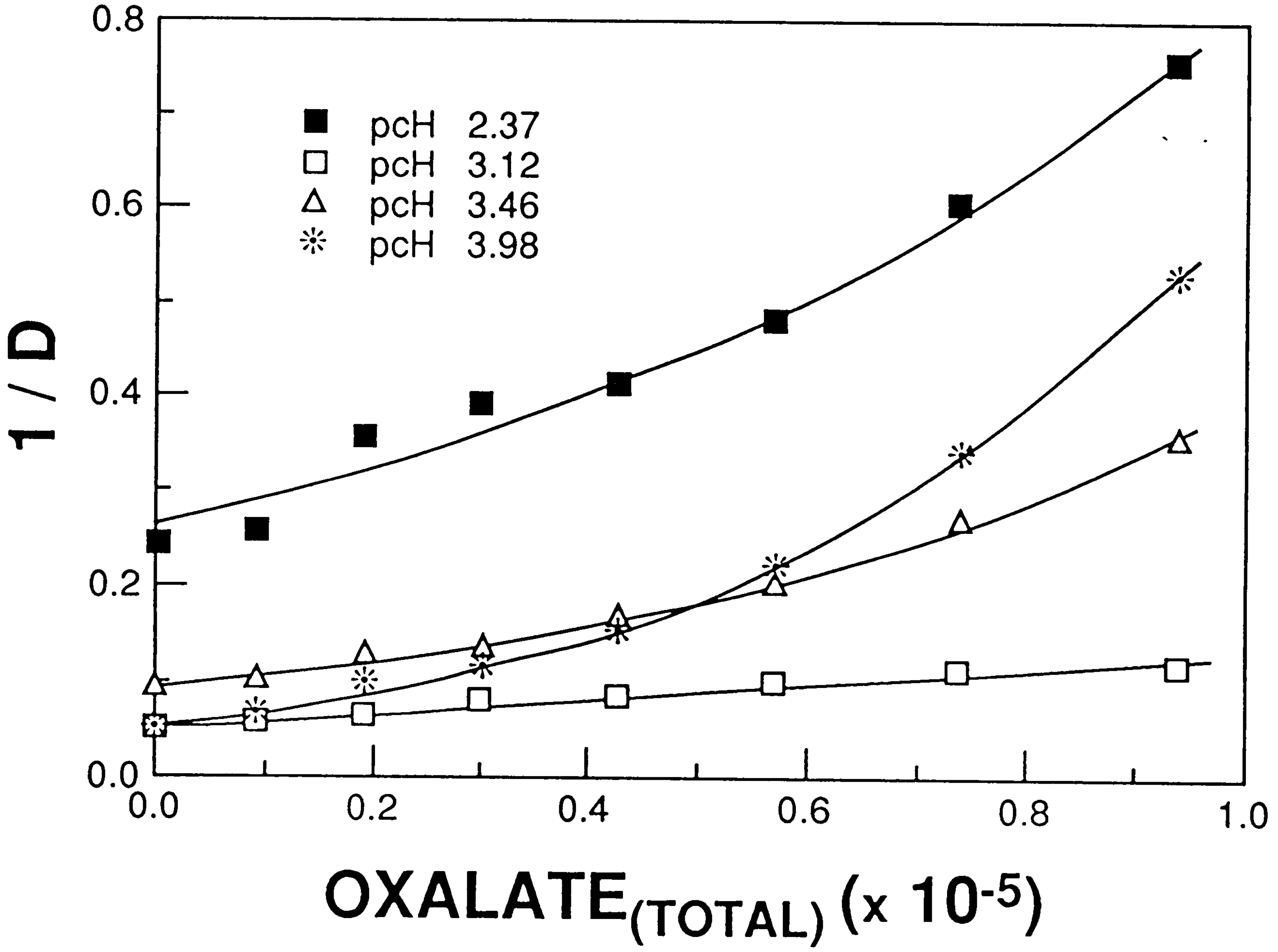
Ionic Strength (M)	Log $^{H}\beta_1$	Log $^{H}\beta_2$	Log $^{OH}\beta_1$
1	-3.77±0.02	-7.63±0.15	10.03±0.02
3	-3.37±0.03	-7.60±0.30	10.83±0.19
5	-3.95±0.02	-	10.75±0.08
7	-4.02±0.07	-	11.18±0.07
9	-4.37±0.04	-	11.28±0.05

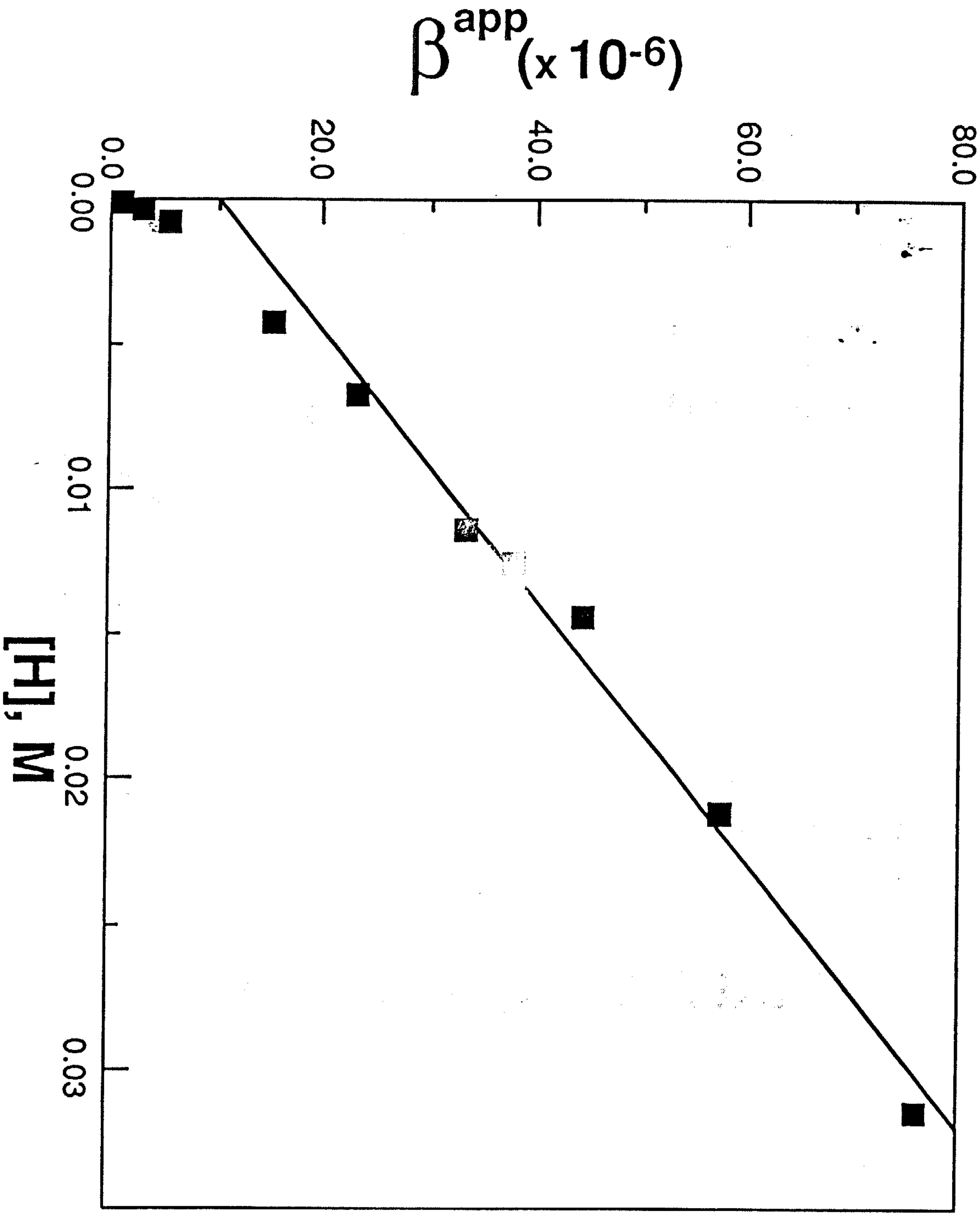
Captions

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

Figure 2. Variation of the apparent stability constant, B_1^{app}, for thorium + oxalate complexes as a function of hydrogen ion concentration at 1 M ionic strength.

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


0.8
0.6
0.4
0.2
0.0
1 / D
■ pcH 2.37
□ pcH 3.12
△ pcH 3.46
❊ pcH 3.98
0.0
0.2
0.4
0.6
0.8
1.0
OXALATE(TOTAL) (x 10-5)


β^{app}(x 10-6)
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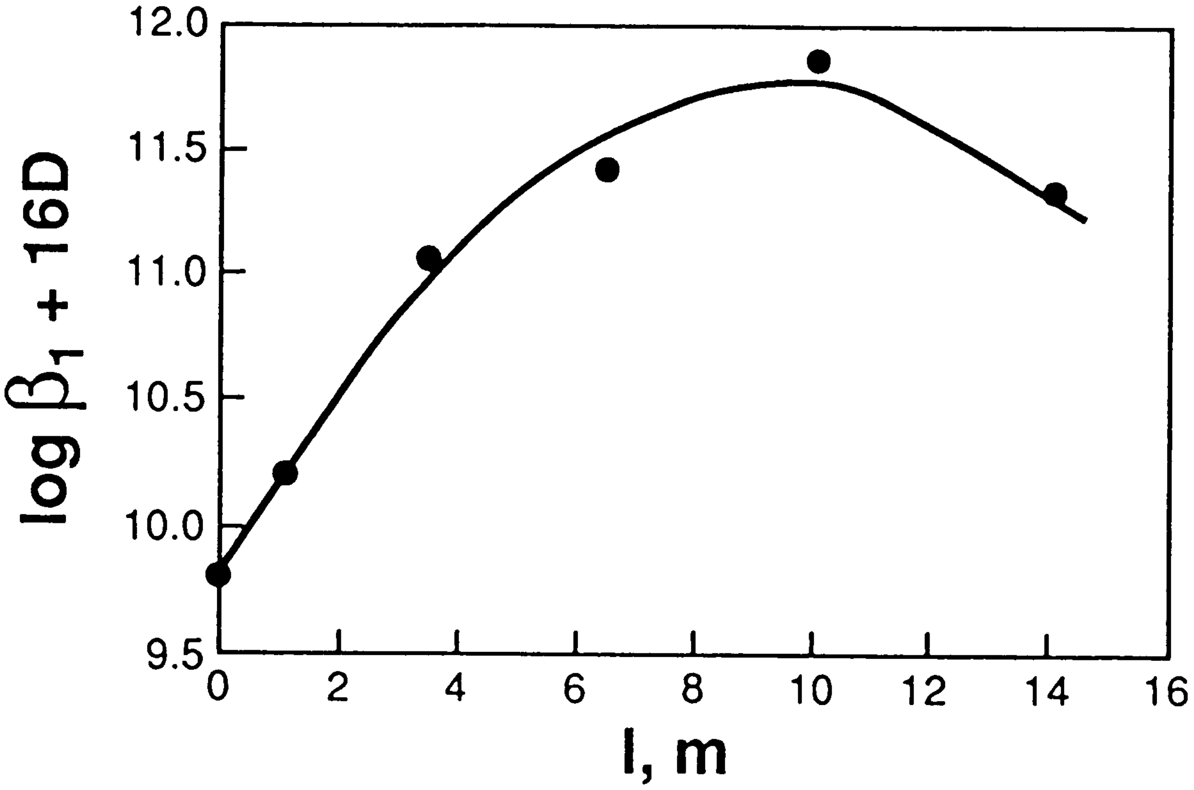
20.0
40.0
60.0
80.0
0.00
0.01
0.02
0.03
[H], M



12.0
11.5
11.0
10.5
10.0
9.5
0
2
4
6
8
10
12
14
16
$\log \beta_1 + 16D$
I, m