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VARIATION OF STABILITY CONSTANTS OF THORIUM CITRATE COMPLEXES  
AND OF THORIUM HYDROLYSIS CONSTANTS WITH IONIC STRENGTH

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ABSTRACT

Citrate is among the organic anions that are expected to be present in the wastes planned for deposition in the Waste Isolation Pilot Plant repository. In this study, a solvent extraction method has been used to measure the stability constants of Thorium(IV)[Th(IV)] with citrate anions in aqueous solutions with (a) NaClO<sub>4</sub> and (b) NaCl as the background electrolytes. The ionic strengths were varied up to 5 m (NaCl) and 14 m (NaClO<sub>4</sub>). The data from the NaClO<sub>4</sub> solutions at varying pH values were used to calculate the hydrolysis constants for formation of Th(OH)<sup>3+</sup> at the different ionic strengths.

**Keywords.** Thorium / Citrate / Complexation / Hydrolysis / Solvent extraction

INTRODUCTION

Underground salt beds are being considered by several countries as the site for disposal of nuclear wastes. In order to assess the probability of release of the long-lived actinide elements into the environment from these repositories, it is necessary to model the chemistry of actinides under conditions encountered in brine solutions. For non-vitrified wastes, the interactions of the actinides with organic compounds present from the processing systems may be significant factors in any migration process. In particular, this study is directed to providing stability constant values for Thorium(IV)[Th(IV)] with the residual citrate anion that may be in the nuclear wastes planned for the deposition in the Waste Isolation Pilot Plant repository. Such constants can be used to obtain estimates of the possible effect on the net Th(IV) solubilities. The data were also provided an estimate of Th(IV) hydrolysis constants in the NaClO<sub>4</sub> solutions.

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The use of the titration method to determine such constants requires relatively high metal ion concentrations that may be prevented by hydrolytic precipitation at higher pH values. In this study, a solvent extraction method [1-5] with radiotracer Th(IV) was used to measure the stability constants with citrate in aqueous solutions with (a) NaClO<sub>4</sub> and (b) NaCl as the background electrolytes. The ionic strengths were varied up to 5 m (NaCl) and 14 m (NaClO<sub>4</sub>). Also, the extraction data in the NaClO<sub>4</sub> solutions at different pH values were used to calculate the hydrolysis constants for formation of Th(OH)<sup>3+</sup> at the different ionic strengths. The complexation equations are described by the equation:



with an overall stability constant  $\beta_{pqr}$  defined as

$$\beta_{pqr} = [M_pH_qL_r] / [M]^p[H]^q[L]^r \quad (2)$$

This symbolism is suitable if protonated and hydrolysed species are involved as in our system. For hydrolysis, a negative q value is used to refer to the hydroxo species. In the pCH (-log [H]) range of 1.5–4.0, the citric acid may form both protonated (ThHCit<sup>+2</sup> and ThH<sub>2</sub>Cit<sup>+3</sup>) and unprotonated (ThCit<sup>+</sup>) complexes.

The equations of the concentrations of the citrate anions are as follows:

$$[Cit^{-3}] = [Cit]_T / (1 + K_1[H] + K_1K_2[H]^2 + K_1K_2K_3[H]^3) \quad (3a)$$

$$[HCit^{-2}] = [Cit]_T / (1 + K_2[H] + K_2K_3[H]^2 + 1/K_1[H]) \quad (3b)$$

$$[H_2Cit^{-1}] = [Cit]_T / (1 + K_3[H] + 1/K_2[H] + 1/K_1K_2[H]^2) \quad (3c)$$

where: [Cit]<sub>T</sub> is the total citrate molarity; K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> are the first, second and third protonation constants of citric acid, respectively and [H] is the hydrogen ion molarity.

In the solvent extraction systems, the distribution constant (D) is defined as

$$D \equiv \Sigma [M]_o / \Sigma [M]_{aq} \quad (4)$$

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Assuming that there is only a single organic(o) phase species,  $MA_n$ , and the presence of various species in the aqueous(aq) phase, eq.4 can thus be expressed by

$$D = [MA_n]_o / ([M]_{aq} + [ML]_{aq} + [MHL]_{aq} + [ML_2]_{aq} + [M(HL)_2]_{aq} + \dots) \quad (5)$$

where L is a complexing anion in the aqueous phase. This equation can be rewritten to include the stability constant of the aqueous complexes [6]:

$$D = [MA_n]_o / [M]_a (1 + \beta_{101} + \beta_{111}[H] + \beta_{121}[H]^2)[L] + (\beta_{102} + \beta_{122}[H]^2 + \beta_{142}[H]^4)[L]^2 \quad (6)$$

For the analysis of the extraction data, apparent stability constants are defined as

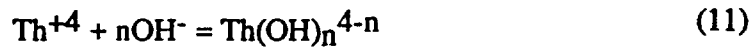
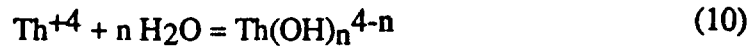
$$\beta_1 \equiv \beta_{101} + \beta_{111}[H] + \beta_{121}[H]^2 \quad (7)$$

$$\beta_2 \equiv \beta_{102} + \beta_{122}[H]^2 + \beta_{142}[H]^4 \quad (8)$$

Using  $D_o$  for the distribution constant in the absence of complexation allows revision of eq.6 in terms of the apparent stability constants:

$$D_o/D = 1 + \beta_1[L] + \beta_2[L]^2 \quad (9)$$

The hydrolysis constants,  $H\beta_n$  and  $OH\beta_n$ , of the Th(IV) ion refer, respectively, to the reactions:



The two hydrolysis constants are related by

$$\log H\beta_n = \log OH\beta_n + n \log K_w \quad (12)$$

where  $K_w$  is the ionization product of water.

The hydrolysis constant for formation of  $Th(OH)^{3+}$  can be calculated from the equation:

$$\beta_{101} (cal) = \beta_{101} (exp) / (1 + OH\beta_1 / [H^+]) \quad (13)$$

where  $\beta_{101}$  (cal) and  $\beta_{101}$  (exp) are the calculated and experimental apparent stability constants, respectively.

## EXPERIMENT

### Reagents and Solutions

Stock solutions of  $1.0 \times 10^{-3}$  M and  $1.6 \times 10^{-4}$  sodium citrate (Aldrich) were prepared. TTA and DBM were purified by sublimation. Stock solutions of 0.01 M TTA and 0.1 M DBM in toluene (Fischer Chemicals) were prepared and stored in the dark. Sodium perchlorate (anhydrous, Mallinckrodt) and sodium chloride (Fisher Chemicals) were used without further purification. All reagents were analytical grade.

$^{230}\text{Th}$  tracer (obtained from Oak Ridge National Laboratory) was prepared in a solution of pH 2 ( $\text{HClO}_4$ ) such that 10  $\mu\text{l}$  of the solution gives approximately 16000 cpm. The  $^{230}\text{Th}$  tracer was checked for radioactive purity by alpha and gamma spectrometry.

To minimize sorption of Th(IV) at pH's where hydrolysis occurs, all solutions used in the experiments were filtered with a 0.2  $\mu\text{m}$  microfiltration system.

### Apparatus and Equipments

A Packard Instrument Tri-Carb 4000 (Hewlett Packard Instruments) Liquid Scintillation Counter was used to count the radioactivity in Ecolume cocktail (ICN Biomedicals Co.). A GeLi Gamma Spectrometer (Canberra) was used to check the radioactive purity.

An Accumet 950 (Fisher Scientific) pH meter was used with a combination of glass electrodes (Corning Semi-Micro Combination). The KCl solution in the salt bridge of the electrode was replaced with a saturated NaCl solution, as the low solubility of  $\text{KClO}_4$  in high ionic strengths of perchlorate solution causes erratic reading. The electrode was calibrated with  $4.00 \pm 0.01$  and  $7.00 \pm 0.01$  pH buffer standard solutions (Fisher Scientific). The pH readings were converted to hydrogen concentration (pCH) using eq. 14 which is described in detail in the Results and Discussion section..

A laminar flow hood (Environmental Air Control Inc.) was used to reduce problems of sorption in solution from suspended particles.

A 655 Dosimat (Metrohm) buret was used to conduct the potentiometric titration in a 30 ml jacketed cell controlled to  $25.0 \pm 0.1^\circ\text{C}$  by water flow from an Isotemp bath.

A water bath (Model 1200-00 Circulator, Cole-Parmer Instrument Company) controlled to  $25.0 \pm 0.1^\circ\text{C}$  was used for the extraction experiments.

## Experimental Procedure

### *Determination of the dissociation constants of citric acid*

The dissociation constants of citric acid, pK values, were determined at different ionic strengths of NaClO<sub>4</sub> and NaCl solutions by potentiometric titration. The titrations were carried out using 10.0 ml solutions in a 30 ml jacketed cell through which water at 25.0 ± 0.1°C was passed. Nitrogen gas was bubbled through the cell solution to remove the dissolved carbon dioxide. A standard solution of 0.03 M NaOH (in NaClO<sub>4</sub> or NaCl of appropriate ionic strength) was titrated against initial volume, V<sub>0</sub>, of NaClO<sub>4</sub> or NaCl of the same ionic strength. In order to maintain a small pH change after each addition of titrant, variable amounts of titrant were used in the additions. A differential graphical technique [7] to analyze the titration data used a plot of  $(dn/d\ln[H^+]) \times C_L$  versus pCH, which allows evaluation of the pK<sub>w</sub> and the acid constants, where n is the ratio of the concentration of proton bounded to ligand and total concentration of ligand, C<sub>L</sub>, is the total concentration of ligand.

### *Extraction Procedure*

For each extraction experiment, 5.00 ml of aqueous solution adjusted to the appropriate pH were placed in vials, which had been silanized as described elsewhere [3]. Aliquots of citric acid stock solution were added to each vial followed by 5.00 ml of TTA or DBM in toluene. The concentration of the organic extractant was adjusted according to the ionic strength and pH of the solution so that D fell between 0.1 and 10. After addition of 10 µl of <sup>230</sup>Th tracer, the vials were shaken for 2-3 hours at room temperature (25±0.1°C). Kinetic studies confirmed that the extraction equilibrium was attained in about 10 minutes. The vials were centrifuged and duplicate aliquots were taken from both phases for scintillation counting and pH measurement.

## RESULTS AND DISCUSSION

### Dissociation Constants of Citric Acid

The dissociation constants of citric acid in different ionic strengths of NaClO<sub>4</sub> and NaCl (in molality, m) solutions are given in Table 1. The pK values at low ionic strengths are reported in the literature [8]. Our values are in agreement with these data. The pH can be converted to pCH using the following calibration equation:

$$p\text{cH} = m \text{pH} + b \quad (14)$$

where  $m$  and  $b$  are constants for a certain ionic strength electrolyte.

The glass electrode calibration coefficient,  $b$  and  $K_w$ , in both electrolytes at different ionic strengths can be simultaneously measured with the dissociation constants from the  $(dn/d\ln[H^+]) \times C_L$  plots (Figure 1). The results are listed in Table 1. The values of citric acid were used in the calculation of free citrate anion.

The  $K_w$  values in different ionic strengths were used to calculate the hydrolysis constants of thorium ion at various ionic strengths of  $\text{NaClO}_4$ .

### Thorium Citrate Complexation

A series of experiments with  $p\text{cH}$  ranging from 1.8 to 4.0 were conducted at ionic strengths of 1.0, 3.5, 6.5, 10.0, and 14.1 m  $\text{NaClO}_4$ ; while for  $\text{NaCl}$  solutions, the  $p\text{cH}$  was kept at 3.0 for the experiments as the ionic strengths varied. The free concentration of citric anion in each extraction vial was calculated from the measured  $p\text{cH}$ , the total concentration of citrate, and the  $p\text{K}_{a1}$ ,  $p\text{K}_{a2}$ , and  $p\text{K}_{a3}$  of citric acid.

Typical curves showing functions of  $D$  vs. citrate anion concentration are shown in Figures 2 and 3. A linear curve for  $1/D$  indicates 1:1 complexes that provide  $\beta_1$  from the slope. If  $(D_0/D-1)/[L]$  is plotted as the ordinate, a linear regression over the appropriate concentration range of  $[\text{Cit}]_f$  gives the second apparent stability constant  $\beta_2$  (eq. 9). From analysis of such curves, the apparent stability constants,  $\beta_1$  and  $\beta_2$ , were obtained in the different ionic strengths of  $\text{NaCl}$  and  $\text{NaClO}_4$  solutions; Table 2 lists these values from at least two extraction experiments. The relationship between the apparent stability constants and the stability constants,  $\beta_{101}$ ,  $\beta_{111}$ ,  $\beta_{102}$ ,  $\beta_{121}$ , are given by eqs. 7 and 8. Using the first two terms of eqs. 7 and 8, respectively, and Quattro Pro for windows program (least square regression and optimizer), the stability constants of various mononuclear thorium-citrate complexes in  $\text{NaClO}_4$  solutions were determined. The values of the constants are given Table 3. The results indicate that the complexation of  $\text{Th(IV)}$  ion with citrate can increase the concentration of  $\text{Th(IV)}$  in the different ionic strengths of  $\text{NaCl}$  and  $\text{NaClO}_4$  solutions, even at quite low concentrations ( $2 \times 10^{-7} \text{M}$ ).

The variation of apparent stability constants of  $\text{Th(IV)}$ -citrate complexes with  $p\text{cH}$  is shown in Figure 4. The effect of hydrolysis on the data above about  $p\text{cH}$  can be seen. The first hydrolysis constants of thorium (IV) cation in various  $\text{NaClO}_4$  media are summarized in Table 4 with the available literature data. The hydrolysis constants obtained in this study using citrate anion



as competing ions agree with those reported in the literature for ionic strength 1 - 3 M [9-14], however, no literature values are reported above 3 M ionic strength.

The bonding of thorium ion to inorganic and organic ligands in complexes can be described well 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 extensive hydrolysis of Th(IV) in even relatively acidic solutions ( $\text{pH} \leq 3$ ) limits complexation studies because most organic ligands with bonding carboxylate groups require pH values of 3 or higher to have ionization of the ligand. This study shows that organic acids can form complexes that are sufficiently strong that they can compete with hydrolysis and increase the net concentration of Th(IV) in neutral solutions. The data is being analyzed further by the Pitzer formalism [15] for a later report.

### ACKNOWLEDGEMENTS

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## Captions

**Figure 1.** Plot of  $(dn/d\ln[H]) \times C_L$  vs. pcH in 5.0 m NaCl solution at 25°C; point is experimental data; solid line is calculated data.

**Figure 2.** Plot of  $1/D$  vs.  $[\text{Citrate}]_f$  in 1.0 m NaCl solution at pcH 3.0; point is experimental data; solid line is calculated data.

**Figure 3.** Plot of  $(D_0/D-1)/[\text{Citrate}]_f$  vs.  $[\text{Citrate}]_f$  in 1.0 m NaCl solution at pcH 3.0; point is experimental data; solid line is calculated data.

**Figure 4.** The first apparent stability constants vs. pcH at 25° C.

**Table 1. Dissociation Constants of Citric Acid in NaCl and NaClO<sub>4</sub> Solutions at Temperature = 25° C.**

Ionic strength ( m )	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>	b <sup>(a)</sup>	pK <sub>w</sub>
	( in sodium perchlorate solutions )				
0.1	2.99±0.01	4.42±0.01	5.70±0.01	0.03±0.01	13.80±0.02
0.3	2.72±0.01	4.19±0.01	5.41±0.01	0.11±0.01	13.75±0.02
0.5	2.92±0.02	4.26±0.01	5.33±0.02	0.14±0.01	13.77±0.01
1.0	2.95±0.01	4.24 ±0.01	5.25±0.01	0.27±0.01	13.82 ±0.02
3.5	2.96±0.01	4.29±0.02	5.22±0.04	0.70±0.01	14.18±0.01
6.5	3.27±0.01	4.63±0.01	5.56±0.01	1.12±0.01	14.70±0.03
10.0	3.51±0.01	4.93±0.01	5.85±0.01	1.52±0.01	15.46±0.01
14.1	3.73±0.02	5.25±0.01	6.31±0.01	2.05±0.01	16.29±0.01
----- ( in sodium chloride solutions )					
0.1	2.93±0.01	4.36±0.01	5.63±0.01	0.04±0.01	13.81±0.01
0.3	2.88±0.02	4.25±0.01	5.38±0.01	0.13±0.01	13.70±0.04
0.5	2.90±0.02	4.23±0.01	5.27±0.01	0.17±0.01	13.72±0.01
1.0	2.88±0.05	4.18±0.01	5.20±0.02	0.35±0.01	13.73±0.02
2.0	2.87±0.01	4.19±0.01	5.12±0.01	0.51±0.01	13.81±0.01
3.0	2.98±0.03	4.28±0.01	5.17±0.01	0.70±0.01	13.96±0.02
5.0	3.13±0.02	4.49±0.01	5.35±0.01	1.09±0.01	14.33±0.01

(a) Values from eq. 14.

**Table 2. Apparent stability constants of Th(IV)-Citrate Complexes at 25°C.**

pH	A. Ionic Strength of NaClO <sub>4</sub> ( m )				
	<u>1.0</u>	<u>3.5</u>	<u>6.5</u>	<u>10.0</u>	<u>14.1</u>
	<b>log β<sub>1</sub></b>				
1.84	10.93±.07	10.02±.07	10.69±.02	11.65±.02	12.68±.04
2.37	9.90±.03	9.23±.04	9.80±.03	10.62±.04	11.24±.03
3.12	9.41±.07	8.97±.09	9.46±.10	10.23±.07	10.99±.05
3.46	9.54±.07	9.13±.06	9.57±.02	9.73±.05	10.57±.07
3.98	8.74±.11	8.65±.07	8.98±.06	8.84±.08	10.43±.09
	<b>log β<sub>2</sub></b>				
1.84	21.27±.19	21.16±.09	22.09±.05	23.04±.01	25.16±.08
2.37	19.30±.12	19.14±.25	19.87±.11	20.91±.09	22.92±.03
3.12	19.06±.03	18.31±.13	18.50±.15	20.24±.02	22.15±.02
3.46	18.27±.04	17.69±.06	19.08±.02	19.85±.03	21.21±.12
3.98	16.94±.03	16.63±.03	17.78±.08	17.53±.05	19.16±.04

**Table 2 (Cont'd). Apparent Stability Constants of Th(IV) - Citrate Complexes at 25°C.**

pH	B. Ionic Strength of NaCl ( m )					
	<u>0.1</u>	<u>0.3</u>	<u>1.0</u>	<u>2.0</u>	<u>3.0</u>	<u>5.0</u>
	$\log \beta_1$					
3.00	10.08±0.07	9.67±0.03	9.56±0.03	9.31±0.04	9.55±0.02	10.18±0.03
	$\log \beta_2$					
3.00	19.05±0.02	18.72±0.04	18.28±0.03	17.41±0.06	17.33±0.04	19.12±0.04

**Table 3. Stability Constants of Th(IV) - Citrate Complexes  
in NaClO<sub>4</sub> Solutions at Temperature = 25°C.**

<b>I,m</b>	<b>log b<sub>101</sub></b>	<b>log b<sub>111</sub></b>	<b>log b<sub>102</sub></b>	<b>log b<sub>122</sub></b>
1.0	9.19±0.13	12.18±0.05	18.62±0.25	23.94±0.03
3.5	8.91±0.09	11.32±0.06	17.83±0.21	23.86±0.15
6.5	9.32±0.11	12.00±0.08	18.64±0.29	24.58±0.04
10.0	9.57±0.05	12.96±0.09	19.85±0.20	25.61±0.02
14.1	10.59±0.08	13.51±0.11	21.61±0.31	27.64±0.05

**Table 4. First hydrolysis constants of Th(IV) cation  
in various NaClO<sub>4</sub> media at 25°C.**

Ionic Strength, m	log H <sub>β1</sub>	Reference
0	-3.20	8
0.01-0.04	-3.61	10
0.05	-3.92	10
0.10	-4.00	10
0.30	-4.12	10
0.51	-4.26	10
1.04	-4.15±0.04	11
1.04	-4.16±0.05	12
3.51	-4.13±0.06	14
1.04	-3.75±0.02	p. w.
3.51	-3.56±0.03	p. w.
6.50	-3.99±0.02	p. w.
10.02	-3.87±0.07	p. w.
14.06	-4.09±0.08	p. w.

p.w.: present work.



