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ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · JULY 2009

Impact Factor: 2.04 · DOI: 10.1021/je9002288

Complex Formation of Thorium(IV) Ion with Glycyl−Glycine and Glycyl−Valine

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The protonation equilibria of glycyl−glycine and glycyl−valine and their complex formation with thorium(IV) ions in aqueous solution were studied over a wide range of pH values (2 to 12) using a combination of potentiometric, cyclic voltametric, and spectrophotometric methods at constant temperature (25 °C) and constant ionic strength (0.1 mol·dm^{-3} sodium perchlorate). The redox properties of the species obtained by the cyclic voltametry technique have confirmed the spectrophotometric results. Least-squares regression calculations are consistent with the formation of the ThL^{3+}, $ThHL_2^{3+}$, and ThL_2^{2+} species for the studied systems, where L represents each peptide. Finally, the species concentrations were plotted at different pH values and discussed.

Introduction

The interaction between amino acids, peptides, and proteins with metal ions plays an important role in biochemistry and biology and has been studied extensively during the last three decades. Complexes of amino acids and oligopeptides are involved in the exchange and transport mechanism of some trace metal ions in the human body.[1−4] Oligopeptides have proved to be the most useful model compounds for such studies since they are able to mimic to a great extent the metal ion binding site of much more complicated protein molecules.[5,6]

Thorium is the most abundant radioactive element in nature [(0.001 to 0.002) % weight of the earth's crust] and is distributed widely at up to 15 ppm in soils.[7,8] The half-life of ^{232}Th is about three times longer than the age of the earth ($1.4 \cdot 10^{10}$ years), but ^{228}Th has a half-life of 1.9 years. ^{230}Th with a half-life of $7.5 \cdot 10^4$ years is the parent of ^{226}Ra and ^{232}Ra.[4] Thorium is used in industry for many purposes including ceramics, gas mantles, nuclear fuel, flame spraying, crucibles, medicine, nonsilica optical glass, catalyst, etc.[9,10] This element and its derivatives have been known as a toxic element for many years.[8] Thorium occurs predominantly as a tetravalent cation, and it is a trace constituent in phosphates, simple and multiples oxides, and silicates. Thorium may be adsorbed in particular and suspended material within water.[11,12] The level of adsorption ranges from (0.003 to 1.72) $\mu g \cdot L^{-1}$ for waterborne Th and (183 to 3445) $\mu g \cdot g^{-1}$ for Th in suspended solids.[13] Thorium can also be found in abundance in lakes that originated from the mining of other metals, which are sometimes converted for use in aquaculture up to 297 $\mu g \cdot L^{-1}$ of dissolved Th in lakes of tin mining.[14] Atmospheric emission and decomposition from industrial sources has resulted in raised levels of this metal in agricultural products. Previous experimental results demonstrated that distribution of thorium in soil and water is highly variable depending on various factors, and an assessment of its distribution in soil−plant systems may be rather complicated.[15] However, small amounts of thorium are ingested and to a lesser extent inhaled by people every day.[8] The United Nations Scientific Committee on the Effects of Atomic Radiations (UNSCEAR) has reported the intake values for natural thorium from drinking water and other foodstuffs in human beings as: ($8.25 \cdot 10^{-3}$, $8.32 \cdot 10^{-3}$, and $4.55 \cdot 10^{-3}$) Bq·d^{-1} for the different isotopes of thorium ^{228}Th, ^{230}Th, and ^{232}Th, respectively.[15] The thorium(IV) ion readily reacts with in vivo amino acids, peptides, nucleic acids, proteins, etc. to form stable complexes which are distributed in the body, primarily in the liver, bone, and kidneys.[16] Thus, the investigation of the pathway of thorium from agricultural products → animals → humans is particularly important as far as the radiological protection of the general population is concerned.

In view of the above, the present work reports a study of thorium(IV) complexes by glycyl−glycine and glycyl−valine as well as the protonation equilibria of the peptides at 25 °C and constant ionic strength (0.1 mol·dm^{-3} $NaClO_4$).

Experimental Section

Chemicals. All the chemicals used were of analytical reagent grade. Glycyl−glycine ($C_4H_8N_2O_3$), gly gly, and glycyl−L-valine ($C_7H_{14}N_2O_3$), gly val, were obtained from Merck and Sigma, respectively. The aqueous stock solutions of the peptides were freshly prepared daily. The NaOH solution was prepared from a titrisol solution (Merck), and its concentration was determined by several titrations with standard HCl. Perchloric acid and thorium nitrate were from Fluka and were used without further purification. Sodium perchlorate was purchased from Merck and was kept in a vacuum at least 72 h before use. All dilute solutions were prepared from double-distilled water with specific conductance equal to (1.3 ± 0.1) $\mu\Omega^{-1} \cdot cm^{-1}$.

Apparatus. A Metrohm pH-meter, 665, was used for pH measurements. A combination Ag/AgCl pH electrode, 6.0228.010 Metrohm, was used for determination of protonation constants of the peptides. All titrations were carried out by a Metrohm automatic titrator unit equipped with a Dosimat automatic buret with five dispenser units, a syringe-buret, and a pH electrode.

Spectrophotometric titrations were performed on a UV−vis Cecil 5000 spectrophotometer with a Pentium 4 computer and using thermostatted matched 10 mm quartz cells. The measurement cell was of a flow type. A Masterflex pump allowed

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10.1021/je9002288 CCC: $40.75
Published on Web 07/31/2009

circulation of the solution under study from the potentiometer cell to the spectrophotometer cell, so the absorbance and the pH of the solution could be measured simultaneously.

In cyclic voltammetry, CV, a cyclic voltammeter, EG & G model 263A, connected to a computer for automated data acquisition was used for current versus potential measurements. Cyclic voltammetry measurements were made using a conventional three-electrode cell: a Ag/AgCl reference electrode, model MF-2052 filled with 3.0 mol·dm^{-3} KCl/saturated AgCl solution, as a reference electrode, a platinum wire as an auxiliary electrode, and a glassy carbon electrode (28 mm^2 surface area) as the working electrode. The working electrode was polished using 0.5 μm of alumina for 2 min and rinsed with distilled water prior to each measurement.

Measurements. All measurements were carried out at (25 ± 0.1) °C. The ionic strength was maintained to 0.1 mol·dm^{-3} with sodium perchlorate. The pH meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol·dm^{-3} perchloric acid solution containing 0.09 mol·dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.1 mol·dm^{-3}). For this standard solution, we set $-\log[H^+] = 2.00$.[17] Junction potential corrections have been calculated from eq 1

$$-\log[H^+]_{real} = -\log[H^+]_{measured} + a + b[H^+]_{measured} \quad (1)$$

where a and b were determined by measuring hydrogen ion concentration for two different solutions of $HClO_4$ or NaOH with sufficient $NaClO_4$ to adjust the ionic strength in solutions. To exclude carbon dioxide and oxygen from the system, a stream of purified nitrogen was passed through a sodium hydroxide solution and then bubbled slowly through the reaction vessel.

Procedure. A 25 mL acidic solution of Th^{4+} [($5.0 \cdot 10^{-4}$ to $1.0 \cdot 10^{-3}$) mol·dm^{-3}] was titrated with an alkali solution (0.1 mol·dm^{-3} NaOH) of the peptides [($5.0 \cdot 10^{-4}$ to $1.0 \cdot 10^{-3}$) mol·dm^{-3}], both of the same ionic strength. The $-\log[H^+]$ and absorbance were measured after addition of a few drops of titrant, and the procedure was extended up to the required $-\log[H^+]$. In all cases, the procedure was repeated at least three times, and the resulting average values and corresponding deviations from the average are shown in the text and tables.

In cyclic voltammetry, a 0.01 mol·dm^{-3} Th^{4+} solution was prepared in acetonitrile−water 60:40 by volume, and its voltammogram was determined. Then, the complexation of Th^{4+} by glycyl−valine and glycyl−glycine has been studied in different concentrations of the ligands [($1.0 \cdot 10^{-5}$, $1.25 \cdot 10^{-5}$, $2.5 \cdot 10^{-4}$, $5.0 \cdot 10^{-4}$, and $1.0 \cdot 10^{-3}$) mol·dm^{-3}] in the same mixture of solvents accompanied by a gentle stirring and an argon purge for 10 min prior to each measurement. In pure water, a well-satisfied voltammogram was not possible to obtain for the Th^{4+} ion ($E_{1/2} = -1.566$ V) because water molecules can create a potential barrier for the Th^{4+} ion voltammograms through a reduction value of about −0.8 V. All measurements were made at scan rates (20, 30, 40, 50, 60, 70, 80, 90, 100, and 150) mV·s^{-1}. $E_{1/2}$ values reported here are defined as the numerical average of the cathodic and anodic peak potentials. All electrochemical potentials measurements are expressed relative to the Ag/AgCl electrode.

Results and Discussion

The species $M_pH_qL_r^{(4p+q-r)}$ formed is characterized by its stoichiometry (p:q:r), where M represents the metal ion. To determine the stability constant of complexation or protonation, eq 2 is defined by β_{pqr}[18]

$$pM^{+4} + qH^+ + rL^- \rightleftarrows M_pH_qL_r^{(4p+q-r)} \quad (2)$$

$$\beta_{pqr} = [M_pH_qL_r^{(4p+q-r)}]/([M^{+4}]^p[H^+]^q[L^-]^r) \quad (3)$$

The protonation constants of the peptides have been used for computation of the stability constant, β_{pqr}, of the metal−ligand. The protonation constants of the ligands have been studied in different kinds of background electrolytes, and the results are reported in the literature.[19−21] In this work, the protonation constants of the peptides were determined using a potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method (Microsoft Excel Solver).[22] These values are listed in Table 1 together with the values reported in the literature, which are in good agreement with those reported earlier.[19−21]

Table 1. Average Values of the Protonation Constants of the Ligands at 25 °C and Constant Ionic Strength (0.1 mol·dm^{-3} $NaClO_4$)[a]

species	log β_{011}	log β_{021}	ref.
gly gly	3.07 ± 0.05	8.16 ± 0.09	this work
gly−L-val	3.15 ± 0.07	8.70 ± 0.09	this work
gly gly	3.10	8.15	19
gly gly	3.13	8.08	20
gly−L-val	3.15	8.11	21

[a] The values reported in the literature are also reported for comparison.

Determination of the formation constant was employed using the method mentioned before.[23] Absorbance, A, and $-\log[H^+]$ were measured by successive addition of an alkali solution of the ligand to the acidic metal ion solution in the UV range (250 to 290) nm; see Experimental Section. Treatment of the spectrophotometric data (every 0.5 nm) obtained during the titrations, as a function of H^+ concentration, was conducted with the computer program Equispec (by using the matrix based in the Matlab environment).[24] The stoichiometric formation constants were computed from the data using the computer program. The number of experimental points (absorbance vs pH) was more than 30 (maximum 50) for each titration. It is most convenient to arrange a series of the measured absorption spectra at different wavelengths and various pH values as the rows of a matrix **Y**. According to Beer−Lambert's law, **Y** can be decomposed into the product of a concentration matrix **C** and a matrix **A** of molar absorptivities. The concentration profiles of the absorbing species form the columns of **C** and the molar absorption spectra form the corresponding rows of **A**. Due to the instrumental and experimental errors, this decomposition is not perfect, the difference being the matrix **E** of residuals. A matrix equation can be written as

$$\mathbf{Y} = \mathbf{CA} + \mathbf{E} \quad (4)$$

Data fitting consists of determining those unknown parameters for which the sum of the squares over all the elements of the matrix **E** of residuals is minimal. Initially, the unknown parameters including the equilibrium constants, a vector **p** of nonlinear parameters, overall formation constants, and all the molar absorptivities of all the components, i.e., the complete matrix **A** of linear parameters, were determined. **C** is defined by the model and the appropriate equilibrium constants and is calculated numerically using the law of mass action and the analytical (total) concentration of each component in solution.[25,26] If the spectra are measured at many wavelengths, the total number of parameters could be very high, and it is crucial to

reduce this number by separation of the linear and nonlinear parameters. For any set of nonlinear parameters, **p**, which defines the concentration matrix **C**, the best set of linear parameters, the matrix **A**, is an explicit least-squares calculation

$$\mathbf{A} = \mathbf{C}^{+}\mathbf{Y} \tag{5}$$

$\mathbf{C}^{+}$ is the pseudoinverse which can be calculated as $\mathbf{C}^{+} = (\mathbf{C}^{t}\mathbf{C})^{-1}\mathbf{C}^{t}$ or preferably using a numerically more stable algorithm (i.e., an algorithm which guarantees to reach physically meaningful final results).[27] **A** is now defined as a function of **p** and consequently **E**, and sums of the squares (ssq) are defined as a function of the nonlinear parameters only

$$\text{ssq} = \sum\sum \mathbf{E}(i,j)^2 = f(\mathbf{Y},\ \text{model},\ \text{parameters}) = f(\mathbf{p}) \tag{6}$$

In the equilibrium condition, the model is a collection of equilibria between the component species, and the parameters are the equilibrium constants. The computation of the pseudoinverse $\mathbf{C}^{+}$ seems to be a trivial task. In equilibrium studies, generally the concentration matrix **C** has, at least theoretically, full rank; i.e., the chemical and mathematical ranks are equal, and the concentration profiles for all species are linearly independent. $\mathbf{C}^{+}$ can be computed, and **A** is determined by eq 5. This is, however, not always the case, and near linear dependency (i.e., when the distribution diagram of some species can be expressed as a linear combination of some other species) and/or species with only very low concentrations result in deficiencies in the equilibrium model. In this status, **C**, then, does not have full rank, and the pseudoinverse, $\mathbf{C}^{+}$, is not or is only poorly defined, which can render its computation difficult to impossible and thus corrupt the resulting **A** as well as the residuals, **E**, and the sum of squares. There are powerful algorithms such as the Newton−Gauss−Levenberg/Marquardt algorithm available for this task.[28]

Considering eq 2, different models including ML, MHL_2, ML_2, and several polynuclear and protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were MHL_3, ML_3, and MH_2L_3 (the charges are omitted for simplicity). A value for MHL species was also calculated by the program, but the species was not considered further because the estimated error in its formation constant was unacceptable, and its inclusion does not improve the goodness of the fit. The models finally chosen, formed by ML, MHL_2, and ML_2 for the studied system, resulted in a satisfactory fitting. The calculated average values of the stability constants for different experiments are listed in Table 2.

In a similar investigation, the stability constant values of Th(IV) and some trivalent lanthanide ions with glycolic acid were determined by the potentiometric titration method. In this paper, the authors proposed the formation of some mono- and binuclear complex species with $\log \beta_{101} = 4.27$, $\log \beta_{102} = 7.66$, $\log \beta_{103} = 10.4$, $\log \beta_{104} = 12.2$, $\log \beta_{222} = 4.48$, $\log \beta_{224} = 11.0$, and $\log \beta_{226} = 15.7$.[29] However, the binuclear species are ruled out in the present work due to the low concentration of the metal ion used. Nourmand and Meissami[30] studied the complexation of thorium(IV) with different enantiomers (D, L, and DL) of a bidentate amino acid, methionine. By the potentiometric titration method, they proposed the formation of two mononuclear complex species of ML and ML_2 with $\log \beta_{101} = 6.88$ and $\log \beta_{102} = 13.58$ (for L species) and a little bit lower for the other enantiomers. In another work, Tewari has found only one complex species in the Th(IV)−methylcysteine system ($\log \beta_{101} = 8.37$) by a paper electrophoretic method at 35 °C.[31] Finally, most of the stability constant values reported in the literature are collected in Table 2 for comparison.[29−37] The reported values are comparable with those obtained in this work. However, the differences are mostly due to the different techniques, various ionic strengths with different background electrolytes, and different temperatures that were used.

Table 2. Average Values of the Formation Constants of Th−gly gly and Th−gly val at 25 °C and Constant Ionic Strength (0.1 mol·dm^{-3} $NaClO_4$) by the Spectrophotometric Method[a]

species	$\log \beta_{101}$	$\log \beta_{112}$	$\log \beta_{102}$	ref.
gly gly	5.46 ± 0.14	18.45 ± 0.20	10.49 ± 0.15	this work
gly-L-val	8.76 ± 0.15	23.85 ± 0.10	14.72 ± 0.17	this work
glycolic acid	4.27	−	7.66	29
L-methionine	6.88	−	13.58	30
methylcysteine	8.37	−	−	31
malonate	7.47	−	12.84	32
D-cysteine	7.51	−	14.80	33
L-leucine	8.25	−	14.14	33
D-serine	8.25	−	16.75	33
D-threonine	7.21	−	14.01	33
DL-alanine	7.18	−	14.51	33
DL-phenylalanine	7.84	−	14.51	33
DL-valine	8.30	−	14.23	33
L-isoleucine	8.26	−	14.22	33
L-lysine	8.52	−	−	34
L-aspartic acid	4.21	−	−	35
glutathione	4.27	−	−	36
glycine	2.55	−	−	37

[a] Some examples of formation constants of thorium are also reported from the literature for comparison.

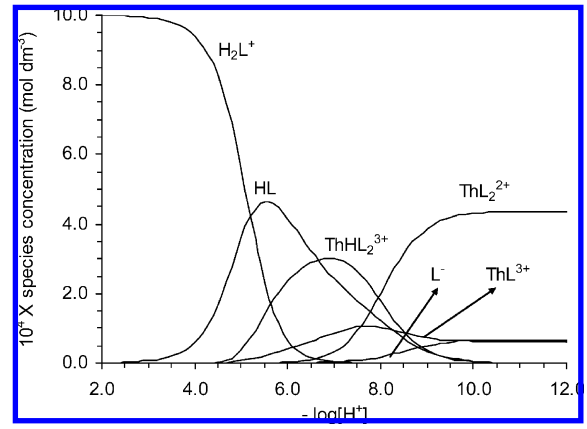

Figure 1. Distribution curves for the system Th−gly gly at 25 °C and constant ionic strength, 0.1 mol·dm^{-3} $NaClO_4$.

In Figures 1 and 2, the equilibrium distributions of various species of Th(IV)−gly gly and Th(IV)−gly val systems are shown as a function of $-\log[H^+]$, respectively. The calculations are based on the stability constant values given in Tables 1 and 2. The curves clearly demonstrate that an increase of the pH is accompanied by an increase in the formation of deprotonated complex species. The most stable complex species at different pH values are: $ThHL_2^{3+}$ at pH ≅ 7 in both cases, ThL_2^{2+} has the highest value around pH ≅ 10 in both cases, but ThL^{3+} occurs at about pH 7.5 in the case of gly gly and at a little higher pH value for gly val.

Cyclic voltammetry can be used to determine the relative stability of Th^{4+} complexes which has been less accessible by other techniques. Shifts in the anodic and cathodic peak potentials of $Th^{4+/0}$−L and the reversibility of the electrochemical processes were studied as a function of concentration of the ligands. The cyclic voltammograms of Th^{4+} obtained at different scan rates are quasireversible with a formal redox potential of

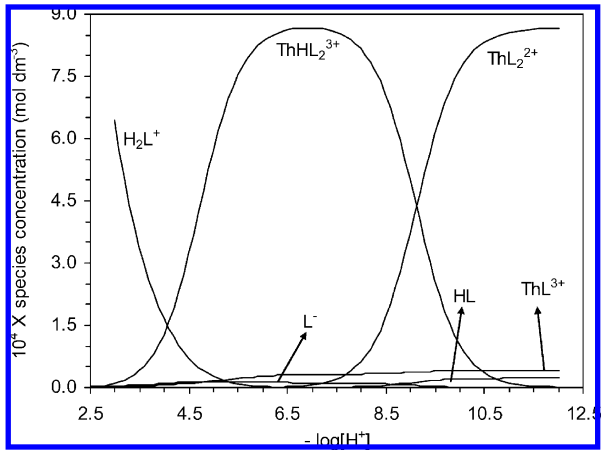

Figure 2. Distribution curves for the system Th−gly val at 25 °C and constant ionic strength, 0.1 mol·dm^{-3} $NaClO_4$.

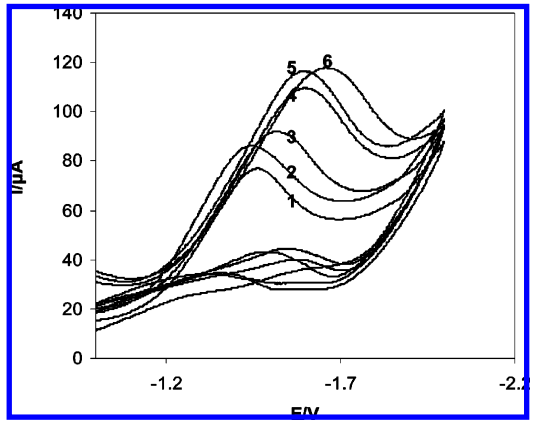

Figure 3. Cyclic voltammograms of Th^{4+} at different scan rates [(1:20, 2:30, 3:40, 4:70, 5:80, and 6:90) mV·s^{-1}], [Th^{4+}] = 0.01 mol·dm^{-3}, and I = 0.01 mol·dm^{-3} $NaClO_4$ on a glassy carbon electrode (28 mm^2 surface).

$E_{1/2}$ = −1.566 V. On the basis of the potentiometric and spectrophotometric measurements described above, the electron-transfer process is attributed to the $Th^{4+/0}$−L redox couple. The effect of the scan rate on the shape of the cyclic voltammograms is shown in Figure 3. In the whole scan rate range, the cathodic peak potential is slightly shifted toward more cathodic potentials with increasing scan rate. The decrease of the cathodic peak potential (a few mV) could be due to a small error provoked by ohmic drop corrections and the uncertainty of the R_e measurement. It can be mentioned that most of the other actinides have shown a reversible behavior at low scan range.[38] The voltammograms of Th^{4+}−gly val and Th^{4+}−gly gly show a reduction wave negatively shifted relative to the reduction wave of $Th^{4+/0}$ (Figure 4). The half-wave potential, $E_{1/2}$, of Th^{4+}−gly val and Th^{4+}−gly gly was found to be somewhat dependent on concentration of the ligands, and these results can be simply explained by their interaction between the metal ion and each ligand. In Figure 5, a shift of $E_{1/2}$ of the Th^{4+}−gly gly couples to less negative values is observed when the concentration of each ligand is increased. The half-wave potentials, $E_{1/2}$, of the $Th^{4+/0}$, $Th^{4+/0}$−gly val, and $Th^{4+/0}$−gly gly couples were determined according to the following equation

$$E_{1/2} = E_{pa} - \Delta E_p/2 \qquad (7)$$

where E_{pa} is the anodic peak potential and ΔE_p is the difference between the anodic and cathodic peak potentials ($\Delta E_p = E_{pa} - E_{pc}$). The stability constants of Th^{4+}−gly val and Th^{4+}−gly gly

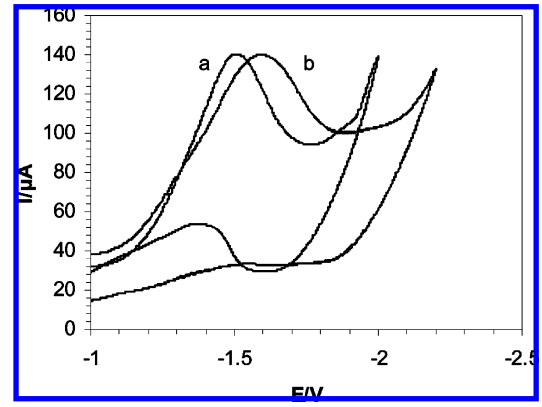

Figure 4. Cyclic voltammograms of Th^{4+} and Th^{4+}/gly gly complex species, (a) [Th^{4+}] = 0.01 mol·dm^{-3} and I = 0.01 mol·dm^{-3} $NaClO_4$ and (b) [Th^{4+}] = 0.01 mol·dm^{-3}, [gly gly] = 0.001 mol·dm^{-3} and I = 0.01 mol·dm^{-3} $NaClO_4$ recorded on a glassy carbon electrode (28 mm^2 surface) at a scan rate of 100 mV·s^{-1}.

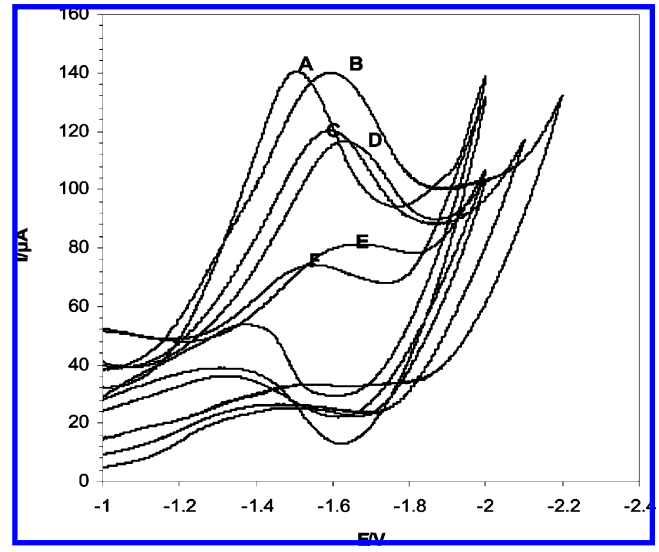

Figure 5. Cyclic voltammograms for $Th^{4+/0}$ complex species recorded on a glassy carbon (28 mm^2 surface) at a scan rate of 100 mV·s^{-1}, experimental conditions are as a function of glycyl−glycine concentration. Gly gly concentration was increased from 0.0 (CV A) to 10^{-3} mol·dm^{-3} (CV B). [Th^{4+}] = 0.01 mol·dm^{-3} and I = 0.01 mol·dm^{-3} $NaClO_4$ (A) [gly gly] = 0.0, (B) [gly gly] = 10^{-3}, (C) [gly gly] = $5\cdot10^{-4}$, (D) [gly gly] = $2.5\cdot10^{-4}$, (E) [gly gly] = $1.25\cdot10^{-5}$, and (F) [gly gly] = 10^{-5} mol·dm^{-3}.

Table 3. Average Values of the Formation Constants of Th−gly gly and Th−gly val at 25 °C and Constant Ionic Strength (0.01 mol·dm^{-3} $NaClO_4$) by the Cyclic Voltammetry Method

species	log β_{101}	log β_{102}
Th−gly gly	6.10 ± 0.11	10.45 ± 0.12
Th−gly val	9.16 ± 0.14	13.74 ± 0.18

were determined at 25 °C by plotting eq 8 to give m and the stability constant, log β, from the slope and the intercept, respectively.

$$\Delta E_{1/2} = 0.0591/n(\log \beta + m \log[L^-]) \qquad (8)$$

where m and n are the ratio of each ligand in the complex species and the electron transferred, respectively. $\Delta E_{1/2}$ is the half-wave potential difference between the metal ion and the complex [$\Delta E_{1/2} = E_{1/2} - E_{1/2}(L)$]. The results of the calculations and the cyclic voltammograms of Th−gly gly and Th−gly val systems are summarized in Table 3. At lower and higher concentration of the ligands, the main species is ML and ML_2,

respectively. There is no evidence of formation of MHL_2, species by the cyclic voltametry method. This could be due to the limitation of changing pH in the cyclic voltammetry method.

Supporting Information Available:

Two tables showing the spectrophotometric titration data of gly gly and gly val with thorium(IV). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Dunnick, J. K.; Fowler, B. A.; Seiler, H. G.; Sigel, H.; Sigel, A. *Handbook on oxicity of inorganic compounds*; Marcel Dekker: New York, 1988.

(2) Catsch, A.; Harmuth-Hoene, A. E. Pharmacology and therapeutic applications of agents used in heavy metal poisoning. *Pharmacol. Ther. A* **1976**, *1*, 1–6.

(3) Bagnall, K. W. The actinide elements. In *topics in inorganic and general chemistry*; Robinson, P. L., Ed.; Monography 15; Elsevier Publishing Co.: New York, 1972.

(4) Li, W. B.; Wahl, W.; Oeh, U.; Hollriegl, V.; Roth, P. Biokinetic modeling of natural thorium in humans by ingestion. *Radiat. Prot. Dosim.* **2007**, *125*, 500–505.

(5) Sanna, D.; Agoston, C.; Micera, G.; Sovago, I. The effect the ring size of fused chelates on the thermodynamic and spectroscopic properties of peptide complexes of copper(II). *Polyhedron* **2001**, *20*, 3079–3090.

(6) Kittl, W. S.; Rode, B. M. Inorg. Chim. Complex formation of copper ion with aliphatic dipeptides. *Acta* **1981**, *55*, 21–27.

(7) Xu, J.; Whisenhunt, D. W., Jr.; Veeck, A. C.; Uhlir, L. C.; Raymond, K. N. Thorium(IV) complexes of bidentate hydroxypyridinonates. *Inorg. Chem.* **2003**, *42*, 2665–2674.

(8) Othmer, K. *Concise encyclopedia of chemical technology*; John Wiley & Sons: New York, 1985.

(9) Hawley, G. G. *The condensed chemical dictionary*, 10th Ed.; Van Nostrand Reinhold Company: New York, 1981.

(10) Roth, P.; Hollriegl, V.; Li, W. B.; Oeh, U.; Schramel, P. Validating an important aspect of new ICRP biokinetic model of thorium. *Health Phys.* **2005**, *88*, 223–228.

(11) Correa, L. M.; Kochhann, D.; Becker, A. G.; Pavanato, M. A.; Liesuy, S. F.; Loro, V. L.; Raabe, A.; Mesko, M. F.; Flores, E. M. M.; Dressler, V. L.; Baldisserotto, B. Biochemistry, cytogenetics and bioaccumulation in silver catfish (Rhamdia quelen) exposed to different thorium concentrations. *Aquat. Toxicol.* **2008**, *88*, 250–256.

(12) Langmuir, D.; Herman, J. S. The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta* **1980**, *44*, 1753–1766.

(13) Ivanovich, M.; Harmon, R. A. *Uranium-series disequilibrium: applications to earth, marine and environmental sciences*; Clarendon Press: Oxford, 1982.

(14) Yusof, A. M.; Mahat, M. N.; Omar, N.; Wood, A. K. H. water quality studies in an aquatic environment of disused tin-mining pools and in drinking water. *Ecol. Eng.* **2001**, *16*, 405–414.

(15) Shtangeeva, I.; Ayrault, S.; Jain, J. Thorium uptake by wheat at different stages of plant growth. *J. Environ. Radioact.* **2005**, *81*, 283–293.

(16) Edington, D. N. The estimation of thorium and uranium as submicrogram level in bone by neutron activation. *Int. J. Appl. Radiat. Isot.* **1967**, *18*, 11–18.

(17) Lagrange, P.; Schneider, M.; Zare, K.; Lagrange, J. Determination and comparison of the stability constants of uranium(VI) and vanadium(V) glycine complexes. *Polyhedron* **1994**, *13*, 861–867.

(18) Beck, M. T.; Nagypal, I. *Chemistry of complex equilibria*; Ellis Harwood: New York, 1990.

(19) Gharib, F.; Nasiri, R. Complex formation of dioxovanadium(V) with glycine and some glycyl peptides. *Rev. Inorg. Chem.* **2005**, *25*, 79–91.

(20) Martell, A. E.; Motekattis, R. J. *The determination of stability constants*, 2nd ed.; VCH: New York, 1992.

(21) Hulanicki, A.; Glab, S.; Ackermann, G. Complexiметric indicators: characteristics and applications. *Pure Appl. Chem.* **1983**, *55*, 1137–1230.

(22) Maleki, N.; Haghighi, B.; Safavi, A. Evaluation of formation constants, molar absortivities of metal complexes, and protonation constants of acids by nonlinear curve fitting using Microsoft Excel Solver. *Microchem. J.* **1999**, *62*, 229–236.

(23) Gharib, F.; Jabbari, M.; Farajtabar, A.; Shamel, A. Solvent effects on protonation and complexation of glutamic and aspartic acids with molybdenum(VI) in different aqueous solutions of methanol. *J. Chem. Eng. Data* **2008**, *53*, 1772–1778.

(24) Bevington, P. R. *Data reduction and error analysis for the physical sciences*; McGraw-Hill: New York, 1969.

(25) Meloun, M.; Havel, J.; Hogfeldt, E. *Computation of solution equilibria*; Ellis Harwood: New York, 1988.

(26) Polster, J.; Lachmann, H. *Spectrometric titrations*; Verlag Chemie: Weinheim, 1989.

(27) Golub, G. H.; Van Loan, C. F. *Matrix computations*, 2nd ed.; John Hopkins Univ. Press: Baltimore, 1989.

(28) Press, W. H.; Vetterling W. T.; Teukolsky, S. A.; Flannery, B. P. *Numerical recipes in C*; Cambridge Univ. Press: Cambridge, 1995.

(29) Toraishi, T.; Farkas, I.; Szabo, Z.; Grenthe, I. Complexation of Th(IV) and various lanthanides(III) by glycolic acid; potentiometric, 13C-NMR and EXAFS studies. *J. Chem. Soc., Dalton Trans.* **2002**, 3805–3812.

(30) Nourmand, M.; Meissami, N. Methionine isomers and the stability of their complexes with uranyl, thorium and some transitional metal ion. *Radiochem. Radioanal. Lett.* **1982**, *55*, 149–154.

(31) Tewari, B. B. Determination of stability constants of metal-methylcysteine and metal-methylcysteine-cysteine complexes by paper ionophoretic technique. *Croat. Chem. Acta* **2005**, *78*, 49–53.

(32) Srinivasan, T. G.; Zanonato, P.; Di Bernardo, P. Complexation of thorium(IV) with malonate at variable temperatures. *J. Alloys Compd.* **2006**, *408*, 1252–1259.

(33) Nourmand, M.; Meissami, N. Complex formation between uranium(VI) and thorium(IV) ions with some α-amino acids. *J. Chem. Soc., Dalton Trans.* **1983**, 1529–1533.

(34) Sharma, U. Stepwise stability constants of uranyl(II) and thorium(IV) complexes of L-lysine monochloride. *Thermochim. Acta* **1986**, *101*, 381–383.

(35) Bismondo, A.; Rizzo, L. Thermodynamic properties of actinide complexes. Uranyl(VI) and thorium(IV) aspartate systems. *Polyhedron* **1989**, *8*, 2233–2236.

(36) Bismondo, A.; Rizzo, L. Thermodynamics of the complex formation of thorium(IV) with glutathione in aqueous solution. *Thermochim. Acta* **1990**, *173*, 43–46.

(37) Bismondo, A.; Rizzo, L.; Tomat, G. Thermodynamic properties of actinide complexes. Uranyl(VI) and thorium(IV) glycine systems. *Inorg. Chim. Acta* **1983**, *74*, 21–24.

(38) Serp, J.; Konings, R. J. M.; Malmbeck, R.; Rebizant, J.; Scheppler, C.; Glatz, J. P. Electrochemical behaviour of plutonium ion in LiCl-KCl eutectic melts. *J. Electroanal. Chem.* **2004**, *561*, 143–148.

Received for review February 28, 2009. Accepted July 18, 2009.

JE9002288