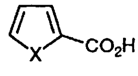
Complexation of Thorium(IV) with 2-Thenoic and 2-Furoic Acids in Aqueous Solution at Low pH[‡]

Jan G. H. du Preez[a] **and Gerhard F. Swiegers**[*,†,b]
[a] *The Uranium Chemistry Research Unit, University of Port Elizabeth, PO Box 1600, Port Elizabeth 6000, South Africa*
[b] *Department of Chemistry, Vista University, Private Bag X613, Port Elizabeth, South Africa*

The aqueous complexation chemistry of thorium(IV) with 2-thenoate and 2-furoate has been studied using precision analytical potentiometry (I = 0.5 mol dm^{-3} $NaClO_4$, 25 °C) in the range pH 1.7–3.0. The best-fit model, which was tested by varying the data and pH range employed, took into account the competitive formation of the conjugate ligand acids and equilibrium hydroxothorium complexes. The formation constants of the complexes obtained, denoted by β_{pqr}, where the subscripts p, q and r refer to the stoichiometric coefficients in the general formula $[L_pTh_qH_r]^{(-p+4q+r)}$ (L = 2-thenoate or 2-furoate) have the values: 2-thenoate, log β_{101} = 3.24 ± 0.00, log β_{110} = 3.04 ± 0.07, log β_{11-1} = 0.39 (invariant), log β_{210} = 5.69 ± 0.05, log β_{312} = 14.16 ± 0.05, log β_{412} = 18.00 ± 0.03; 2-furoate, log β_{101} = 3.01 ± 0.00, log β_{110} = 2.85 ± 0.04, log β_{210} = 5.11 ± 0.07, log β_{312} = 12.78 ± 0.06, log β_{410} = 10.07 ± 0.03, log β_{412} = 15.14 ± 0.07. These results suggest that higher species of the type ThL_n^{x+} (n = 3 or 4) are partially protonated at the pH necessary to avoid hydrolytic precipitation of the actinide.

Investigation of the aqueous solution chemistry of actinide(IV) ions constitutes a significant challenge; most of these ions are stable only in strongly acidic solutions in which the available protons can compete very effectively for co-ordination of most common ligands. Previous studies provide an illustration of this point; published formation constants for many systems, including numerous fundamental and otherwise well studied ligands, are poorly defined and disagree significantly when different measurement techniques have been used.[1] In addition, the formation constants of higher metal–ligand species (such as ML_n, n = 3 or 4 for L = bidentate ligand) are often either unavailable or calculated with excessively large statistical errors.

In the representative case of the thorium(IV) monocarboxylates[2-6] the difficulties involved can be illustrated by the fact that simple carboxylates, such as acetate, have protonation constants (log K_a) of *ca.* 4.0–5.0. By contrast, the formation constants of their first complexes, $[ThL]^{3+}$, are generally an order of magnitude smaller, so that, at the low pH required to prevent hydrolysis of the actinide, metal chelate species are almost completely absent. To determine stability constants by a competition method entailing potentiometric titration of metal and ligand at a buffered pH of around 1.5, as has previously been necessary,[2-4] consequently relies on the tiny proportion of metal chelate present in the experimental solution. In the acetate case, the $[Th(O_2CMe)]^{3+}$ formed in 2 : 1 ligand : metal solutions represents less than 2% of the total metal and ligand; even in 20 : 1 solutions $[Th(O_2CMe)]^{3+}$ exists as only 20% of the total thorium available. All higher complexes occur in extremely low proportions of the total metal or ligand under these conditions. Yet attempts to work at higher pH led to unexpected precipitations related to the buffer concentration.[2-4]



X = O or S

A more reasonable method of studying such systems involves undertaking a series of precision potentiometric titrations at various fixed ligand : metal ratios in which the acidity is swept from low pH upwards through the entire pH range available. Points at which the competition of protons for the ligand is smallest (*i.e.* just prior to hydrolysis of the actinide) can then be included in the data analysis. While previously applied in similar cases,[7] such an approach has, to the best of our knowledge, not been attempted with an actinide(IV)–ligand system.

We have studied the aqueous chemistry of Th^{4+} with 2-thenoic acid and 2-furoic acid using this method within the limitations imposed by both the system and the technique itself.

Experimental

All chemicals were used as analytical reagents except for 2-furoic acid (provided by C. G. Smith, Durban, South Africa) which was purified by repeated recrystallisation from boiling water until the melting point was 130 °C. Solutions were prepared using distilled and degassed water; all solution manipulations were performed under an inert atmosphere.

Solution Preparations.—A 3 mol dm^{-3} $NaClO_4$ solution was prepared by addition of an appropriate amount of $HClO_4$ and (CO_2-free) NaOH solution; neutralisation of residual acidity was monitored by using a pH meter. The solution was analysed per unit weight for sodium using atomic absorption measurements and for perchlorate using a gravimetric technique.[8] A 1 mol dm^{-3} $HClO_4$ solution was prepared and standardised by weight against a NaOH solution of known concentration. A *ca.* 0.1 mol dm^{-3} solution of $Th(ClO_4)_4 \cdot xH_2O$ was prepared. The following solutions were then made up to I = 0.5 mol dm^{-3} by addition of appropriate weights of the 3 mol dm^{-3} $NaClO_4$ solution to the above solutions: (a) 0.1 mol

---

[†] *Present address:* Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.

[‡] *Supplementary data available* (No. SUP 57088, 36 pp.): titration data, results of calculations and distribution curves. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

dm^{-3} NaOH, (b) 0.1 mol dm^{-3} HClO$_4$, (c) 0.02 mol dm^{-3} ligand acid, and (d) 0.1 mol dm^{-3} HClO$_4$ containing 0.01 mol dm^{-3} Th(ClO$_4$)$_4$·xH$_2$O. Solution (a) was standardised by titration with potassium hydrogen phthalate, (b) and (c) by titration with a NaOH solution of known concentration. Solution (d) was analysed, by weight, for Th^{IV} using a back titration of ethylenediaminetetraacetic acid (H$_4$edta) with an excess of a zinc(II) solution of known concentration, and for HClO$_4$ by titration with a NaOH solution of known concentration.

Potentiometric Titrations.—Mixtures of solutions (c) and (d) above were titrated with solution (a) in double-walled beakers, thermostatted with circulating water to 25.0 ± 0.1 °C, using a fully automated Metrohm-Herisau 670 Titroprocessor equipped with a glass and Ag–AgCl reference electrode (filled with 3 mol dm^{-3} NaClO$_4$ solution). A presaturated (by bubbling through a 3 mol dm^3 NaClO$_4$ solution) flow of nitrogen was maintained over all titration solutions. The entire apparatus was housed in a constant-temperature room at 25 °C. Potentiometric titrations involving the following initial concentrations of Th^{4+} and ligand acid were undertaken in, at least, duplicate: *ca.* 0.000, 0.007 (ligand only); 0.007, 0.007; 0.005, 0.010; 0.005, 0.015; 0.003, 0.012 (furoic acid only); 0.003, 0.015 (furoic acid only) and 0.003, 0.013 mol dm^{-3} (thenoic acid only). The free hydrogen-ion concentration, h, was determined using equation (1). For brevity, $-\log h$ is abbreviated as pH$_c$.

$$E = E^\circ + 59.16 \log h + E_j \qquad (1)$$

All titration solutions were initially *ca.* pH$_c$ 1.5–1.7. Precipitation was observed to commence in the range pH$_c$ 2.70–2.95. Data corresponding to the last 0.05 pH$_c$ units prior to the first indications of precipitation were routinely discarded to ensure the exclusive use of equilibrium points. In all titrations equilibrium was established within 2–3 s of addition of base, with no observable drift in potential.

Electrode Calibrations and Calculations.—Electrode calibrations were carried out from acid–base titrations (I = 0.5 mol dm^{-3}, NaClO$_4$) performed immediately before/after each titration. A sequential application of the program MAGEC,[9] including Gran-plot and alkali-correction procedures, produced three separate, but narrowly consistent sets of optimised values for E°, pK_w and the experimental Nernstian slope. The same data in the region pH$_c$ 1.50–2.35 were then plotted as (E − 59.16 log h) *vs.* h, yielding the junction potential (E_j) and further confirmation of E°.[10] As an additional precaution, each set of metal–ligand titration data was subdivided into the following pH$_c$ ranges: (*a*) *ca.* 2.35 to precipitation (E_j ignored), (*b*) *ca.* 2.00 to precipitation (E_j taken into account) and (*c*) *ca.* 1.70 to precipitation (E_j taken into account). Model testing was then performed on both individual and combinations[11] of collected titration data in each of these ranges using the program SUPERQUAD.[12] Consistent calculation results were taken as an indication of correct calibration and the absence of undetected but significant species with narrowly overlapping equilibria at the boundaries of the pH$_c$ range. Dissociation constants of the ligand acids were determined as an integral part of the entire calculations[11] and were in agreement (furoic acid)[6,13] or marginally lower (thenoic acid)[6] than previously reported.

Results and Discussion

For the purposes of this study the individual carboxylic acids were selected since they are more acidic than most carboxylates (the 10–90% protonation range lies within the range pH$_c$ 2–4). The reaction of Th^{IV} with the acids can be represented by equation (2), with individual formation constants, β_{pqr}, denoted by the coefficients describing their stoichiometry, *i.e.* $[p, q, r]^{(-p+4q+r)}$.

$$pL^- + q\text{Th}^{4+} + r\text{H}^+ \longrightarrow [\text{L}_p\text{Th}_q\text{H}_r]^{(-p+4q+r)} \qquad (2)$$

Table 1 gives the best-fit models and calculated formation constants for the combination of all data for each thorium(IV)–ligand acid system. Simple monomeric complexes $[1,1,0]^{3+}$ and $[2,1,0]^{2+}$ were obtained for the first and second species with formation constants of a similar order to those of comparable thorium(IV) carboxylate complexes (Table 1). However, despite exhaustive testing, β_{310} could not be obtained as part of the best-fit model from an overall combination of titration data for either system, nor β_{410} for Th^{IV} and thenoic acid. Instead β_{312} and β_{412} were found consistently to provide the best fit of both the individual and combined data for Th^{IV} and both acids along with β_{410} for Th^{IV} and furoic acid. The sample standard deviation statistic, s, for each of the models is excellent and the χ^2 residual statistics are within the 95% confidence level.[12,14] The proportions of metal chelate species in the various individual titrations are significantly higher than previously obtained (Fig. 1).

These results suggest the existence of protonated complexes within the pH$_c$ range examined, a finding supported by a previously noted (from thermodynamic measurements), but unexplained change in the nature of co-ordination corresponding to K_3 in the thorium(IV)–acetate system.[2] Qualitatively similar complexes have been postulated and observed for thorium(IV)–nitrate systems at higher acidity.[15] Despite the relative acidity of thorium(IV), its chelates appear to be protonated in this case once the charge on the species has been reduced by the co-ordination of three or more ligands. This is significant since techniques requiring an assumption of 4:1:0 and 3:1:0 stoichiometry would not provide accurate formation

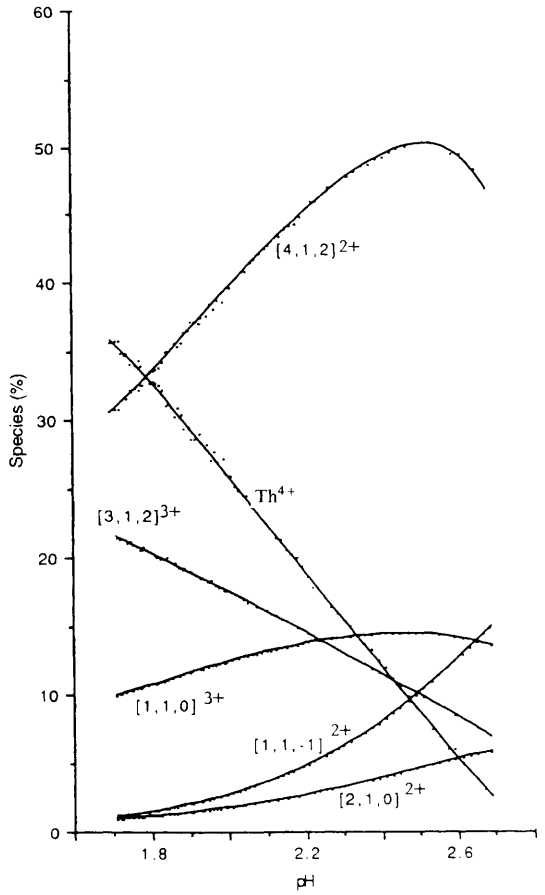


Fig. 1 Percentage of metal chelate species relative to the total thorium as a function of pH in the titration of Th^{4+} and 2-thenoic acid having the initial concentrations 0.003 and 0.013 mol dm^{-3} respectively

Table 1 Formation constants (log β) for species $[L_pTh_qH_r]^{(-p+4q+r)}$ with 2-thenoic acid and 2-furoic acid ($NaClO_4$, I = 0.5 mol dm^{-3}) and other ligands (I = 1.0 mol dm^{-3})

Complex	2-Thenoic acid[a]	2-Furoic acid[b]	Formate[c]	Acetate[c]	Propionate[c]	Sulfanylacetate[d]
[1,0,1]	3.24 ± 0.00	3.01 ± 0.00	3.49	4.58	4.68	3.53
$[1,1,0]^{3+}$	3.04 ± 0.07	2.85 ± 0.04	3.09	3.89	3.94	3.22
$[1,1,-1]^{2+}$	0.39[e]					
$[2,1,0]^{2+}$	5.69 ± 0.05	5.11 ± 0.07	5.15	6.94	7.25	5.69
$[3,1,0]^{+}$			6.73	9.01	9.44	7.20
$[3,1,2]^{3+}$	14.16 ± 0.05	12.78 ± 0.06				
[4,1,0]		10.07 ± 0.03		10.3	11.20	8.54
$[4,1,2]^{2+}$	18.00 ± 0.03	15.14 ± 0.07				
Ref.	This work	This work	3	4	3	6

[a] χ^2 = 11.33, s = 0.36, 292 points. [b] χ^2 = 8.30, s = 0.35, 363 points. [c] 1 mol dm^{-3} $NaClO_4$, 25 °C. [d] I = 1.0 mol dm^{-3}, 25 °C. [e] Invariant.

constants in these circumstances.[16] Furthermore, repeating a particular potentiometric titration of ligand and metal at differingly low, buffered pH_c values as previously described [2-4] would not constitute an accurate check for the presence of protonated species as they may exist over the entire pH_c range available and their proportions may be extremely low, depending on the conditions employed.

Two equilibrium hydrolytic species, which appear to exist reversibly in the early stages of hydrolysis,[17] were observed; constants β_{11-1} and β_{41-2} were calculated as part of the best-fit model for individual titration data in the thorium(IV)–thenoic acid system. The latter complex existed only in low proportions in an extremely narrow pH_c range (2.50–2.70) immediately prior to precipitation. It could therefore be safely excluded from the overall best-fit model, without change in the remaining calculated constants. The former species existed in a much larger pH_c range, again in relatively small proportions. Attempts similarly to ignore it led, however, to a significant change in the value of β_{110}, so that β_{11-1}, calculated with a consistent value from various individual and combinations of titration data at low ligand:metal ratios, was included as invariant in the final calculations.

The similarity of these water-soluble carboxylic acids to the well known water-insoluble β-diketones 2-thenoyl- and 2-furoyl-trifluoroacetone, which are exceptionally efficient extractants of Th^{IV} in the range pH 1.7–2.4,[18] suggests Scheme 1 as a possible mechanism for the solvent-extraction process.

$$\begin{array}{ccc} Th^{4+}(aq) + 4\,Htfta(org) & \longrightarrow & H_2Th(tfta)_4{}^{2+}(aq) + 2H^+(aq) \\ & & \downarrow\uparrow \\ Th(tfta)_4(org) + 4H^+(aq) & \longleftarrow & Th(tfta)_4(aq) + 4H^+(aq) \end{array}$$

Scheme 1 Htfta = Trifluoro-2-thenoylacetone

The thermodynamic stability of the $[4,1,2]^{2+}$ complex would in this case be entirely compensated for by the higher solubility in the organic phase and large Nernst distribution constant, K_{D4}, of the [4,1,0] species, thereby plausibly accounting for the enhancement of the extractive ability of β-diketones when particular organic solvents, such as benzene, are used.[1,18]

Acknowledgements

The assistance of Dr. B. J. A. M. van Brecht is gratefully acknowledged.

References

1 S. Ahrland, in *The Chemistry of the Actinide Elements*, eds. J. J. Katz, G. T. Seaborg and L. R. Morris, 2nd edn., Chapman and Hall, New York, 1986, ch. 21 and refs. therein.
2 R. Portanova, P. DiBernardo, O. Traverso, G. A. Mazzocchin and L. Magon, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2177; A. Bismondo and L. Rizzo, *Polyhedron*, 1989, **8**, 2233.
3 R. Portanova, G. Tomat, A. Cassol and L. Magon, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1685.
4 L. Magon, A. Bismondo, L. Maresca, G. Tomat and R. Portanova, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4237.
5 A. I. Moskvin and L. N. Essen, *Russ. J. Inorg. Chem., (Engl. Transl.)*, 1967, **12**, 359.
6 *Critical Stability Constants*, eds. R. M. Smith and A. E. Martell, Plenum, New York, 1989, vols. 3, 5 and 6.
7 For example, F. J. C. Rossotti and R. J. Whewell, *J. Chem. Soc., Dalton Trans.*, 1977, 1223.
8 A. I. Vogel, *A Textbook of Inorganic Analysis*, 3rd edn., Longman, London, 1961.
9 P. M. May, D. R. Williams, P. W. Linder and R. G. Torrington, *Talanta*, 1982, **29**, 249.
10 H. Rossotti, *Talanta*, 1974, **21**, 809.
11 A. Braibanti, G. Ostacoli, P. Paoletti, L. D. Pettit and S. Sammartano, *Pure Appl. Chem.*, 1987, **59**, 1722; G. H. Nancollas and M. B. Tomson, *Pure Appl. Chem.*, 1982, **54**, 2675.
12 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
13 P. Lumme, *Suom. Kemistil. B*, 1960, **33**, 87.
14 A. Vacca, A. Sabatini and M. A. Gristina, *Coord. Chem. Rev.*, 1975, **15**, 161.
15 J. L. Ryan, *J. Phys. Chem.*, 1960, **64**, 1375 and ref. therein; P. T. Moseley, S. W. Sanderson and V. J. Wheeler, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3975.
16 F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants and Other Equilibrium Constants*, McGraw-Hill, New York, 1961.
17 C. F. Baes, N. J. Meyer and C. E. Roberts, *Inorg. Chem.*, 1965, **4**, 518; S. Hieranen, *Acta Chem. Scand.*, 1954, **8**, 1626; K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, 1954, **58**, 325.
18 J. Stary, *The Extraction of Metal Chelates*, Pergamon, Oxford, 1964; A. M. Poskanzer and B. M. Foreman, *J. Inorg. Nucl. Chem.*, 1961, **16**, 323.

Received 3rd *March* 1995; *Paper* 5/01308I