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Complexation of Plutonium and Thorium in Aqueous Environments*

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The release of radionuclides from a radioactive waste repository to the environment is predominantly governed by their formation of aqueous complexes with both inorganic and organic ligands [1]. Examining these systems is difficult because of their diversity and the long time scales involved. However, modern geochemical computer programs, incorporating large thermodynamic formation constant databases may be used to model radionuclide speciation, although the resulting predictions are only as good as the input parameters to the models. Thus, poorly characterised and inaccurate formation constant data are likely to produce considerable errors in the results. Therefore, the acquisition of such data, whether it be taken from the literature or determined experimentally, is a preliminary objective in modelling these radioactive waste scenarios.

The presence of organic ligands can affect the solubility of actinides and, hence, their mobilisation from the repository through the geosphere, the biosphere and eventually to man. This was demonstrated in an initial study involving the complexation of plutonium, neptunium and americium by EDTA, citrate and acetate under typical repository conditions [2]. The predictions were based on literature values of formation constants. It became apparent during their acquisition, however, that data for actinide–organic complexes was sparse and on the whole unreliable. This is probably due to the high radiotoxicity and the complicated solution chemistry of the actinides. For instance, in solution plutonium can exist simultaneously in up to four oxidation sates corresponding to the Pu^{3+}, Pu^{4+}, PuO_2^+ and PuO_2^{2+} ions [3].

One possible approach which can be used in circumventing these difficulties is to employ chemical analogues of the actinides in question. For example, thorium(IV) closely approximates the chemical behaviour of the plutonium(IV) oxidation state [4].

Citrate is present in both the waste, as a decontamination agent [5], and in ground/fresh waters as a naturally occurring ligand [6]. It also plays a major role in biological systems as a major low molecular weight ligand [3].

Therefore, the major aim of this study was to investigate the interaction of thorium(IV) with citrate using potentiometry in aqueous solution at 25 °C with a background electrolyte of 100 mmol dm^{-3} chloride. This method generally yields more thermodynamically significant constants as the values are based on activities rather than concentrations. The only other published results for this system [7] may be considered unreliable because they have been calculated on the assumption that no protonated or hydroxy species were formed. Yet this study has shown that utilisation of modern computer optimisation techniques for titration data analysis enables species of these types to be identified, along with their formation constants.

The formation constants for the species thus identified were then used to model the effect of citrate on the solubility of plutonium in (a) alkaline concrete porewaters pertaining to a radioactive waste repository and (b) near neutral ground/fresh waters.

Experimental

Materials

Citric acid (Analar, BDH Ltd.) was used without further purification. *Anal.* (C, H), Found: C, 34.4; H, 4.7. Calculated for $C_6H_8O_7 \cdot H_2O$: C, 34.3; H, 4.8%.

Standard stock solutions of thorium chloride were prepared from thorium nitrate (Analar, BDH Ltd.) in the following manner:

(i) The nitrate was dissolved in a minimum quantity of water and thorium hydroxide was precipitated by the addition of sodium hydroxide.

(ii) The aqueous phase was removed by centrifuging and decanting. The precipitate was then resuspended in water several times to remove nitrate. (This was done rapidly to prevent the formation of insoluble thorium hydroxide polymers.)

(iii) Finally, the precipitate was dissolved in a known quantity of hydrochloric acid to produce the thorium chloride stock solution. The thorium concentration was determined by EDTA complexometric titrations using catechol violet indicator [8] and the hydrogen ion concentration by strong acid/strong base titrations [9].

Sodium hydroxide and hydrochloric acid solutions were freshly prepared from concentrated ampoules (BDH).

All solutions were prepared using distilled degassed doubly-deionized water and maintained at an ionic strength of 100 mmol dm^{-3} by the addition of sodium chloride (Analar, BDH).

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Method

Citrate protonation constants and thorium–citrate formation constants were determined by glass electrode (Russell) potentiometric titration in a vessel thermostatted at 25 °C. The electrodes were calibrated, with respect to the hydrogen ion, by performing strong acid/strong base titrations [9].

Protonation curves for the ligand were obtained at a variety of different total citrate concentrations. Similarly, the metal complex formation curves were obtained at different citrate:thorium ratios and for different total citrate and thorium concentrations.

Titration Data Analysis

A general equilibria involving Th^{4+} cations (M); Cit^{3-} anions (L); and H^+ ions and its overall formation constant can be expressed thus:

$$pM + qL + rH \rightleftharpoons M_pL_qH_r;$$

$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \qquad (1)$$

The equilibria for the interaction of Th^{4+}, Cit^{3-} and OH^- ions and its overall formation constant is represented thus:

$$pM + qL + rH_2O \rightleftharpoons M_pL_q(OH)_r + rH;$$

$$\beta_{pqr} = \frac{[M_pL_q(OH)_r]\,[H]^r}{[M]^p[L]^q} \qquad (2)$$

Square brackets indicate free concentrations and charges have been omitted for simplicity.

An average value for the dissociation constant of water ($pK_w = -13.72$) determined in this laboratory was used.

Thorium hydrolysis data were included, as these species could affect complexation with citrate. The mononuclear species, $ThOH^{3+}$ and $Th(OH)_2{}^{2+}$ suggested by Hietanen and Sillén [10] in Cl^- background are only approximations. Formation constants for these two complexes were taken from results in a 1 mol dm^{-3} $ClO_4{}^-$ background [11]. The polynuclear species, $Th_2(OH)_2{}^{6+}$, $Th_2(OH)_3{}^{5+}$ and $Th_6(OH)_{14}{}^{10+}$ are dominant for Cl^- backgrounds [12]. The first two complexes were taken from a study at 0.5 mol dm^{-3} Cl^- [13], whilst the third was omitted due to the fact that it was unlikely to occur in this study.

Protonation and metal–ligand formation curves were generated using the ESTA* suite of computer programs [14]. These are represented by $\bar{z}_H$ (the average number of protons bound per ligand) against $-\log[H^+]$ for the citrate protonation; and $\bar{z}_M$ (the average number of ligands bound per metal) against $-\log[\text{Citrate}]$ for the thorium–citrate interactions.

The formation constants for the selected models of species were refined using the optimisation mode of ESTA with a weighted least-squares objective function (U) defined as:

$$U = \frac{\Sigma_n w(\text{e.m.f.}^o - \text{e.m.f.}^c)^2}{N - n_p} \qquad (3)$$

where N is the total number of titration points; n_p is the total number of optimised parameters (formation constants and other titration variables) and $\Sigma_n w(\text{e.m.f.}^o - \text{e.m.f.}^c)^2$ is the sum of squared e.m.f. residuals.

Concrete and Ground/Fresh Water Simulations

The geochemical computer code MINEQL [15] was used to model the solubility and speciation of plutonium in concrete and ground/fresh waters.

Results and Discussion

Citrate Protonation

The three protonation constants of citrate were measured (Table I) optimising simultaneously with electrode intercept and initial ligand concentration. These values compare favourably with those found by other groups [16, 17].

Thorium–Citrate Interactions

The experimental formation curve (Fig. 1) for the thorium–citrate interactions shows the results of six different titrations detailed in the legend. These curves are non-superimposable, exhibiting 'spreading' and 'curl-back' indicating the possible presence of protonated, hydroxy and polynuclear species.

TABLE I. Refined Citrate Protonation and Thorium–Citrate Formation Constants at 25 °C and 100 mmol dm^{-3} Cl^-

Species			$\log \beta_{pqr}$ $(\sigma)^a$	U	No. data points	No. titrations
p	q	r				
Citrate protonation						
0	1	1	5.650 (0.001)	50.7	608	8
0	1	2	9.973 (0.001)			
0	1	3	12.883 (0.002)			
Thorium–citrate (best model)						
1	1	0	11.611 (0.039)	11.0	225	6
1	2	0	21.139 (0.057)			
1	2	1	23.637 (0.035)			
1	2	−2	12.572 (0.077)			
1	3	0	26.113 (0.075)			
1	3	1	30.374 (0.069)			

[a] Standard deviation.

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*Equilibrium Simulation for Titration Analysis.

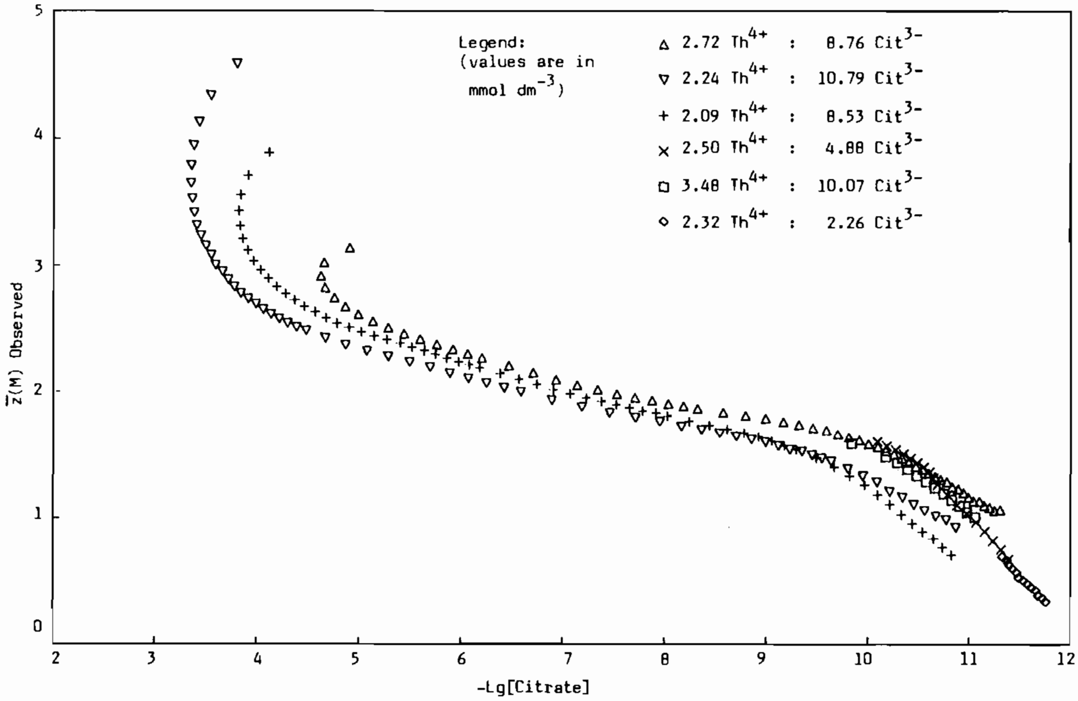

Fig. 1. Thorium–citrate experimental formation curve.

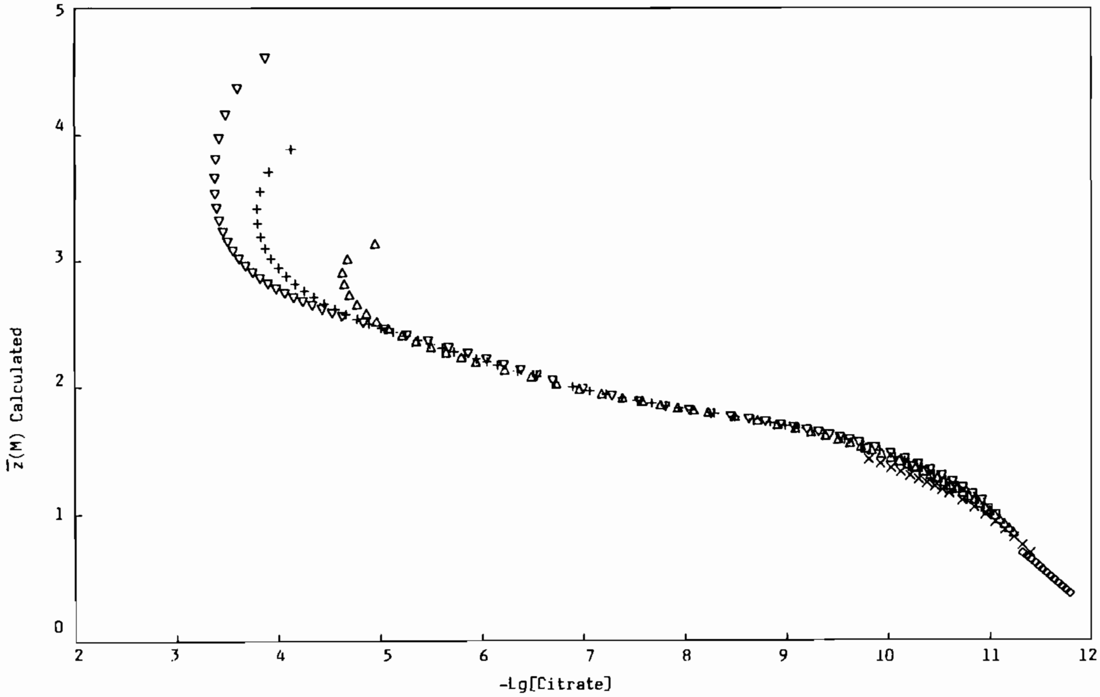

Fig. 2. Thorium–citrate simulated formation curve (best model).

A process of refining formation constants and subsequent simulation of experimental data was used to determine the 'best' model of the species present (Table I). The optimised formation constants of these complexes were used to produce the simulated formation curve (Fig. 2).

This model was chosen over others because of (a) good correlation between experimental and

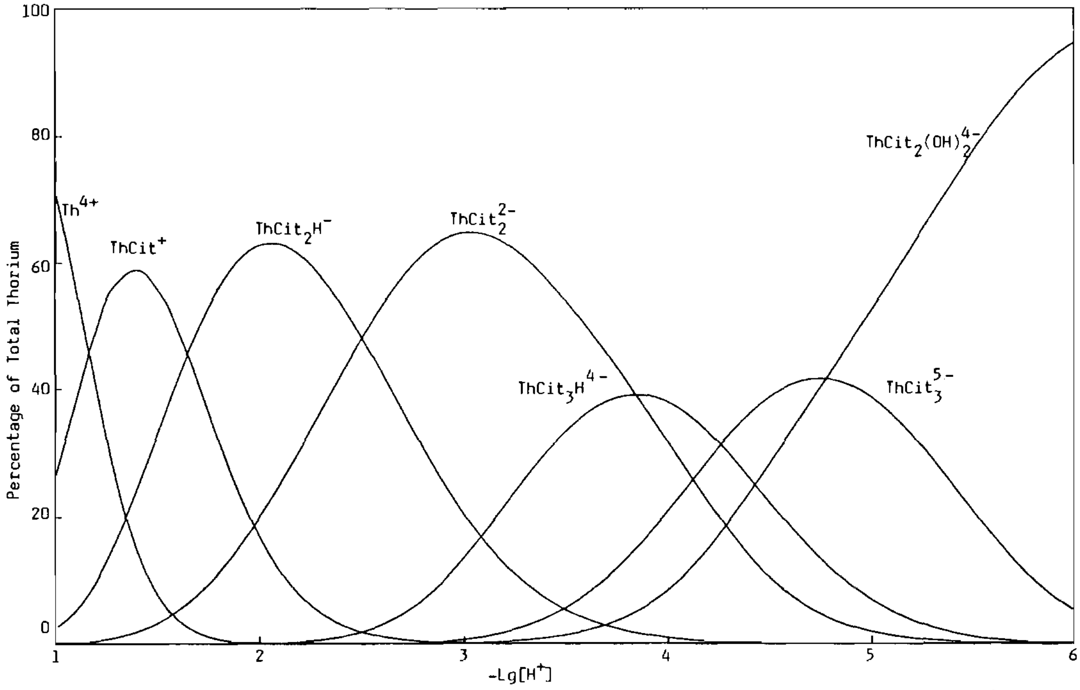

Fig. 3. Species distribution plot for thorium–citrate ($[Th^{4+}]$ = 2.5 mmol dm^{-3}; $[Cit^{3-}]$ = 7.5 mmol dm^{-3}).

TABLE II. A Comparison of Thorium(IV) and Plutonium(IV)–Citrate Constants at 25 °C and Corrected to Zero Ionic Strength

Species	Formation constants (log β) for M–L		
	Th–Cit (this work)	Th–Cit (Nebel and Urban [7])	Pu–Cit (Metivier and Guillaumont [18])
ML	14.13	16.17	14.71
MLH			16.26
MLH_2			16.86
MLOH			9.21
$ML(OH)_2$			4.96
ML_2	24.29	24.94	19.92
ML_2H	27.21		
ML_2H_2			29.52
ML_2H_4			31.32
ML_2H_5			31.42
$ML_2(OH)_2$	14.67		9.82
ML_3	28.00		
ML_3H	33.31		

simulated formation curves, and (b) lower standard deviations and overall objective function.

A species distribution plot based on the determined formation constants and a mean thorium–citrate concentration ratio can be shown (Fig. 3) for the pH range from 1 to 6 in this study.

Plutonium Modelling

The validity of the thorium–citrate constants determined and their use as an analogue for plutonium can be assessed by comparison with the work of other groups [7, 18]. The species and formation constants reported previously along with the model determined in this study have been summarised (Table II).

The thorium–citrate ML and ML_2 formation constants reported here are in good agreement with those of Nebel and Urban [7] even though these authors found no protonated or hydroxy species.

Comparison of the plutonium data of Metivier and Guillaumont with thorium–citrate data illustrates the apparent effect of the larger ionic radius of Th^{4+} over Pu^{4+}. This is demonstrated by the formation of ML_3 species with Th^{4+} but not with Pu^{4+}. It was thus decided to use both sets of formation constant data in the computer modelling studies described below so that areas of ambiguity could be highlighted and the appropriateness of Th^{4+} as an analogue for Pu^{4+} assessed.

A typical chemical composition of concrete [2] and ground/fresh [6] waters were used and only the major ions were included (Table III) so as to provide a simplified model of each system. Approximate pH and redox potential (E_h) typical to the situations used were also required as input.

Modelling studies using the MINEQL computer code were performed using the two different sets

TABLE III. Typical Concrete and Ground/Fresh Water Compositions used in Computer Simulations

Component	Concentration (mol dm^{-3})	
	Concrete water	Ground/fresh water
Ca^{2+}	1×10^{-4}	1×10^{-3}
Na^{+}	5×10^{-5}	5×10^{-4}
Mg^{2+}	5×10^{-6}	2.5×10^{-4}
Cl^{-}	2×10^{-3}	7.5×10^{-4}
$SO_4{}^{2-}$	3×10^{-3}	3×10^{-4}
$CO_3{}^{2-}$	3×10^{-5}	1×10^{-3}
pH	12.0	8.0
E_h (redox potential)	−300 mV	+200 mV

TABLE IV. The Effect of Citrate Concentration[a] on the Maximum Solubility of Plutonium[a] in Concrete and Ground/Fresh Waters

log[Citrate]	log[Pu solubility]			
	Concrete water		Ground/fresh water	
	Pu–Cit data [18]	Th–Cit data [this work]	Pu–Cit data [18]	Th–Cit data [this work]
−6.0	−9.27	−9.27	−9.54	−9.54
−5.0	−9.27	−9.27	−9.54	−9.54
−4.0	−9.27	−9.27	−9.54	−9.54
−3.0	−9.26	−9.26	−9.50	−7.80
−2.0	−9.23	−9.23	−9.12	−4.77
−1.0	−9.18	−9.17	−7.71	−2.91

[a] In mol dm^{-3}.

of 'Pu(IV)–citrate' data (*vide supra*). The maximum solubility of plutonium was calculated by equilibration with a $Pu(OH)_{4(s)}$ mineral phase, for a range of citrate concentrations from 10^{-6} to 10^{-1} mol dm^{-3} (Table IV). This range was chosen to include the values found in natural waters and the likelihood of localised high concentrations within the waste itself.

There is little enhanced solubility of plutonium within a concrete water for either set of formation constant data. However, in the case of ground/fresh waters a significant increase is observed with increased citrate concentration. The $PuCit_2(OH)_2{}^{4-}$ species is responsible for this in both cases, with the greater change shown by the Th–Cit data. The formation constant for the $ThCit_2(OH)_2{}^{4-}$ species is far greater than that measured for its plutonium analogue.

Conclusions

This computer simulation exercise has highlighted the need for reliable data for the actinides with organic ligands involved in the pathways from repository to man. Many constants are measured at low pH ranges, such as in this study, whereas, in general, modelling studies consider higher pH values than this. Thus, future studies must include this higher range so that the contributions of hydroxy species to complexation can be understood. These mixed ligand–hydroxy species are essential in the speciation of the actinides.

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