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Effect of temperature on the hydrolysis of actinide elements in solution

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(Article begins on next page)

Complexation of Th(IV) with sulfate in aqueous solution at 10-70 °C

Plinio [Di Bernardo](#)^a

Francesco [Endrizzi](#)^{a, b}

Andrea [Melchior](#)^c

Zhicheng [Zhang](#)^d

Pier Luigi [Zanonato](#)^{a, *}

Linfeng [Rao](#)^{d, *}

lrao@lbl.gov

^aDipartimento di Scienze Chimiche, University of Padova, Via Marzolo 1, 35131 Padova, Italy

^bKarlsruhe Institute of Technology, Hermann-von-Helmholtz Platz, 1, 76344 Eggenstein-Leopoldshafen, Germany

^cDipartimento Politecnico di Ingegneria e Architettura, Laboratori di Chimica, Via delle Scienze 99, 33100 Udine, Italy

^dLawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

*Corresponding authors.

Abstract

The applicability of spectrophotometry or H⁺-potentiometry to the studies of the complexation of thorium(IV) in aqueous solutions is limited because Th(IV) does not have characteristic optical [absorption](#) in UV/Vis/Near IR region and H⁺-electrode is not sensitive in solutions of high acidity that needs to be maintained to prevent the hydrolysis of Th(IV). In the present work, the technique of calorimetric titration was used to determine the heat of reaction for the complexation of Th(IV) with sulfate in the temperature range of 10-70 °C. The [equilibrium](#) constants and enthalpy of complexation were determined simultaneously from the calorimetric data. It was observed that the enthalpy of complexation is endothermic at 10 °C, and become more endothermic as the temperature is increased. Despite of this, the complexes, Th(SO₄)²⁻ and Th(SO₄)₂(aq), become more stable at higher temperatures due to the increasingly more positive entropy of complexation that exceeds the increase of enthalpy. The trends in the stability of sulfate complexes with tetravalent actinides (Th⁴⁺, U⁴⁺, Np⁴⁺, and Pu⁴⁺) are discussed in terms of electrostatic interactions that correlate with the ionic radii of the metal cations.

Keywords: Thorium; Sulfate; Complexation; Temperature effect; Calorimetry

1 Introduction

Modelling the behavior of actinides under environmental conditions requires a thorough knowledge of the thermodynamic properties of the metal ions involved with a multitude of potential ligands which can influence the migration of the metal ions into the environment.

Thorium, a member of the actinide family, has a relatively high natural abundance on Earth: about 6000 ppb, three times higher than that of uranium. Like uranium, thorium is also a source of nuclear energy that could be generated in nuclear fuel cycles based on thorium [1]. In recent years, there has been renewed and additional interest in thorium fuel cycle because of several advantages such as the intrinsic proliferation resistance due to the presence of ²³²U and its strong gamma emitting daughter products, and the generation of lesser long lived minor actinides than the traditional uranium fuel cycle.[†] Fundamental understanding of the behavior of thorium in the used fuel reprocessing and in environmental transport is critically important to the development of safe and sustainable nuclear fuel cycle based on thorium. Therefore, thermodynamic data concerning the interactions of thorium with various ligands are needed.

Thorium is found in nature only as tetravalent Th(IV), which can be mobilized through complexation with inorganic and organic ligands. Though inorganic ligands are usually weaker complexants with Th(IV) than organic ligands, it was estimated that, in the absence of organic complexants and below pH 3, the $\text{Th}(\text{SO}_4)_2(\text{aq})$ complex is the most important in solutions containing F^- , Cl^- , PO_4^{3-} , and SO_4^{2-} in concentrations typical of ground waters (estimated concentration of sulfate could be 250 mg/L or greater). Hence, knowledge of the thermodynamic data for the complexation of Th(IV) with sulfate is important for the modelling of the Th(IV) behaviour in acidic systems such as mine water and raffinates, acidic sulfate soils, and sulfuric acid leachates from hydrothermal uranium ores. In addition, because the temperature in some of these systems could be significantly higher than the ambient, data concerning the thermodynamic properties of Th(IV) sulfate complexes at high temperatures are also needed to predict the behaviour of thorium.

Studies of complexation of Th(IV) with sulfate have been recently [reviewed](#) [2]. Nearly all past studies used the distribution method, including ion exchange and solvent extraction. The data in the literature clearly show that, at relatively high acidities and nearly constant ionic strength, $\text{Th}(\text{SO}_4)^{2+}$ and $\text{Th}(\text{SO}_4)_2(\text{aq})$ are the predominant species in solutions containing Th(IV) and sulfate up to 0.5 M. All the past studies, except the study by Patil et al. [3] at 10, 25 and 40 °C and some solubility studies twenty years ago [4], refer to room temperature. Based on the equilibrium constants at 10–40 °C, Patil et al. estimated the enthalpies and entropies of complexation [3]. In only one case the enthalpy and entropy of complexation were determined by calorimetry at 25 °C and ionic strength 2 M [5]. No literature data are available at temperatures higher than 40 °C. Therefore, as it is well-known that thermodynamic parameters could vary significantly with temperature, in this work a microcalorimetric method was used to determine simultaneously the equilibrium constants and corresponding enthalpy of complexation for Th(IV)/sulphate complexes in 1 M $(\text{Na,H})\text{ClO}_4$ at different temperatures (10, 25, 40, 55, 70 °C). In order to obtain reliable values for the complexation reactions, the study was extended to the simultaneous determination of the [free energy](#) and enthalpy of protonation of sulphate at the same temperatures and ionic medium.

2 Experimental

All chemicals are of reagent grade. MilliQ water was used to prepare all solutions. The stock solution of sodium sulfate was prepared by dissolving weighed quantities of Na_2SO_4 in water. The stock solution of Th(IV) was prepared based on the procedure described elsewhere [6]. The concentrations of thorium and the excess perchloric acid in the stock solution were determined by EDTA titration complexometry and Gran's potentiometric method [7,8], respectively. The ionic strength of all working solutions was adjusted to 1.00 mol dm^{-3} at 25 °C, equivalent to 1.05 mol kg^{-1} at different temperatures, by adding appropriate amounts of NaClO_4 .

Microcalorimetric titrations were performed at the selected temperatures with a Thermometric 2277 isothermal microcalorimeter. The performance of the calorimeter was validated by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM) at 25 °C. The obtained value ($-47.6 \pm 0.3 \text{ kJ mol}^{-1}$) is in excellent agreement with the literature data [9]. Detailed description of the calorimeter was described elsewhere [6].

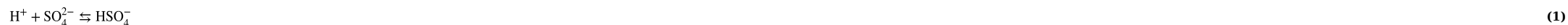
The protonation of sulfate was studied by adding either a solution of sulfate (40–80 mM) to $\sim 2.7 \text{ mL}$ of a solution of perchloric acid (20–100 mM) or a solution 100 mM of perchloric acid to $\sim 2.7 \text{ mL}$ of a solution of sodium sulfate (10–200 mM). The complexation of sulfate with Th(IV) was followed by adding a sodium sulfate solution (50 or 200 mM) to $\sim 2.7 \text{ mL}$ of a solution of Th(IV) containing an excess of perchloric acid to prevent metal ion hydrolysis. The concentrations of Th(IV) and H^+ in the microcalorimeter cup ranged from 1 to 5 mM and from 6 to 25 mM, respectively.

Multiple titrations were conducted at each temperature. For each titration, n experimental values of the heat generated in the reaction cell ($Q_{\text{ex},j}$, where $j = 1$ to n) were collected. In order to obtain the net complex formation heat at the j -th point ($Q_{\text{cpx},j}$), the values of $Q_{\text{ex},j}$ were corrected for the heat of dilution of the titrant solution ($Q_{\text{dil},j}$), determined in separate runs, and for the heat due to the protonation of sulfate ($Q_{\text{p},j}$), calculated by the minimization program with the protonation thermodynamic parameters obtained in a separate study. The equilibrium constants and enthalpy of complexation, β_j and ΔH_j , were simultaneously obtained by a computer program [10,11] that basically uses the Letagrop approach [12] to minimize the sum of the error squares on the total complexation heat per mole of Th(IV): $\Delta h_{v,j} = \sum Q_{\text{cpx},j}/n_{\text{Th}}$, where n_{Th} is the moles of Th(IV) in the titration cell.

3 Results and discussion

3.1 Protonation of sulfate at 10 to 70 °C

Only the first protonation reaction (described by Eq. (1)) was studied in this work.[‡] Representative protonation titrations are shown in Fig. 1 as the total reaction heat as a function of the volume of titrant added. The protonation parameters in Table 1 were obtained by fitting the titration data with the minimization program where the values of equilibrium constant and the corresponding protonation enthalpy were optimized simultaneously. The entropy of protonation was accordingly calculated from the equilibrium constant and enthalpy of protonation, as summarized in Table 1.



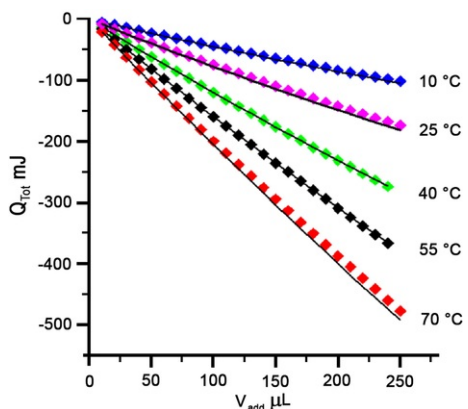


Fig. 1 Total reaction heat (Q_{tot}) for the protonation of sulfate as a function of the volume of titrant added. Cell solution: ~ 2.7 mL, ~ 50 mM Na_2SO_4 in 1.05 m $\text{Na}(\text{ClO}_4^-, \text{SO}_4^{2-})$; titrant: ~ 100 mM. HClO_4 . The negative sign stands for an endothermic reaction. Symbols: experimental data; solid lines: fit.

Table 1 Thermodynamic parameters for the protonation of sulfate and the complexation of sulfate with Th(IV) at different temperatures in $1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}(\text{ClO}_4/\text{SO}_4^{2-})$. All errors represent $\pm 3\sigma \log\beta$ on the molarity scale and $\log\beta$ at infinite dilution calculated on the basis of the Specific Ion Interaction Theory (SIT).

Reaction	$\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$						Ref.
	$I = 1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$			$I = 0$			
T °C	$\log \beta$	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	$T\Delta S$ $\text{kJ}\cdot\text{mol}^{-1}$	$\log \beta^\circ$	ΔH° $\text{kJ}\cdot\text{mol}^{-1}$	$T\Delta S^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	
10	0.84 ± 0.02	21.8 ± 0.9	26.4 ± 1.0	1.61 ± 0.07			p.w.
25	1.11 ± 0.01	23.2 ± 0.9	29.5 ± 0.9	1.90 ± 0.07	25.6 ± 0.9	36.4 ± 0.9	p.w.
				1.98 ± 0.05			[2]
40	1.26 ± 0.02	26.0 ± 0.3	33.6 ± 0.4	2.07 ± 0.07			p.w.
55	1.45 ± 0.01	28.3 ± 0.2	37.4 ± 0.3	2.28 ± 0.07			p.w.
70	1.61 ± 0.02	30.9 ± 0.6	41.5 ± 0.7	2.47 ± 0.07			p.w.
Reaction	$\text{Th}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{Th}(\text{SO}_4)^{2+}$						
10	3.14 ± 0.01	19.5 ± 0.3	36.5 ± 0.4	6.07 ± 0.09			p.w.
25	3.36 ± 0.02	22.7 ± 0.4	41.9 ± 0.5	6.30 ± 0.09	32.3 ± 0.4	68.4 ± 0.5	p.w.
		20.92 ± 0.74	56.14 ± 1.97	6.17 ± 0.32			[2]
40	3.54 ± 0.02	26.3 ± 0.5	47.5 ± 0.6	6.64 ± 0.09			p.w.
55	3.68 ± 0.04	29.7 ± 0.3	52.8 ± 0.8	6.86 ± 0.10			p.w.
70	3.80 ± 0.03	33.0 ± 0.3	58.0 ± 0.7	7.10 ± 0.10			p.w.
Reaction	$\text{Th}^{4+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Th}(\text{SO}_4)_2$						

10	5.13 ± 0.02	38.5 ± 0.7	66.3 ± 0.8	9.48 ± 0.09			p.w.
25	5.54 ± 0.03	43.5 ± 0.7	75.1 ± 0.8	9.99 ± 0.10	57.9 ± 0.7	114.91 ± 0.8	p.w.
		40.38 ± 1.08	95.69 ± 1.88	9.69 ± 0.27			[2]
40	5.85 ± 0.03	51.6 ± 0.8	86.7 ± 1.0	10.45 ± 0.10			p.w.
55	5.83 ± 0.05	58.2 ± 1.5	94.8 ± 1.7	10.56 ± 0.10			p.w.
70	6.20 ± 0.04	64.5 ± 2.4	105.2 ± 2.5	11.10 ± 0.10			p.w.

As shown in Table 1, the enthalpy of protonation of sulfate is endothermic and becomes more endothermic at higher temperatures (from $21.8 \text{ kJ}\cdot\text{mol}^{-1}$ at $10 \text{ }^\circ\text{C}$ to $30.9 \text{ kJ}\cdot\text{mol}^{-1}$ at $70 \text{ }^\circ\text{C}$). From the enthalpies of protonation in the temperature range from $10 \text{ }^\circ\text{C}$ to $70 \text{ }^\circ\text{C}$, the heat capacity of the sulfate protonation was calculated to be $169 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Despite that the enthalpy of protonation becomes more unfavorable at higher temperatures, the protonation constant of sulfate at $70 \text{ }^\circ\text{C}$ is about six times higher than that at $10 \text{ }^\circ\text{C}$ because, as the temperature is increased, the entropy term ($T\Delta S$) increases more significantly than the enthalpy and, accordingly, the free energy of protonation becomes more favorable.

It is worth noting that the protonation constants obtained with the present calorimetric study are in excellent agreement with previous results of a very accurate potentiometric study, in which a nine terms empirical equation was elaborated to obtain the protonation constants of sulfate in a wide range of temperatures ($0\text{-}250 \text{ }^\circ\text{C}$) and ionic media ($0\text{-}5 \text{ mol}\cdot\text{kg}^{-1}$ NaCl) [13]. The excellent agreement between the values obtained by two different techniques, calorimetry in the present work and potentiometry in the literature [13], at the same ionic strength of 1 M (NaClO_4 in the present work and NaCl in the literature [13]) is shown in Fig. 2.

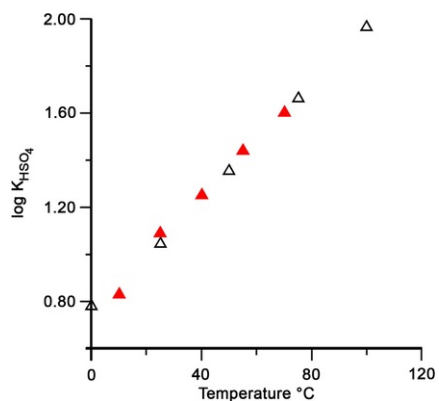


Fig. 2 The protonation constants of sulfate in 1 M NaCl [13] (Δ) and 1 M NaClO_4 (\blacktriangle) (present work) at different temperatures.

In the previous potentiometric study, the enthalpies of protonation were also calculated from the numerical differentiation of the nine terms equation [13]. Considering the different experimental techniques and the difference of ionic media, the values from Ref. [13] are in fair agreement with the enthalpies of protonation measured by calorimetry in the present work: the latter values are about 10–15% higher than the former. Interestingly, the heat capacity of sulfate protonation, calculated from the linear correlation of enthalpy with temperature in the two studies, agrees within 4% ($176 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $169 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in Ref. [13] and present work, respectively).

3.2 Complexation of sulfate with Th(IV) at 10 to 70 °C

The experimental data of the calorimetric titrations are shown in Fig. 3, in the form of Δh_{vj} vs. n_{bar} , where $n_{\text{bar}} = ([\text{Th}(\text{SO}_4)^{2+}] + 2[\text{Th}(\text{SO}_4)_2(\text{aq})])/[\text{Th}]_{\text{total}}$. In this case, the best fit of titration data was obtained by maintaining the protonation constant and enthalpy as fixed parameters in the minimization program and changing simultaneously the equilibrium constants and the enthalpies of reaction for the Th(IV)/sulfate complexation. The values of n_{bar} were calculated using the formation constants and the analytical concentrations of thorium, proton and sulfate present in solution at each step of the titration. Several schemes of speciation, including the formation of $\text{Th}(\text{SO}_4)_3^{2-}$ and $\text{Th}(\text{SO}_4)_4^{4-}$ complexes suggested by earlier studies in the literature [2], were tested by the minimization program. In all cases, the best fit was obtained by assuming the formation of only two complexes, $\text{Th}(\text{SO}_4)^{2+}$ and $\text{Th}(\text{SO}_4)_2(\text{aq})$, according to Eqs. (2) and (3).

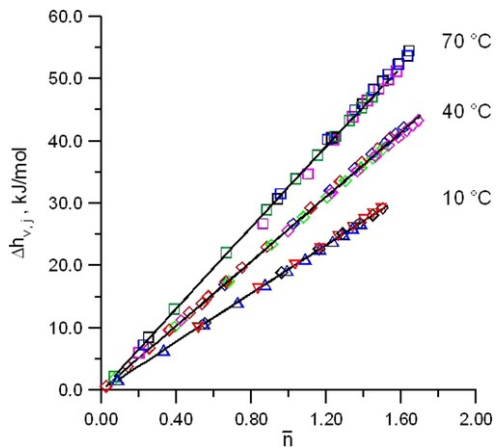
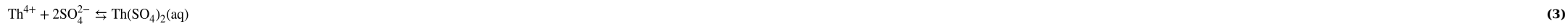
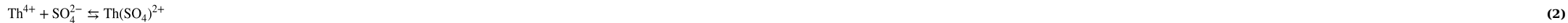


Fig. 3 Calorimetric titrations of the thorium sulfate system: total enthalpy changes per mole of thorium as a function of n_{bar} . $I = 1.05 \text{ mol kg}^{-1} \text{ NaClO}_4$. Symbols with different color and shape represent multiple titrations with different conditions.

The best-fit parameters are summarized in Table 1. From these data, curves simulating the calorimetric titrations were calculated and shown in Fig. 3. The excellent agreement between the calculated curves and the experimental points testifies the quality of the fit and is a direct confirmation of the reliability of the data used to calculate the sulfate protonation heat.

Data in Table 1 indicate that, similar to the trend observed for the protonation of sulfate, though the enthalpy of complexation becomes more unfavorable to the complexation as the temperature is elevated, the complexes are more stable at higher temperatures because of the increasingly more positive entropy of complexation. With the increase of temperature, the increase of the entropy term ($T\Delta S$) exceeds the increase of enthalpy (ΔH), resulting in more negative Gibbs free energy. The increase of entropy with temperature can be interpreted as a result of the increase of entropy of the water molecules released from the highly-ordered solvation shells of Th(IV) and sulfate ions to a bulk solvent that, due to the increase of thermal movements, is more disordered at higher temperatures. From the best linear fit of the enthalpies of complexation as a function of temperature, the heat capacities of complexation were calculated to be: 227 ± 2 and $445 \pm 16 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, for reactions (2) and (3), respectively.

The similarity in the trends of Gibbs free energy, enthalpy and entropy as a function of temperature between the protonation of sulfate and the complexation of sulfate with Th(IV) suggests that the interaction between sulfate and Th(IV) is dominantly electrostatic in nature. Therefore, the stronger protonation and complexation of sulfate with Th(IV) at higher temperatures could be understood in terms of the change of dielectric constant of water that decreases by 30% as the temperature is increased from 0 to 100 °C.

3.3 Calculation of equilibrium constants and enthalpy of protonation and complexation of sulfate with Th(IV) at infinite dilution

The equilibrium constants of protonation and complexation of sulfate with Th(IV) at infinite dilution ($\log \beta^\circ$) were calculated with the Specific Ion Interaction Theory (SIT) [14–16], using Eq. (4),

$$\log \beta^\circ = \log \beta_m - \Delta Z^2 D + \Delta \epsilon I_m \quad (4)$$

where β_m is the equilibrium constant (in molality)⁸ at the ionic strength of I_m , ΔZ^2 is the difference between the sums of the squares of product and reactant ionic charges in reactions 1, 2, and 3, D is the Debye-Hückel term used in the SIT method ($D = A I_m^{1/2} / (1 + B a_j I_m^{1/2})$). Parameters A and $B a_j$ in D are temperature-pressure-dependent constants and are available in the literature [14–16] ($A = 0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ and $B a_j = 1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ at 25 °C and 1 bar). The specific ion interaction terms, $\Delta \epsilon$ at 25 °C for reactions 1, 2, and 3 are calculated with Eqs. (5)–(7), respectively, using the interaction parameters^{9,10} from the literature [2].

$$\Delta \epsilon(1) = \epsilon(\text{Na}^+, \text{HSO}_4^-) - \epsilon(\text{H}^+, \text{ClO}_4^-) - \epsilon(\text{Na}^+, \text{SO}_4^{2-}) = -(0.05 \pm 0.02) \quad (5)$$

$$\Delta \epsilon(2) = \epsilon(\text{ThSO}_4^{2+}, \text{ClO}_4^-) - \epsilon(\text{Th}^{4+}, \text{ClO}_4^-) - \epsilon(\text{Na}^+, \text{SO}_4^{2-}) = -(0.22 \pm 0.12) \quad (6)$$

$$\Delta \epsilon(3) = -\epsilon(\text{Th}^{4+}, \text{ClO}_4^-) - 2\epsilon(\text{Na}^+, \text{SO}_4^{2-}) = -(0.33 \pm 0.1) \quad (7)$$

For the calculation of $\log\beta^\circ$ at temperatures other than 25 °C, the following approaches were adopted: (1) using $\log\beta$ (molarity) in Table 1 as $\log\beta$ (molality) without correction because the correction is smaller than the magnitude of experimental uncertainties; (2) using the values of A at different temperatures from the literature [16], and a constant value of $B_{a_1} = 1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ for all temperatures as recommended by the NEA review [16]; (3) using the values of $\Delta\varepsilon$ at 25 °C (Eqs. (5)-(7)) for all temperatures, because the values at other temperatures were not known and the errors thus introduced are probably quite small.^{††} Besides, the values of $(\partial\varepsilon/\partial T)_p$ for the reactants and products may balance out each other so that $\Delta\varepsilon$ for many reactions remains approximately constant up to 100 °C [17]. The calculated values of $\log\beta^\circ$ are summarized in Table 1. The values for the protonation and complexation of sulfate with Th(IV) at 25 °C agree with those recommended by the NEA review within the error limits.

The enthalpy of complexation can be corrected to infinite dilution by the method described in the literature [18]. For a system studied at tracer concentrations, the correction can be expressed by Eq. (8), where $\Delta_r H_m$ and $\Delta_r H_m^\circ$ are the enthalpies of reaction at ionic strengths of I_m and zero, respectively; L_1 is the relative partial molar enthalpy of water and r is the stoichiometric coefficient of water in the reaction involved; A_L is the Debye-Hückel parameter for the enthalpy ($A_L = 1.986 \text{ kJ}\cdot\text{kg}^{0.5}\cdot\text{mol}^{-1.5}$ at 25 °C and 1 atm); ΔZ^2 is the difference between the sums of the squares of product and reactant ionic charges in the reactions; m is the concentration of the background electrolyte in molality (for a 1-1 electrolyte such as NaClO_4 , $I_m = m$); $\Delta\varepsilon_L$ is an ion interaction term and equals to $\sum \nu_i \varepsilon_L(i,j)$, where ν_i is the stoichiometric reaction coefficients (positive for the products and negative for the reactants) and $\varepsilon_L = (\partial\varepsilon/\partial T)_p$.

$$\Delta_r H_m - rL_1 = \Delta_r H_m^\circ + \frac{3A_L \Delta(Z^2) \sqrt{I_m}}{4(1 + 1.5\sqrt{I_m})} - RT^2 m \Delta\varepsilon_L \quad (8)$$

The value of L_1 in a 1-1 ionic medium (e.g., NaClO_4 in the present work) can be expressed by Eq. (9):

$$L_1 \approx \frac{M_W}{1000} \left[-\frac{3A_L}{2(1.5^3)} \left(t - 2\ln t - \frac{1}{t} \right) \right] \quad (9)$$

where $t = (1 + 1.5I_m^{0.5})$. At $I_m = 1.05 \text{ mol}\cdot\text{kg}^{-1}$, the value of L_1 is small. Also, because no water molecules are involved in reactions (1), (2), and (3), $r = 0$. As a result, the second term on the left side of Eq. (8) can be neglected.

In addition, the third term on the right side of Eq. (8) can be neglected because $(\partial\varepsilon/\partial T)_p$ is small and the values of $(\partial\varepsilon/\partial T)_p$ for the reactants and products may balance out each other [17]. As a result, the difference between $\Delta_r H_m$ and $\Delta_r H_m^\circ$ is determined by the second term on the right side of Eq. (8), an ionic strength term depending on I_m and ΔZ^2 .

It should be noted that the complexation of Th(IV)/sulfate studied in the present work is not a system with the reactants and products at trace concentrations. Therefore, the applicability of Eqs. (8) and (9) to the present work may be limited. However, on the assumption that the ionic strength term in Eq. (8) is still the dominant correction term, it is estimated that, at 25 °C, the values of $\Delta_r H_m$ should be corrected by $-(0.6 \times \Delta Z^2) \text{ kJ}\cdot\text{mol}^{-1}$ to obtain $\Delta_r H_m^\circ$ for the system in the present study ($I = 1.05 \text{ mol}\cdot\text{kg}^{-1}$). The enthalpies of reaction at 25 °C for reactions (1), (2), and (3), with $\Delta Z^2 = -4$, -16 , and -24 , respectively, were accordingly corrected to infinite dilution and listed in Table 1, together with the corresponding values of $T\Delta S^\circ$.

3.4 Trends in complexation of sulfate with Th(IV), U(IV), Np(IV), and Pu(IV)

The similarity in the trends of Gibbs free energy, enthalpy and entropy as a function of temperature between the protonation of sulfate and the complexation of sulfate with Th(IV) suggests that the interaction between sulfate and Th(IV) is dominantly electrostatic in nature. Therefore, across the actinide series from Th^{4+} , U^{4+} , Np^{4+} , and Pu^{4+} as the ionic radii are decreased, the stability of the sulfate complexes is expected to increase and a linear correlation could exist between the thermodynamic functions and the ionic radii. Fig. 4 shows the plots of Gibbs free energy, enthalpy, and entropy of the monosulfate complexes of the tetravalent actinide cations (at 25 °C and zero ionic strength) as a function of the ionic radii. The data for Th^{4+} are from the present work. The values of $\log\beta^\circ$ for U^{4+} , Np^{4+} and Pu^{4+} , and the value of ΔH° for U^{4+} and Np^{4+} are all from two critical comprehensive reviews on these elements [14,15]. The value of enthalpy for Pu^{4+} is taken from a recent publication [19]. The values of ionic radii are for the tetravalent actinide cations with coordination number of 8 and are taken from the literature [20].

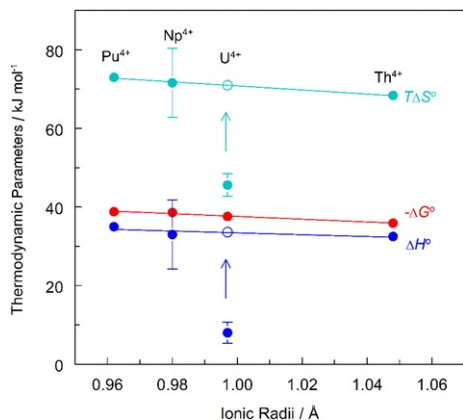


Fig. 4 Thermodynamic parameters for the formation of monosulfate complexes of tetravalent actinide ions at infinite dilution vs. ionic radii. The open circles represent the values of ΔH° and $T\Delta S^\circ$ for USO_4^{2+} complex suggested by the present study on the basis of the correlation.

Fig. 4 shows very good linear relationships between the thermodynamic functions of complexation and the ionic radii of tetravalent actinide ions, except U^{4+} . Evidently, the Gibbs free energy for USO_4^{2+} fits well with the correlation but the value of enthalpy for USO_4^{2+} is significantly off from the correlation, which accordingly results in the entropy term ($T\Delta S^\circ$) that is also off from the correlation. This observation strongly suggests that the stability constant (and so the Gibbs free energy) recommended for USO_4^{2+} by the review [14,15] is reliable, but the value of enthalpy (and so the entropy) recommended for USO_4^{2+} by the review ($8.0 \pm 2.7 \text{ kJ}\cdot\text{mol}^{-1}$ [14,15]) probably needs re-evaluation. It should be noted that this value was calculated by the review [14,15] using the temperature dependence (10, 25, and 40 °C) of the equilibrium constants ($\text{U}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{USO}_4^{2+} + \text{H}^+$) measured by solvent extraction [21]. We recommend using calorimetric measurements similar to those for Th(IV)/sulfate in the present work to determine the reaction heat and re-evaluate the enthalpy of complexation for U(IV)/sulfate.

Data in Fig. 4 also shows that the enthalpy (ΔH°) and entropy (ΔS°) of complexation between sulfate and the tetravalent actinide cations increase as the ionic radii decrease along the An^{4+} series from Th^{4+} to Pu^{4+} . These trends could be due to the stronger interactions between water molecules and smaller An^{4+} ions that make the hydration sphere around Pu^{4+} “tighter” and more organized than that around Th^{4+} . As a result, upon complexation with sulfate, more energy is required to dehydrate Pu^{4+} than Th^{4+} (more positive enthalpy for the former), and higher degree of disorder is created in the system of Pu^{4+} than Th^{4+} (more positive entropy for the former) because the more ordered water molecules from Pu^{4+} are released into the bulk water.

5 Conclusion

In the temperature range 10–70 °C, Th(IV) forms two mononuclear successive sulphate complexes in aqueous solution of 1 M NaClO_4 . The stability of the complexes increases as the temperature is increased. The complexation reactions ($\text{Th}^{4+} + q\text{SO}_4^{2-} \rightleftharpoons \text{Th}(\text{SO}_4)_q^{(4-2q)+}$, where $q = 1$ and 2) are endothermic and become more endothermic at higher temperatures. Despite of this trend in the enthalpy, the formation of Th(IV)/sulfate complexes is favoured at high temperatures because the entropy term ($T\Delta S$) also increases with temperature and the increase in $T\Delta S$ exceeds the increase in ΔH as the temperature is increased. Excellent linear relationships exist between the thermodynamic functions for the complexation of sulfate with tetravalent actinides (Th^{4+} , Np^{4+} , and Pu^{4+}) and their ionic radii, reflecting the prevalently electrostatic nature of the complexes. The deviation of the data for U^{4+} from the linear correlation suggests that the values of enthalpy of complexation for $\text{U}^{4+}/\text{SO}_4^{2-}$ complexes in the literature are questionable and should be re-evaluated when calorimetric data become available.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jct.2017.09.025>.

References

- [1] IAEA, Thorium fuel cycle—Potential benefits and challenges, IAEA-TECDOC-1450, 2005, International Atomic Energy Agency; Vienna.
- [2] F.J. Mompean, J. Perrone and M. Illemassène, (Eds.), *Chemical Thermodynamics of Thorium* **vol. 11**, 2007, OECD Publishing.
- [3] S.K. Patil and V.V. Ramakrishna, *Radiochim. Acta* **18**, 1972, 190–192.
- [4] J. Hála and H. Miyamoto, *J. Phys. Chem. Ref. Data* **36**, 2007, 1417–1736.
- [5] A.J. Zielen, *J. Am. Chem. Soc.* **8**, 1959, 5022–5028.
- [6] P. Di Bernardo, P. Zanonato, L. Rao, A. Bismondo and F. Endrizzi, *Dalton Trans.* **40**, 2011, 9101–9105.
- [7] G.H. Jeffrey, J. Bassett, J. Mendham, R.C. Denney, Vogel’s Textbook of Quantitative Chemical Analysis, John Wiley & Sons, fifth ed., vol. 14, 1990.
- [8] G. Gran, *Analyst* **77**, 1952, 661–671.
- [9] (a) J.J. Christensen, L.D. Hansen and R.M. Izatt, Handbook of Proton Ionization Heats and Related Thermodynamic Quantities, 1976, John Wiley and Sons; New York;
(b) Z. Zhang, G. Helms, S.B. Clark, G. Tian, P.L. Zanonato and L. Rao, *Inorg. Chem.* **48**, 2009, 3814–3824.
- [10] P. Zanonato, P. Di Bernardo, A. Bismondo, G. Liu, X. Chen and L. Rao, *J. Am. Chem. Soc.* **126**, 2004, 5515–5522.
- [11] L. Rao, T.G. Srinivasan, A. Yu Garnov, P. Zanonato, P. Di Bernardo and A. Bismondo, *Geochim. Cosmochim. Acta* **68**, 2004, 4821–4830.
- [12] R. Arnek, *Ark. Kemi.* **32**, 1970, 81–88.
- [13] A.G. Dickson, D.J. Wesolowski, D.A. Palmer and R. Mesmer, *J. Phys. Chem.* **94**, 1990, 7978–7985.
- [14] F.J. Mompean, M. Illemassene, C. Domenech-Orti and K. Ben Said, (Eds.), *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium* 2003, Elsevier B.V.; Amsterdam.
- [15] H. Wanner and I. Forest, (Eds.), *Chemical Thermodynamics of Uranium* **vol. 1**, 1992, North Holland Elsevier Science Publishers B. V.,; Amsterdam, The Netherlands.
- [16] F.J. Mompean and M. Illemassène, J. Perrone, (Eds.), *Chemical Thermodynamics of complexes and compounds of U, Np, Pu, Am, Tc, Zr, Ni and Se with selected organic ligands* **vol. 9**, 2005, North Holland Elsevier Science Publishers B. V.; Amsterdam, The Netherlands.
- [17] A.V. Plyasunov and I. Grenthe, *Geochim. Cosmochim. Acta* **58**, 1994, 3561–3582.
- [18] I. Grenthe, K. Spahiu and A.V. Plyasunov, Estimations of Medium Effects on Thermodynamic Data, Chapt. IX1997, NEA/OECD; Paris, 412.
- [19] Y.X. Xia, J.I. Friese, D.A. Moore, P.P. Bachelor and L. Rao, *J. Radioanal. Nucl. Chem.* **274**, 2007, 79–86.
- [20] G.R. Choppin, E.N. Rizkalla, Solution chemistry of actinides and lanthanides, in: K.A. Gschneidner, Jr., L. Eyring, G.R. Choppin, G.H. Lander (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 18 Lanthanides/Actinides Chemistry, Elsevier Science B. V., 1994 (Chapter 128).
- [21] R.A. Day, R.N. Wilhite and F.D. Hamilton, *J. Am. Chem. Soc.* **77**, 1955, 3180–3182.

Footnotes

[†]The high gamma radiation associated with the short lived daughter products of ²³²U is also a disadvantage of the thorium fuel cycle because it necessitates remote reprocessing and refabrication of fuel.

[‡]The second protonation ($\text{H}^+ + \text{HSO}_4^- \rightleftharpoons \text{H}_2\text{SO}_4$) is very weak and can be ignored in this study.

[§]The constants in molarity, β_M , are converted to those in molality, β_m , according to the literature [16].

**(Na^+ , HSO_4^-) = $-(0.01 \pm 0.02)$, (H^+ , ClO_4^-) = 0.14 ± 0.02 , (Na^+ , SO_4^{2-}) = $-(0.184 \pm 0.002)$ (omitting the ₂ term), (ThSO_4^{2+} , ClO_4^-) = 0.3 ± 0.1 , (Th^{4+} , ClO_4^-) = 0.7 ± 0.1 [2].

^{††}The values of $(\partial\epsilon/\partial T)_p$ are usually $\leq 0.005 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for temperatures below 200 °C [14].

Appendix A. Supplementary data

[Multimedia Component 1](#)

Supplementary data

Highlights

- Complexation of Th(IV) with sulfate is enhanced at higher temperatures.
 - The enhancement is mainly due to ~~the~~ increasingly more positive entropy of complexation ~~that exceeds the increase of enthalpy~~.
 - ~~The enthalpy of Th(IV)/sulfate complexation from this work~~Data suggests ~~re-evaluation of that~~ the enthalpy of U(IV)/sulfate in the literature ~~my need to be re-evaluated~~.
-

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