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

CrossMark

Plinio Di Bernardo [a], Francesco Endrizzi [a,b], Andrea Melchior [c], Zhicheng Zhang [d], Pier Luigi Zanonato [a,*], Linfeng Rao [d,*]

[a] *Dipartimento di Scienze Chimiche, University of Padova, Via Marzolo 1, 35131 Padova, Italy*
[b] *Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz, 1, 76344 Eggenstein-Leopoldshafen, Germany*
[c] *Dipartimento Politecnico di Ingegneria e Architettura, Laboratori di Chimica, Via delle Scienze 99, 33100 Udine, Italy*
[d] *Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

ARTICLE INFO

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, $Th(SO_4)^{2+}$ and $Th(SO_4)_2(aq)$, 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 (Th^{4+}, U^{4+}, Np^{4+}, and Pu^{4+}) are discussed in terms of electrostatic interactions that correlate with the ionic radii of the metal cations.

© 2017 Elsevier Ltd.

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 [232]U 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 trans-

port 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 $Th(SO_4)_2(aq)$ 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

* Corresponding authors.
  E-mail address: lrao@lbl.gov (L. Rao).
  [†] The high gamma radiation associated with the short lived daughter products of [232]U is also a disadvantage of the thorium fuel cycle because it necessitates remote reprocessing and refabrication of fuel.

method, including ion exchange and solvent extraction. The data in the literature clearly show that, at relatively high acidities and nearly constant ionic strength, $Th(SO_4)^{2+}$ and $Th(SO_4)_2(aq)$ 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 el 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 that 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 (Na,H)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 ± 0.3 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 ~2.7 mL of a solution of perchloric acid (20–100 mM) or a solution 100 mM of perchloric acid to ~2.7 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 ~2.7 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 ($Q_{ex,j}$, where $j = 1$ to n) were collected. In order to obtain the net complex formation heat at the j-th point ($Q_{cpx,j}$), the values of $Q_{ex,j}$ were corrected for the heat of dilution of the titrant solution ($Q_{dil,j}$), determined in separate runs, and for the heat due to the protonation of sulfate ($Q_{p,j}$), 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): $\Delta h_{v,j} = \sum Q_{cpx,j}/n_{Th}$, 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.

$$H^+ + SO_4^{2-} \leftrightarrows HSO_4^- \tag{1}$$

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

Despite that the enthalpy of protonation becomes more unfavorable at higher temperatures, the protonation constant of sulfate at 70 °C is about six times higher than that at 10 °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 (0–250 °C) and ionic media (0–5 mol·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.

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 J·K^{-1}·mol^{-1} and 169 J·K^{-1}·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 $\Delta h_{v,j}$ vs. n_{bar}, where $n_{bar} = ([Th(SO_4)^{2+}] + 2[Th(SO_4)_2(aq)])/[Th]_{total}$. 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

---

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