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### **Title**

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# Spectrophotometric and Calorimetric Studies of U(VI) Complexation with Sulfate at 25-70°C

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## ABSTRACT

Sulfate, one of the inorganic constituents in the groundwater of nuclear waste repository, could affect the migration of radioactive materials by forming complexes. Spectrophotometric and microcalorimetric titrations were performed to identify the U(VI)/sulfate complexes and determine the equilibrium constants and enthalpy of complexation at 25 – 70°C. Results show that U(VI) forms moderately strong complexes with sulfate, i.e.,  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$ , in this temperature range and the complexes become stronger as the temperature is increased: 2-fold and 10-fold increases in the stability constants of  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$ , respectively, when the temperature is increased from 25°C to 70°C. The complexation is endothermic and entropy-driven, showing typical characteristics of inner-sphere complexation and “hard acid”/“hard base” interactions. The thermodynamic trends are discussed in terms of dehydration of both the cation ( $\text{UO}_2^{2+}$ ) and the anion ( $\text{SO}_4^{2-}$ ) as well as the effect of temperature on the structure of water.

*Key Words:* Uranium, sulfate, complexation, temperature effect

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## 1. INTRODUCTION

One of the approaches to safe management of high-level nuclear wastes (HLW) calls for the disposal of HLW in geological repositories. Though the engineered barrier systems are expected to last a very long time after the repository is closed, they may gradually deteriorate and eventually lose integrity. Consequently, water could contact the waste, dissolve it, and carry radionuclides out of the repository. Since uranium is the most abundant radionuclide in nuclear wastes and is most likely to be in the hexavalent state under environmental conditions, the migration of U(VI) in the postclosure chemical environment of the repository is a great concern to long-term repository performance.

Because the temperature of the HLW repository could remain significantly higher than the ambient even thousands of years after the closure of the repository, predictions of the chemical behavior of U(VI) in the repository cannot be made without reliable thermodynamic data concerning the interactions of U(VI) with the ligands that exist in the groundwater of the repository (e.g.,  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$ ) at elevated temperatures. At present, thermodynamic data on actinide complexation at elevated temperatures are scarce and highly scattered [1-3]. For example, the stability constants ( $\log \beta$ ) of the U(VI)/sulfate complexes in the literature range from 1.7 to 3.8 for  $\text{UO}_2\text{SO}_4(\text{aq})$  and 2.4 to 4.4 for  $\text{UO}_2(\text{SO}_4)_2^{2-}$  at or near 20 – 25°C [1,4-11]. The enthalpy of complexation derived from the temperature dependency of stability constants [12] was found to differ significantly from those obtained by calorimetry [13-15]. The lack of reliable geochemical thermodynamic data could lead to conservative decisions that have too big safety margins and raise the cost of the project. To help with the performance assessment of the HLW repository and fill the gap in thermodynamic data on actinide complexation at elevated temperatures, we have studied the complexation of actinides (Th, U,

Np and Pu) with selected organic and inorganic ligands at elevated temperatures. This paper summarizes the results of the complexation of U(VI) with sulfate at 25 - 70°C.

## **2. EXPERIMENTAL**

### **2.1 Chemicals**

All chemicals except uranium were reagent grade or higher. Water from a Milli-Q system was used in preparing all solutions. Details on the preparation and standardization of the U(VI) stock solution were provided elsewhere [16]. Solutions of sulfate were prepared by dissolving solid Na<sub>2</sub>SO<sub>4</sub> in water. NaClO<sub>4</sub> was used as background electrolyte to maintain the ionic strength of working solutions. Due to the use of Na<sub>2</sub>SO<sub>4</sub> as the titrant in the spectrophotometric and calorimetric titrations, the ionic strength of the working solutions may deviate from 1.0 mol·dm<sup>-3</sup>, but the concentration of sodium ion remains constant at 1.0 mol·dm<sup>-3</sup> (25°C).

### **2.2 Spectrophotometry**

UV/Vis absorption spectra of U(VI) (380 - 480 nm, 0.2 nm interval) were collected on a Varian Cary-5G spectrophotometer equipped with sample holders that were maintained at constant temperatures by a 1×1 Peltier controller. 10 mm quartz cells were used. Multiple titrations with different concentrations of U(VI) were performed. The initial concentrations of U(VI) in the cells ranged from 0.0177 to 0.0708 mol·dm<sup>-3</sup>. In each titration, appropriate aliquots of the titrant (0.500 mol·dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>) were added into the cell and mixed thoroughly before the absorption spectrum was collected. Usually 10 - 15 additions were made, thus generating a set of 10 - 15 spectra in each titration. The stability constant of the U(VI)/sulfate complex (on the molarity scale) was calculated by non-linear least-square regression using the Hyperquad program [17].

### **2.3 Microcalorimetry**

Calorimetric titrations were conducted at 25, 40, 55 and 70°C with an isothermal microcalorimeter (Model ITC 4200, Calorimetry Sciences Corp). The microcalorimeter uses a “twin” heat flow design to reach maximum sensitivity. The reaction heat is measured from the difference in the heat flows between the sample and the reference cells. The volume of the cells is about 1.2 cm<sup>3</sup>. The titrant is delivered into the sample cell through a long and thin needle from a 100 µl or 250 µl syringe. The syringe is driven by a precision stepper motor that guarantees accurate delivery of the titrant. The performance of the calorimeter has been tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The results (in kJ·mol<sup>-1</sup>) are  $-47.7 \pm 0.3$  (25 °C),  $-46.8 \pm 0.2$  (40 °C),  $-45.8 \pm 0.5$  (55 °C) and  $-45.2 \pm 0.5$  (70 °C), compared well with the values in the literature:  $-46.0 \pm 0.3$  at 45 °C and  $-46.2 \pm 0.3$  at 70 °C [18],  $-46.81 \pm 0.02$  at 35 °C and  $-46.0 \pm 0.02$  at 50 °C [19].

Multiple titrations with different initial concentrations of U(VI) were conducted at each temperature. For each titration,  $n$  additions were made (usually  $n = 40 - 50$ ), resulting in  $n$  experimental values of the heat generated in the reaction cell ( $Q_{\text{ex},j}$ , where  $j = 1$  to  $n$ ). These values were corrected for the heat of dilution of the titrant ( $Q_{\text{dil},j}$ ), which was determined in separate runs. The net reaction heat at the  $j$ -th point ( $Q_{\text{r},j}$ ) was obtained from the difference:  $Q_{\text{r},j} = Q_{\text{ex},j} - Q_{\text{dil},j}$ . The program Letagrop [20] was used to analyze the data and calculate the thermodynamic parameters.

### 3. RESULTS AND DISCUSSION

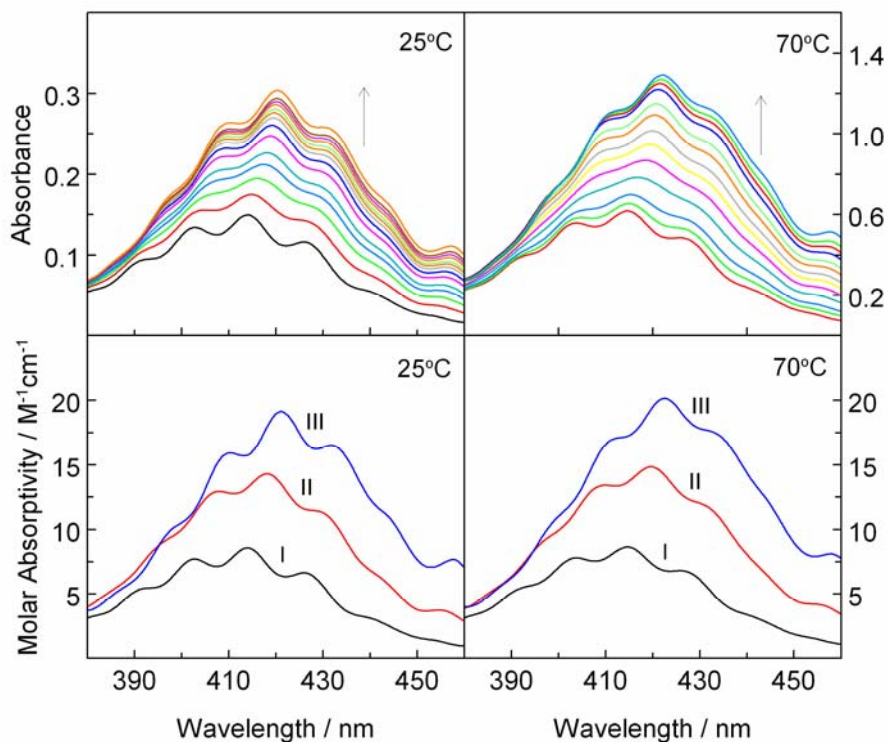
#### 3.1 Stability constants of U(VI)/sulfate complexes at variable temperatures

The absorption spectra of two representative spectrophotometric titrations at 25 and 70°C are shown in Figure 1. The spectra at 40 and 55°C are not shown, but the trends in the spectra

features at each temperature are similar, i.e., the absorption bands of  $\text{UO}_2^{2+}$  were red-shifted and the absorbance intensified as the concentration of sulfate was increased. Analysis by the Hyperquad program indicated that there are three absorbing species of U(VI) and the spectra were best-fitted with the formation of two successive complexes:



The formation constants of  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  at 25, 40, 55 and 70°C were calculated and listed in Table 1. In the calculation, the protonation constants of sulfate at different temperatures from the literature [21] were used. The uncertainties of  $\log \beta_M$  in the table are “composite” values obtained by taking into consideration the statistic deviations of repetitive titrations at each temperature. The “composite” uncertainties are about 2 – 4 times larger than the standard deviations calculated by the Hyperquad program. The latter are usually quite small (< 0.01) and probably unrealistic.



**Fig. 1** Representative spectrophotometric titrations of U(VI)/sulfate complexation.  $I = 1.0 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}(\text{ClO}_4/\text{SO}_4)$ . Upper figures – normalized absorption spectra collected in the titration at 25 and 70°C. Titrant:  $0.500 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{SO}_4$ .  $C_{\text{Na}_2\text{SO}_4} = 0 - 0.22 \text{ mol}\cdot\text{dm}^{-3}$  in the titration. Initial solution in cuvette: 2.50 mL;  $1.77 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3} \text{ UO}_2(\text{ClO}_4)_2/2.12 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$  (25°C),  $7.08 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3} \text{ UO}_2(\text{ClO}_4)_2/8.48 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$  (70°C). Lower figures – calculated molar absorptivity of  $\text{UO}_2^{2+}$  (I),  $\text{UO}_2\text{SO}_4(\text{aq})$  (II) and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  (III) at 25 and 70°C.

**Table 1** Thermodynamic parameters for the complexation of U(VI) with sulfate,  $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$   $\text{Na}(\text{ClO}_4/\text{SO}_4)$ . (sp – spectrophotometry, cal – calorimetry, sx – solvent extraction; p.w. – present work).

Reaction	$t$ °C	Method	$\log \beta_M$	$\log \beta_m$	$\text{Log } \beta^0$ (by SIT)	$\Delta H$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Ref.
$\text{UO}_2^{2+} + \text{SO}_4^{2-} = \text{UO}_2\text{SO}_4(\text{aq})$	25	sp, cal	$1.96 \pm 0.06$	$1.94 \pm 0.06$	$3.23 \pm 0.08$	$17.7 \pm 0.3$	$96 \pm 1$	p.w.
						$16.1 \pm 1.7^*$		p.w.
					$3.15 \pm 0.02$	$19.5 \pm 1.6$		[1]
	40	sp, cal	$2.04 \pm 0.06$	$2.02 \pm 0.06$	$3.35 \pm 0.08$	$21.0 \pm 0.4$	$106 \pm 1$	p.w.
	55	sp, cal	$2.20 \pm 0.06$	$2.18 \pm 0.06$	$3.56 \pm 0.08$	$22.8 \pm 0.6$	$111 \pm 2$	p.w.
	70	sp, cal	$2.32 \pm 0.03$	$2.30 \pm 0.03$	$3.74 \pm 0.08$	$25.9 \pm 0.7$	$120 \pm 2$	p.w.
$\text{UO}_2^{2+} + 2\text{SO}_4^{2-} = \text{UO}_2(\text{SO}_4)_2^{2-}$	25	sp, cal	$2.97 \pm 0.03$	$2.93 \pm 0.03$	$4.22 \pm 0.15$	$43.2 \pm 0.9$	$201 \pm 3$	p.w.
						$43.0 \pm 2.1^*$		p.w.
					$4.14 \pm 0.07$	$35.1 \pm 1.0$		[1]
	40	sp, cal	$3.34 \pm 0.03$	$3.30 \pm 0.03$	$4.63 \pm 0.15$	$37.8 \pm 0.4$	$184 \pm 1$	p.w.
	55	sp, cal	$3.71 \pm 0.06$	$3.67 \pm 0.06$	$5.06 \pm 0.16$	$38.2 \pm 1.2$	$187 \pm 4$	p.w.
	70	sp, cal	$3.94 \pm 0.15$	$3.90 \pm 0.15$	$5.34 \pm 0.16$	$37.5 \pm 0.7$	$184 \pm 2$	p.w.
$\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$	25	cal	$1.07 \pm 0.09$			$22.7 \pm 0.3$	$97 \pm 3$	[21]
	40	cal	$1.14 \pm 0.12$			$32 \pm 2$	$124 \pm 10$	
	55	cal	$1.28 \pm 0.09$			$40 \pm 5$	$146 \pm 18$	
	70	cal	$1.38 \pm 0.09$			$50 \pm 5$	$172 \pm 18$	

\* Values obtained by the van't Hoff plot using the stability constants at variable temperatures.

To allow the comparison of stability constants at different temperatures, the constants in molarity need to be converted to the constants in molality according to eq.(3) [22],

$$\log \beta_m = \log \beta_M + \sum_r \nu_r \log \mathcal{G} \quad (3)$$

where  $\beta_m$  and  $\beta_M$  are the equilibrium constants of a reaction in molality and molarity, respectively,  $\mathcal{G}$  is the ratio of the values of molality to molarity for the specific ionic medium.

For  $1.0 \text{ mol}\cdot\text{dm}^{-3}$   $\text{NaClO}_4$ ,  $\mathcal{G}$  equals  $1.05 \text{ dm}^3$  of solution per kg of water.  $\sum_r \nu_r$  is the sum of



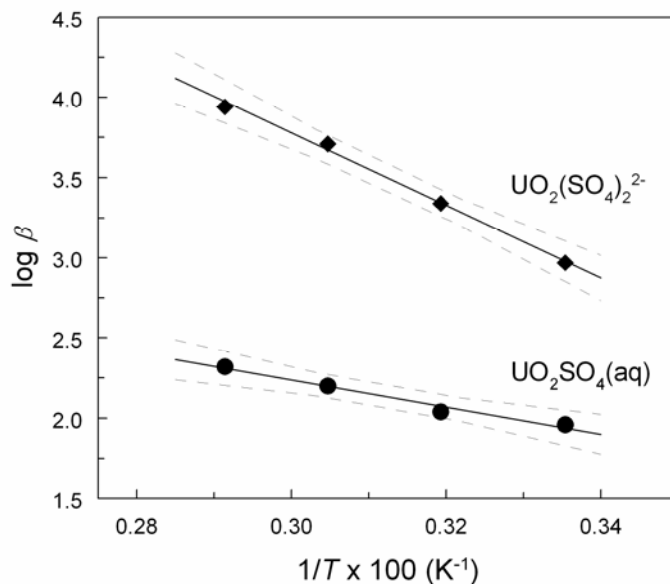
stoichiometric coefficients of the reaction ( $\nu_i$  is positive for products and negative for reactants). The converted stability constants ( $\log \beta_m$ ) are shown in Table 1.

Data in Table 1 indicate that U(VI) forms sulfate complexes with moderate strength and the complexes become stronger as the temperature is increased – 2-fold and 10-fold increases in the stability constants of  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$ , respectively, as the temperature is increased from 25 to 70°C. The enhancement of complexation by the increase of temperature is also suggested by the deconvoluted spectra of  $\text{UO}_2^{2+}$ ,  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  shown in the lower part of Fig.1. The shift of wavelength of maximum absorption ( $\Delta\lambda$ ) and the increase in the molar absorptivity ( $\Delta\varepsilon$ ) due to complexation are all larger at 70°C than those at 25°C as summarized in Table 2.

**Table 2** Features of absorption spectra of  $\text{UO}_2^{2+}$ ,  $\text{UO}_2(\text{SO}_4)(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  at 25 and 70°C,  $I = 1.0 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}(\text{ClO}_4/\text{SO}_4)$ .  $\lambda$  - wavelength of maximum absorption,  $\varepsilon$  - molar absorptivity at the wavelength of maximum absorption.

$t, ^\circ\text{C}$	$\lambda \text{ (nm)} / \varepsilon \text{ (M}^{-1}\text{cm}^{-1}\text{)}$			$\Delta\lambda \text{ (nm)}$		$\Delta\varepsilon \text{ (M}^{-1}\text{cm}^{-1}\text{)}$	
	$\text{UO}_2^{2+}$	$\text{UO}_2(\text{SO}_4)$	$\text{UO}_2(\text{SO}_4)_2^{2-}$	$\text{UO}_2^{2+} \rightarrow \text{UO}_2(\text{SO}_4)$	$\text{UO}_2^{2+} \rightarrow \text{UO}_2(\text{SO}_4)_2^{2-}$	$\text{UO}_2^{2+} \rightarrow \text{UO}_2(\text{SO}_4)$	$\text{UO}_2^{2+} \rightarrow \text{UO}_2(\text{SO}_4)_2^{2-}$
25	414.0 / 8.58	418.1 / 14.30	421.0 / 19.14	4.1	7.0	5.72	10.56
70	414.6 / 8.65	419.6 / 14.85	422.4 / 20.15	5.3	7.8	6.20	11.50

The van't Hoff plot ( $\log \beta_M$  vs.  $1/T$ ) is shown in Fig. 2. From the slope of the linear fit (weighted by the uncertainties), the “average” enthalpies of complexation in the temperature range (25 – 70°C) were calculated to be  $(16.1 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$  and  $(43.0 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$  for reactions (1) and (2), respectively.

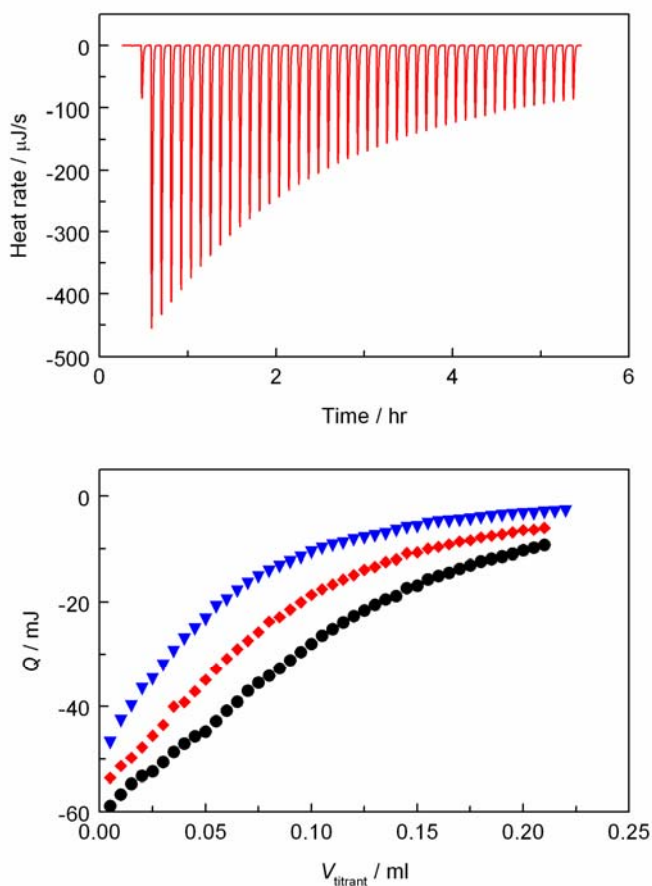


**Fig. 2**  $\log \beta$  vs.  $1/T$  for the complexation of U(VI) with sulfate. Solid symbols (●, ◆): experimental data ( $I = 1.0 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}(\text{ClO}_4/\text{SO}_4)$ ); Solid line – weighted (by uncertainty) linear fit; dashed lines – upper and lower limits of the confidence band at the 95% level.

### 3.2 Enthalpy of complexation between U(VI) and sulfate at elevated temperatures

Figure 3 shows a representative calorimetric titration of the complexation of U(VI) with sulfate at 70°C. The observed reaction heat includes the contributions from several reactions including the protonation of sulfate and the complexation of U(VI) with sulfate. Thus, to calculate the enthalpy of U(VI)/sulfate complexation from the reaction heat, a number of parameters, including the protonation constant and enthalpy of sulfate and the stability constants of  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  must be known. In this work, we have used the protonation constants and enthalpy of sulfate previously reported [21] and the stability constants of  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  determined by spectrophotometry in this work (Table 1). The enthalpies of complexation at 25, 40, 55 and 70°C, as well as the entropies of complexation calculated accordingly, are summarized in Table 1. The enthalpies of complexation at 25°C

directly determined by calorimetry in this work ( $17.7 \pm 0.3$  and  $43.2 \pm 0.9$   $\text{kJ}\cdot\text{mol}^{-1}$  for  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$ ) are in excellent agreement with those obtained by the van't Hoff plot ( $16.1 \pm 1.7$  and  $43.0 \pm 2.1$   $\text{kJ}\cdot\text{mol}^{-1}$  for  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$ ), and in fairly good agreement with those selected by the NEA review for infinitely dilute solutions ( $19.5 \pm 1.6$  and  $35.1 \pm 1.0$   $\text{kJ}\cdot\text{mol}^{-1}$  for  $\text{UO}_2\text{SO}_4(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$ ) [1].

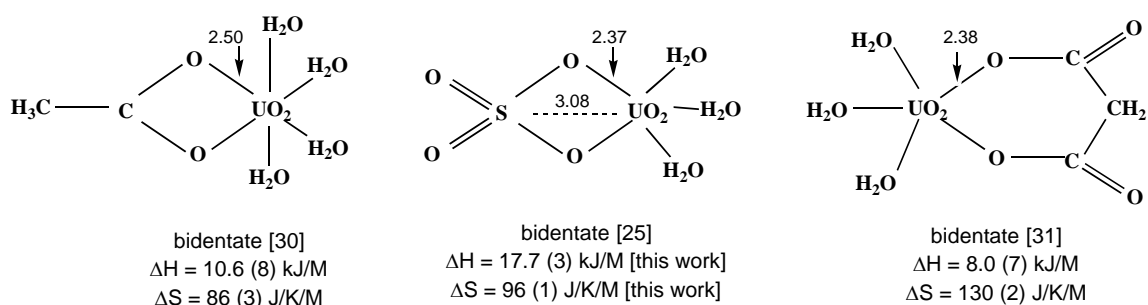


**Fig. 3** Calorimetric titration of U(VI) sulfate complexation. (top) A representative thermogram of titration; (bottom) Stepwise heat vs. titrant volume.  $I = 1.0$   $\text{mol}\cdot\text{dm}^{-3}$   $\text{Na}(\text{ClO}_4/\text{SO}_4)$ ,  $t = 70^\circ\text{C}$ . Cup: 0.900 mL,  $C_{\text{U}}/C_{\text{H}}$  ( $\text{mol}\cdot\text{dm}^{-3}$ ) =  $1.97 \times 10^{-2}/2.36 \times 10^{-2}$  (●),  $1.475 \times 10^{-2}/1.77 \times 10^{-2}$  (◆),  $9.85 \times 10^{-3}/1.18 \times 10^{-2}$  (▼); titrant:  $0.500$   $\text{mol}\cdot\text{dm}^{-3}$   $\text{Na}_2\text{SO}_4$ ,  $5$   $\mu\text{L}/\text{addition}$ .

Data in Table 1 show that, in the temperature range from 25 °C to 70 °C, both the enthalpy and entropy of complexation are positive. The complexation is entropy-driven, characteristic of "hard acid" and "hard base" interactions and inner-sphere complexation [23]. Dehydration of both the cations ( $\text{UO}_2^{2+}$ ) and anions ( $\text{SO}_4^{2-}$ ) plays the most significant roles in the complexation, the energy required for dehydration contributing to the positive enthalpy and the number of water molecules released from the hydration sphere contributing to the positive entropy. For the formation of  $\text{UO}_2\text{SO}_4(\text{aq})$ , both the enthalpy and entropy of complexation increases as the temperature is increased, making opposite contributions to the temperature effect on the Gibbs free energy (and thus on the stability of the complex). The complexation is enhanced at higher temperatures because increase in the entropy term ( $T\Delta S$ ) exceeds the increase in the enthalpy. The increase of entropy with the temperature could be the consequence of a more disordered bulk water structure at higher temperatures due to the perturbation by thermal movements. In the process of complexation, the solvating water molecules are released to an already expanded and more disordered bulk solvent [24]. As a result, the net gain in the complexation entropy is larger at higher temperatures.

Whether the sulfate ion is bidentate or monodentate in the U(VI)/sulfate complexes is another subject of discussion [25-29]. Both modes of coordination have been found in the structures of U(VI)/sulfate complexes in solid [26,27] and in solution [28,29]. Quantum chemical calculations at the DFT and MP2 levels reveal that there are several possible isomers of the complexes  $\text{UO}_2\text{SO}_4$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  that have very similar energy, but bidentate coordination of the sulfate group is always preferred over monodentate coordination [25]. The thermodynamic data from this study seem to support that, in both  $\text{UO}_2\text{SO}_4$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$ , the sulfate ion is probably bidentate. As shown in Table 1, the stepwise enthalpies and entropies of complexation

are 17.7 kJ/M and 96 J/K/M for  $\text{UO}_2\text{SO}_4$ , and 25.5 kJ/M and 105 J/K/M for  $\text{UO}_2(\text{SO}_4)_2^{2-}$ , respectively. The magnitude of the enthalpy and entropy is informative of the denticity in complexes, especially the entropy because it is directly related to the number of water molecules that the ligand replaces. The entropy values for  $\text{UO}_2\text{SO}_4$  and  $\text{UO}_2(\text{SO}_4)_2^{2-}$  are comparable to those of known bidentate inner-sphere complexes such as U(VI)/acetate [30] and U(VI)/malonate [31] (Fig. 4).



**Fig. 4** Coordination modes in  $\text{UO}_2(\text{acetate})^+$  (left),  $\text{UO}_2\text{SO}_4(\text{aq})$  (center), and  $\text{UO}_2(\text{malonate})(\text{aq})$  (right).

### 3.3 Calculation of stability constants at variable temperatures to infinitely dilute solutions:

#### Analysis by the Specific Ion Interaction approach (SIT)

The SIT (Specific Ion Interaction) approach originated from the Brønsted-Guggenheim-Scatchard model [32-34] can be used to calculate the equilibrium constants at zero ionic strength from experimental data at other ionic strengths. For reactions (1) and (2), the equilibrium constants at  $I = 0$  ( $\log \beta^0$ ) are related to  $\log \beta$  at other ionic strengths by eq. (4):

$$\log \beta - \Delta Z^2 \times D = \log \beta^0 - \Delta \varepsilon I_m \quad (4)$$

where  $\Delta Z^2 = \{\Sigma(Z_{\text{products}}^2) - \Sigma(Z_{\text{reactants}}^2)\}$ , and equals -8 for both reactions (1) and (2).  $D$  is the Debye-Huckel term used in the SIT method and  $D = AI_m^{1/2}/(1 + 1.5I_m^{1/2})$ ,  $I_m$  is the ionic strength

in molality, and  $\varepsilon$  is the ion interaction parameter used in the SIT method [1]. For reaction (1),  $\Delta\varepsilon(25^\circ\text{C}, \text{kg mol}^{-1}) = -\varepsilon(\text{Na}^+, \text{SO}_4^{2-}) - \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = - (0.34 \pm 0.07)$  [1]. For reaction (2),  $\Delta\varepsilon(25^\circ\text{C}, \text{kg mol}^{-1}) = \varepsilon(\text{Na}^+, \text{UO}_2(\text{SO}_4)_2^{2-}) - 2\varepsilon(\text{Na}^+, \text{SO}_4^{2-}) - \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = - (0.34 \pm 0.14)$  [1]. For the calculation of  $\log K^0$  at temperatures other than  $25^\circ\text{C}$ , we used the values of  $A$  at different temperatures tabulated in the literature [22] and the value of  $\Delta\varepsilon$  at  $25^\circ\text{C}$  for all temperatures, because the values at other temperatures were not known and the errors thus introduced are probably quite small, since the values of  $(\partial\varepsilon/\partial T)_p$  are usually  $\leq 0.005 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  for temperatures below  $200^\circ\text{C}$  [22]. 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  $100^\circ\text{C}$  [35]. The calculated  $\log \beta^0$  are summarized in Table 1 (the error limits were obtained by propagation of the uncertainties in the experimental values of  $\log \beta_M$  and the uncertainties in  $\Delta\varepsilon$  at  $25^\circ\text{C}$ ). The values of  $\log \beta^0(\text{UO}_2\text{SO}_4(\text{aq}))$  and  $\log \beta^0(\text{UO}_2(\text{SO}_4)_2^{2-})$  at  $25^\circ\text{C}$  ( $3.23 \pm 0.08$  and  $4.22 \pm 0.08$ ) from this work agree very well with those recommended by the NEA review within the error limits ( $3.15 \pm 0.02$  and  $4.14 \pm 0.07$ ) [1].

#### 4. SUMMARY

Complexation of  $\text{UO}_2^{2+}$  with  $\text{SO}_4^{2-}$  in aqueous solutions is enhanced at elevated temperatures. Thermodynamic parameters of complexation ( $\Delta H$  and  $\Delta S$ ) suggest that dehydration of both  $\text{UO}_2^{2+}$  and  $\text{SO}_4^{2-}$  plays major roles in the energetics and disorder of the complex system. The enthalpy and entropy of complexation both increase as the temperature is increased. The complexes become more stable at higher temperatures because the increase in the entropy term dominates in the overall energetics of the complexation.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Grenthe, I.; Fuger, J.; Konings, R. J. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. “*Chemical thermodynamics of uranium*”, (Wanner, H., Forest, I., eds.), Amsterdam: Elsevier Science Publishers B.V., 1992.
2. R. Guillaumont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D. A. Palmer, M. H. Rand, “*Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*”, (Mompean, F. J.; Illemassene, M.; Domenech-Orti, C.; Ben Said, K. eds.), Amsterdam: Elsevier B.V. (2003).
3. L. Rao, *Chem. Soc. Rev.* 36 (2007) 881.
4. S. Ahrland, *Acta Chem. Scand.* 5 (1951) 1151.
5. R. D. Brown, W. B. Bunger, W. L. Marshall, C. H. Secoy, *J. Am. Chem. Soc.* 76 (1954) 1532.
6. E. W. Davies, C. B. Monk, *Trans. Faraday Soc.* 53 (1957) 442.
7. M. H. Lietzke, R. W. Stoughton, *J. Phys. Chem.* 64 (1960) 816.
8. S. Matsuo, *J. Chem. Soc. Japan* 81 (1960) 833.
9. D. Banerjea, K. K. Tripathi, *J. Inorg. Nucl. Chem.* 18 (1961) 199.
10. B. G. Pozharskii, T. N. Sterlingova, A. E. Petrova, *Russ. J. Inorg. Chem.* 8 (1963) 831.

11. R. M. Wallace, *J. Phys. Chem.* 71 (1967) 1271.
12. T. Vercouter, P. Vitorge, B. Amekraz, C. Moulin, *Inorg. Chem.* 47 (2008) 2180.
13. S. Ahrland, L. Kellberg, *Acta Chem. Scand.* 25 (1971) 3677.
14. A. R. Bailey, J. W. Larson, *J. Phys. Chem.* 75 (1971) 2368.
15. W. J. Ullman, F. Schreiner, *Radiochim. Acta* 40 (1986) 179.
16. L. Rao, G. Tian, *J. Chem. Thermodynamics* 40 (2008) 1001.
17. P. Gans, A. Sabatini and A. Vacca, *Talanta* 43 (1996) 1739.
18. R. Smith, P. Zanonato and G. R. Choppin, *J. Chem. Thermodyn.* 24 (1992) 99.
19. I. Grenthe, I., H. Ots and O. Ginstrup, *Acta Chem. Scand.* 24 (1970) 1067.
20. R. Arnek, *Arkiv Kemi* 32 (1970) 81.
21. L. Rao, G. Tian, Y. Xia and J. I. Friese, *Thermodynamics of neptunium(V) fluoride and sulfate at elevated temperatures*, in Proceedings of the 11<sup>th</sup> International High-Level Radioactive Waste Management Conference (IHLRWM), April 30 – May 4, 2006, Las Vegas, Nevada, pp.374-378.
22. W. Hummel, G. Anderegg, I. Puigdomènech, L. Rao and O. Tochiyama, “*Chemical Thermodynamics of Compounds and Complexes of: U, Np, Pu, Am, Tc, Zr, Ni and Se with Selected Organic Ligands*”, (Mompean, F. J.; Illemassene, M.; Perrone, J. eds.), Amsterdam: Elsevier B.V. (2005).
23. G. R. Choppin, E. N. Rizkalla, *Solution Chemistry of Actinides and Lanthanides*, in “*Handbook on the Physics and Chemistry of Rare Earths, Vol. 18 – Lanthanides/Actinides: Chemistry*”, Eds. K. A. Gschneider, Jr., L. Eyring, G. R. Choppin, G. H. Lander, Elsevier Science B.V., New York, 1994.



24. P. Di Bernardo, P. Zanonato, A. Bismondo, H. Jiang, A. Yu. Garnov, J. Jiang, L. Rao, *Eur. J. Inorg. Chem.* (2006) 4533.
25. V. Vallet, I. Grenthe, *C. R. Chimie* 10 (2007) 905.
26. A. Zalkin, H. Ruben, D. H. Templeton, *Inorg. Chem.* 17 (1977) 3701.
27. L. A. Hayden, P. C. Burns, *J. Solid State Chem.* 163 (2002) 313.
28. H. Moll, T. Reich, C. Hennig, A. Rossberg, Z. Szabó, I. Grenthe, *Radiochim. Acta* 88 (2000) 559.
29. J. Neuefeind, S. Skanthakumar, L. Soderholm, *Inorg. Chem.* 43 (2004) 2422.
30. J. Jiang, L. Rao, P. Di Bernardo, P. Zanonato, A. Bismondo, *J. Chem. Soc. Dalton Trans.* (2002) 1832.
31. L. Rao, J. Jiang, P. Zanonato, P. Di Bernardo, A. Bismondo, A. Yu. Garnov; *Radiochimica Acta* 90 (2002) 581.
32. (a) J. N. Brønsted, *J. Am. Chem. Soc.* 44 (1922) 877; (b) J. N. Brønsted, *J. Am. Chem. Soc.* 44 (1922) 938.
33. E. A. Guggenheim, *Philos. Mag.* 57 (seventh series) (1935) 588.
34. G. Scatchard, *Chem. Rev.* 19 (1936) 309.
35. A. V. Plyasunov, I. Grenthe, *Geochim. Cosmochim. Acta* 58 (1994) 3561.