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Stoichiometries and Thermodynamic Stabilities for Aqueous Sulfate Complexes of U(VI)

Thomas Vercouter,*[*] Pierre Vitorge, Badia Amekraz, and Christophe Moulin

CEA Saclay DEN-DANS/DPC/SECR/LSRM, 91191 Gif-sur-Yvette cedex, France

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The formation constants of UO_2SO_4 (aq), $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$ were measured in aqueous solutions from 10 to 75 °C by time-resolved laser-induced fluorescence spectroscopy (TRLFS). A constant enthalpy of reaction approach was satisfactorily used to fit the thermodynamic parameters of stepwise complex formation reactions in a 0.1 M Na^+ ionic medium: $\log_{10} K_1(25\ °C) = 2.45 \pm 0.05$, $\Delta_r H_1 = 29.1 \pm 4.0\ kJ \cdot mol^{-1}$, $\log_{10} K_2(25\ °C) = 1.03 \pm 0.04$, and $\Delta_r H_2 = 16.6 \pm 4.5\ kJ \cdot mol^{-1}$. While the enthalpy of the $UO_2(SO_4)_2^{2-}$ formation reaction is in good agreement with calorimetric data, that for UO_2SO_4 (aq) is higher than other values by a few kilojoules per mole. Incomplete knowledge of the speciation may have led to an underestimation of $\Delta_r H_1$ in previous calorimetric studies. In fact, one of the published calorimetric determinations of $\Delta_r H_1$ is here supported by the TRLFS results only when reinterpreted with a more correct equilibrium constant value, which shifts the fitted $\Delta_r H_1$ value up by 9 $kJ \cdot mol^{-1}$. $UO_2(SO_4)_3^{4-}$ was evidenced in a 3 M Na^+ ionic medium: $\log_{10} K_3(25\ °C) = 0.76 \pm 0.20$ and $\Delta_r H_3 = 11 \pm 8$ $kJ \cdot mol^{-1}$ were obtained. The fluorescence features of the sulfate complexes were observed to depend on the ionic conditions. Changes in the coordination mode (mono- and bidentate) of the sulfate ligands may explain these observations, in line with recent structural data.

1. Introduction

Chemical speciation of heavy and radioactive metal ions in ground or surface waters is an important issue for the modeling of their transport from polluted soils or radioactive waste storage sites into the environment.[1] A considerable effort has been spent to better understand the interactions of complexing agents present in soils with metal ions, and particularly with uranium. Sulfate anions can be found at relatively high concentration in natural waters and can participate in the dissemination of uranium. For instance, sulfate concentrations higher than 10 mM were evaluated in the pore water of clay-rich rocks that may host a deep geological repository of high-level radioactive waste;[2] an environmental concern is also the uranium contamination of drinking water reservoirs near sites where uranium ore has been exploited by leaching with concentrated sulfuric acid.[3,4] Consequently, geochemical modeling of the transport of uranium through natural aquifers must account for sulfate complexation.

Binary uranyl sulfate complexes may be dominant species under acidic conditions, while ternary uranyl hydroxo-sulfate complexes are stable at low to near-neutral pH conditions.[5] Despite a large number of investigations on the sulfate complexation of U(VI), the stoichiometries of the complexes are still debated, and discrepancies are observed in their formation data.[6,7] Moreover, most of the data have been obtained at ambient temperatures, while various temperatures may be expected under environmental conditions; especially higher temperatures could be reached in the vicinity of a

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[*] Author to whom correspondence should be addressed. Phone: +33-1-69-08-26-59. Fax: +33-1-69-08-54-11. E-mail: thomas.vercouter@cea.fr.

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radioactive waste repository due to the radioactive decay energy. In this work, we have studied the formation of binary uranyl sulfate complexes as a function of the temperature.

The enthalpies of complex formation or dissociation reactions for UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ have been determined by calorimetry[8–10] and from the temperature coefficients of complexation constants.[11–13] The critical compilation of thermochemical data by the Nuclear Energy Agency (NEA) revealed a fair agreement between the data obtained by the former method, while larger discrepancies were observed for the data obtained by the latter one.[7,14] Indeed, calorimetric measurements provide precise enthalpy changes of reaction when the speciation is well defined. On the contrary, uncertain speciation may affect the Δ_rH determinations. Calorimetric results will be discussed here in more detail because possible misinterpretations are suspected due to either the choice of the $\beta_1°$ value[9] or the possible influence of polynuclear uranyl species.[10]

The third complex, $UO_2(SO_4)_3^{4-}$, has usually been neglected in the interpretations of experimental data because its existence has been difficult to prove. Indeed, this complex should form at high ionic strengths and high sulfate concentrations, while most of the studies were carried out in more dilute solutions. More recently, the formation of $UO_2(SO_4)_3^{4-}$ in concentrated Na_2SO_4 solutions was suggested by time-resolved laser-induced fluorescence spectroscopy (TRLFS), and its formation constant β_3 was estimated at ambient temperature.[15]

TRLFS has already been successfully used to determine the influence of the temperature on the carbonate complexation of Cm(III) in concentrated solutions and to derive enthalpy and entropy changes of reaction from the temperature coefficient of the equilibrium constant.[16] TRLFS combines very low detection limits and a high sensitivity toward U(VI) complex formation in aqueous solutions,[17,18] which enables an avoidance of the formation of polycationic complexes. In the present study, sulfate complexation of uranyl was investigated at variable temperatures between 10 and 75 °C at low and high ionic strengths by TRLFS. We report new determinations of thermodynamic parameters and discuss the coordination of the UO_2^{2+} ion in the sulfate complexes.

2. Experimental Section

2.1. Materials. Millipore deionized water (Alpha-Q, 18.2 MΩ cm) was used throughout the preparations. A stock solution of natural uranium was prepared by the dissolution of U_3O_8 in a hot perchloric acid solution. The uranium concentration was measured by inductively coupled plasma mass spectrometry. The uranium concentration in the test solutions was obtained by adequate dilution of this stock solution. $NaClO_4$, H_2O, and Na_2SO_4 were purchased from Merck (R.P. Normapur) and used without further purification. Perchloric acid and sodium hydroxide were used for $[H^+]$ adjustments.

2.2. $[H^+]$ Measurements and Sulfate Speciation. $[H^+]$ was measured using combined glass microelectrodes (Radiometer Analytical, XC161). The original solution of the reference compartment was replaced with either a 0.1 or 3 M $NaClO_4$ aqueous solution containing 0.01 M NaCl. Calibrations were performed with solutions of known $[H^+]$ in 0.1 or 3 M ionic media, as detailed elsewhere.[19] $[H^+]$ was measured at the temperature of the laboratory (23 ± 1 °C), at the beginning and at the end of each titration experiment, to ensure that heating did not alter the solution compositions by evaporation. The HSO_4^- dissociation constant, $K_a(T,I)$, was calculated for each temperature and each ionic strength using $K_a°(T)$ values from Dickson et al.,[20] and using the formula of specific ion interaction theory (SIT).[7] The parameters in the Debye–Hückel term are calculated at each temperature as detailed elsewhere.[16] The ion interaction coefficients are taken from the literature.[7] They are assumed to be temperature-independent in the range 10–75 °C. This approximation has little impact on our calculations because all titrations were carried out in a H^+ range where SO_4^{2-} predominates over HSO_4^- ($-\log_{10}[H^+] > 2.7$). At each temperature, the concentrations of H^+, HSO_4^-, and SO_4^{2-} in the solutions were calculated from the mass conservation and electroneutrality relationships, and $K_a(T,I)$.

2.3. Time-Resolved Laser-Induced Fluorescence Spectroscopy. A 1.5 mL solution of U(VI) was placed in a quartz cell and titrated by the addition of adequate volumes of a sulfate solution with the same U(VI) concentration. The temperature of the solution was equilibrated for at least 15 min after each addition and maintained at ±0.3 °C using water circulation in the cell holder. The laser excitation source is a Nd:YAG Laser (Minilite II, Continuum, U.S.A.) delivering an energy of 4 mJ at 355 nm. The repetition rate was 10 Hz, and the pulse duration was about 5 ns. The fluorescence from the solution sample was focused on the entrance slit of a monochromator spectrograph (Acton 300i, Roper Scientific, U.S.A.) using a combination of mirrors and lenses. It was detected by an intensified CCD camera (Andor, U.K.) that was triggered by the delayed output of the laser pulse. The fluorescence spectra had a resolution better than 0.2 nm. The error on the measured fluorescence intensity was estimated to be less than 2% from the standard deviation of the fluorescence intensity of a reference Eu(III) solution that was regularly measured.

Fluorescence lifetimes were derived from the decay of the intensity $F(\lambda,D,W)$ measured at given wavelengths λ as a function of the gate delay D and for a given gate width W. The decay curves were fitted using eq 1, which results from the time integration of the expression of the fluorescence signal when prefilter and postfilter effects are neglected:[18]

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$$F(\lambda,D,W) = k \times \sum_{s=0}^{N} \left\{ [s] \times f_{s}^{0}(\lambda) \times \tau_{s} \times \exp\left(-\frac{D}{\tau_{s}}\right) \times \left[1 - \exp\left(-\frac{W}{\tau_{s}}\right)\right]\right\} \quad (1)$$

where k is an apparatus factor, N is the number of fluorescing species, and τ_S and $f_S{}^0(\lambda)$ are the fluorescence lifetime and molar fluorescence intensity at $D = 0$ of the species S, respectively. The parameters τ_S and $f_S{}^0(\lambda)$ were simultaneously fitted on decay curves at three to five different emission wavelengths corresponding to maximum intensity peaks.

Fluorescence spectra were recorded with a gate delay D of 0.5 μs after the laser pulse and a gate width W of 400 μs in order to collect the largest part of the fluorescence of U(VI) species. The gate width was voluntarily large in order to detect the possible presence of hydroxide complexes of U(VI), which may have high lifetime values, compared to UO_2^{2+} and the sulfate complexes.[15,18] Then, eq 1 becomes

$$F(\lambda,0.5,400) = k \times \sum_{s=0}^{N} \left\{[s] \times F_{s}^{0}(\lambda)\right\} \quad (2)$$

where $F_S{}^0(\lambda)$ is the molar spectral contribution of the species S at these acquisition parameters. The amplitude factors $k \times [s]$ of each spectral contribution are then proportional to the species concentrations. $F_S{}^0(\lambda)$ was represented with a sum of five Gaussian–Lorentzian functions in the range 465–565 nm. The contributions of each species were determined by nonlinear curve fitting using the OriginPro 7.5 software (OriginLab Corp., U.S.A.). In a first step, only the spectra which exhibited isobestic points were simultaneously fitted to determine the two spectral components. In a second step, the remaining spectra of the experimental set were fitted by adding a spectral component. The errors on the amplitude factors were estimated from the reproducibility of the fluorescence measurements, and from the standard deviations in the fit of the experimental spectra with two or three spectral components.

3. Thermodynamic Description

3.1. Equilibrium Constants. Formations of sulfate complexes of UO_2^{2+} are described with the following stepwise reactions:

$$UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4\,(aq) \quad (3)$$

$$UO_2SO_4\,(aq) + SO_4^{2-} \rightleftharpoons UO_2(SO_4)_2^{2-} \quad (4)$$

$$UO_2(SO_4)_2^{2-} + SO_4^{2-} \rightleftharpoons UO_2(SO_4)_3^{4-} \quad (5)$$

and the conditional equilibrium constants (in kg·mol^{-1}) with $i = 1-3$:

$$K_i = \frac{[UO_2(SO_4)_i^{2-2i}]}{[UO_2(SO_4)_{i-1}^{4-2i}]\,m_{SO_4^{2-}}} \quad (6)$$

where m is the molality (mol·kg^{-1}) and [ ] are molarities (mol·L^{-1}). K_1 is also noted β_1. The choice of the concentration units in eq 6 is convenient for our purpose because the fluorescence of the uranyl species is proportional to their molarities (mol·L^{-1}), but ionic medium corrections on K_i should be made in the molality unit (mol·kg^{-1}). The validity of the speciation model was also graphically checked with the rearranged expression of eq 6:

$$\log_{10}\left(\frac{[UO_2(SO_4)_i^{2-2i}]}{[UO_2(SO_4)_{i-1}^{4-2i}]}\right) = \log_{10} m_{SO_4^{2-}} + \log_{10} K_i \quad (7)$$

The left-side member was determined from the ratios of the amplitude factors of the corresponding fluorescence contributions. The values of $\log_{10} K_i$ were obtained by a least-squares analysis on the $1/\sigma^2$-weighted data points (where σ is the evaluated error on the ratios), and accounting for the effect of the ionic medium change, as explained in the next section. The error on $\log_{10} K_i$ was calculated from the standard deviation multiplied by the appropriate value of the Student parameter for a 95% confidence interval.

The dependence of K_i ($i = 1-3$) on temperature was modeled by integrating the van't Hoff isochore, which involves the enthalpy $\Delta_r H_i$ and the heat capacity $\Delta_r C_{p,i}$ of the reaction:

$$\log_{10} K_i(T) = \log_{10} K_i(T^\circ) - \frac{\Delta_r H_i(T^\circ)}{R\ln(10)}\left(\frac{1}{T} - \frac{1}{T^\circ}\right) + \frac{\Delta_r C_{p,i}}{R\ln(10)}\left[\frac{T^\circ}{T} - 1 + \ln\left(\frac{T}{T^\circ}\right)\right] \quad (8)$$

where R is the molar gas constant and $T^\circ = 298.15$ K. $\Delta_r C_{p,i}$ contributes to a second-order term in eq 8 and can sometimes be neglected.

3.2. Ionic Medium Corrections. The constants K_i are dependent on the activity coefficients of the reactants and products, which were kept almost constant by using a supporting electrolyte ($NaClO_4$). In fact, the titration experiments were performed so as to maintain constant [Na^+] by appropriate mixing of the two $NaClO_4$ and Na_2SO_4 salts. When [SO_4^{2-}] was not negligible as compared to [ClO_4^-], ionic medium effects had to be explicitly taken into account. Thus, the dependence of K_i on the change of the ionic medium was calculated using the SIT formula:

$$\log_{10} K_i - 8(i-2)D_{D-H} = \log_{10} K_i{}^\circ - \sum_j \{[\epsilon(i,j) - \epsilon(i-1,j)]m_j\} + \epsilon(Na^+, SO_4^{2-})\,m_{Na+} \quad (9)$$

where m_j is the molality of the ion j, and $\epsilon(k,j)$ is the SIT coefficient for the interaction between $UO_2(SO_4)_k^{2-2k}$ and the ion j.

The Debye–Hückel term, D_{D-H}, was calculated at each temperature, as in section 2.2; the ion interaction coefficients for U(VI) ions and SO_4^{2-} with the medium ions Na^+, ClO_4^-, and SO_4^{2-} were taken from the work by Geipel et al.,[15] while $\epsilon(UO_2^{2+}, SO_4^{2-}) = 0.12$ kg·mol^{-1} was arbitrarily fixed according to Grenthe and Lagerman.[5] Their temperature dependence was neglected in a first approximation, which is relevant for solutions with 0.1 M ionic strength due to the weak influence of the SIT terms. The SIT formula was also used in the same manner to extrapolate the $\log_{10} K_i$ values to $I = 0$. The factors of molar-to-molal conversion were calculated for each solution at 25 °C by a weighed average of the factors for the single salts.[7]

Table 1. Main Fluorescence Features of Complexes of U(VI) at 20 °C

	main emission wavelengths (nm)	medium	lifetime (μs)
UO_2^{2+}	471−488−510−534−560	0.01 M $HClO_4$	2.3 ± 0.2
UO_2SO_4 (aq)	477−493−515−538−565	Na_2SO_4−$NaClO_4$, $I = 0.1$ M	n.d.
$UO_2(SO_4)_2^{2-}$	481−496−518−542−569	Na_2SO_4−$NaClO_4$, $I = 0.1$ M	n.d.
$UO_2(SO_4)_3^{4-}$	477−494−516−539−565	1.5 M Na_2SO_4	18.1 ± 0.8[a]
UO_2OH^+	482−498−520−544−n.d.	$NaClO_4$, $I = 0.1$ M, pH 2.7	30 ± 3

[a] Estimation from measurements in solutions in which the complex dominates; the value might not correspond to a true fluorescence decay process (see text).

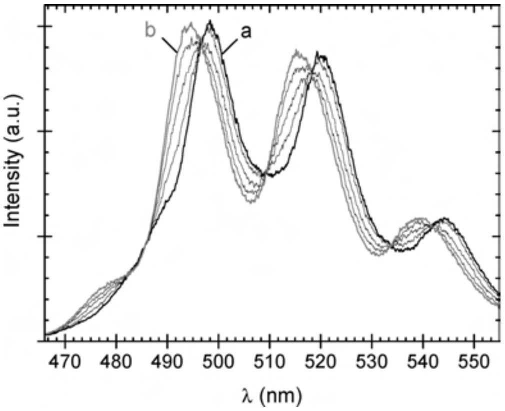

Figure 1. Fluorescence spectra of 4.2 μM U(VI) in Na_2SO_4/$NaClO_4$ solutions ($[Na^+] = 0.1$ M, $-\log_{10} [H^+] = 2.7$) measured at 10 °C as a function of $[SO_4^{2-}]$ from 0 (spectrum a) to 4.33 mM (spectrum b).

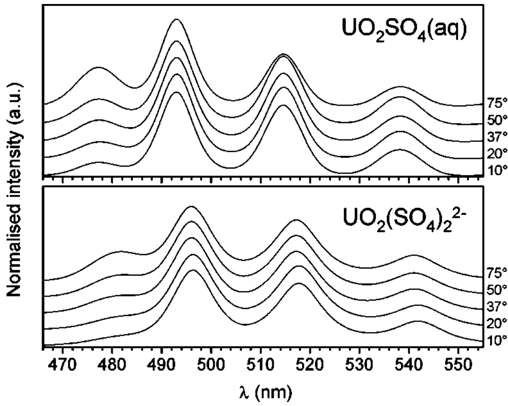

Figure 2. Fluorescence spectra assigned to UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ at different temperatures in solutions with $[Na^+] = 0.1$ M from spectral decomposition.

4. Results

4.1. Speciation of U(VI) in a 0.1 M Na^+ Ionic Medium.

The first series of experiments was carried out by titrating a 0.1 M $NaClO_4$ solution with a 0.05 M Na_2SO_4 solution, both with $[U(VI)] = 4.2$ μM. Despite the acidic conditions, the initial spectrum of the uncomplexed U(VI) was found to be very similar to the one of UO_2OH^+, with a smaller contribution from the spectrum of UO_2^{2+} (more than 10 times lower). The fluorescence yield of UO_2OH^+ is usually much higher than that of other species, and UO_2OH^+ can be detected at very low concentrations.[21] Although the hydrolysis constant is increased by approximately 1 order of magnitude from 25 to 70 °C,[22] $[UO_2OH^+]$ still remains negligible under our conditions compared with $[UO_2^{2+}]$, even at 75 °C. These two spectral components were determined by an adequate choice of the acquisition parameters (Table 1). Their measured lifetimes lie in the range of published values.[23,24] The important fluorescence signal due to UO_2OH^+ was actually used as a measure of the concentration of the uncomplexed U(VI), because the ratio $[UO_2OH^+]/[UO_2^{2+}]$ is constant at constant pH. Therefore, the measured signal was corrected to account for the small variations of $[H^+]$ along the titration. Indeed, at the beginning of the titrations, $-\log_{10} [H^+]$ equaled 2.7 for each temperature investigated and slightly increased with the additions of significant volumes of the titrating solution: the final values of $-\log_{10} [H^+]$ were 2.7, 2.9, 3.0, 3.0, and 3.2 for 10, 20, 37, 50, and 75 °C, respectively.

With the addition of sulfate to the solution, the fluorescence peaks of UO_2OH^+ tend to decrease while other peaks appear. For $\log_{10} m_{SO_4^{2-}} < -2.4$, several isobestic points are observed, which suggests the formation of UO_2SO_4 (aq) (Figure 1). For higher sulfate concentrations, spectral changes indicate that another U(VI) species exists in solution, as expected with the formation of $UO_2(SO_4)_2^{2-}$.

The decomposed fluorescence spectra of the two complexes are presented in Figure 2 for each temperature. The total intensity decreases when the temperature is increased because the fluorescence lifetime decreases according to the Arrhenius law. The positions of the peak maxima and the widths at midheight appear to be unaltered in the temperature range studied, except for the emissions at about 477 and 481 nm for UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$, respectively; these emissions actually originate from a different excited state of U(VI), with all the other emissions at higher wavelengths,[25] which explains why the temperature effect has no reason to be the same for them. The wavelengths of the main fluorescence bands are given in Table 1. The spectrum assigned to UO_2SO_4 (aq) at 75 °C shows less favorable emissions at 515 and 538 nm compared to that at 493 nm. Conversely, the relative intensities in the spectrum assigned to the second complex $UO_2(SO_4)_2^{2-}$ remain the same whatever the temperature. Temperature changes affect the

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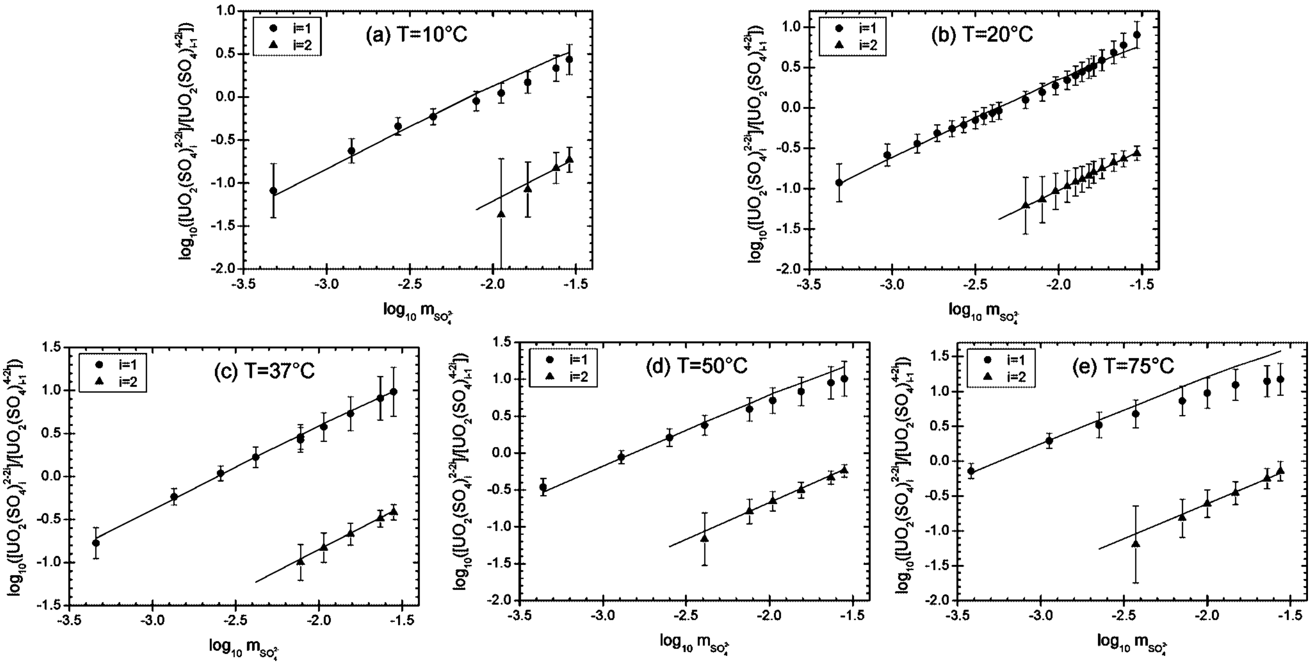

Figure 3. Validation of the speciation model at [Na$^+$] = 0.1 M with the formation of UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ at different temperatures.

probability of the radiative transitions and usually induce a decrease of the fluorescence yield. The decreased relative intensities of the 515 and 538 nm peaks of UO_2SO_4 (aq) at 75 °C do not result from a less-reliable spectral decomposition, although the fluorescence signal was much lower at 75 °C than that at lower temperatures: indeed, when forcing the spectrum of UO_2SO_4 (aq) at 75 °C to have the same relative intensities as those at the lower temperatures, the fit of the measured spectra was totally unsatisfactory. Despite insufficient information to discuss this spectroscopic observation further, we believe that it is not an artifact of the fit, but that it is rather related to slight changes in the surroundings of the UO_2^{2+} ion in UO_2SO_4 (aq) at 75 °C.

The attribution of the decomposed spectra to the UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ complexes was confirmed by the dependence of the ratios of the U(VI) species concentrations on $m_{SO_4^{2-}}$ using log–log representations (Figure 3). For each temperature, linear variations with slopes of 1 well described the data in accordance with eq 7 for $i = 1$ and 2. This slope analysis is a validation of the speciation model that was considered (eqs 3 and 4), which is also in agreement with the expected stoichiometries at 20 °C for such sulfate concentrations.[7] For $i = 1$, the fitted curves slightly deviate from a straight line at the highest sulfate concentrations because of eq 9, which predicts a decrease of $\log_{10} K_1$ (by 0.18 at most) due to the medium effect. No indication of the presence of $UO_2(SO_4)_3^{4-}$ was found since the fit was not improved by introducing eq 5 in the model. At 75 °C, the data points for $i = 1$ fall under the straight line by more than their error bars for $\log_{10} m_{SO_4^{2-}} > -1.6$ (Figure 3e). This deviation cannot be explained by a variation of the specific ion interaction coefficients at 75 °C, because their influence in a 0.1 M Na$^+$ ionic medium is small. Since the concentration of the free uranyl is determined from the fluorescence contributions of UO_2OH^+, it is more likely that the correction that we made to account for [H$^+$] variations induces larger uncertainties on [UO_2^{2+}] at 75 °C than at lower temperatures because a significant increase of pH from 2.7 to 3.2 was expected. Moreover, no significant deviation is observed for $i = 2$ for which the UO_2OH^+ fluorescence contribution has little impact. Consequently, the data points at low $\log_{10} m_{SO_4^{2-}}$ and 75 °C were given more weight in the fit.

The dependence of the resulting $\log_{10} K_i$ values on the temperature is represented in Figure 4a. An increase of the temperature from 10 to 75 °C enhances the stability of the mono- and disulfate complexes of U(VI) by an order of magnitude, at most, on the K values. Consequently, when the temperature is increased, complexation occurs at lower sulfate concentrations. The corresponding thermodynamic parameters at 25 °C were fitted on the basis of eq 8 with heat capacities of reaction, $\Delta_rC_{p,1}$ and $\Delta_rC_{p,2}$, held at zero: $\log_{10} K_1 = 2.45 \pm 0.05$, $\Delta_rH_1 = 29.1 \pm 4.0$ kJ·mol^{-1}, $\log_{10} K_2 = 1.03 \pm 0.04$, and $\Delta_rH_2 = 16.6 \pm 4.5$ kJ·mol^{-1}. According to the uncertainties assigned to the $\log_{10} K_i$ values, the enthalpies of reaction were assumed to be temperature-independent. Thus, $\Delta_rC_{p,1}$ and $\Delta_rC_{p,2}$ could not be accurately determined with our data sets.

4.2. Speciation of U(VI) in a 3 M Na$^+$ Ionic Medium. The formation of $UO_2(SO_4)_3^{4-}$ was investigated by additional experiments at higher ionic strengths, which enables a higher reach of sulfate concentrations and usually stabilizes highly charged species. Similarly to the previous series, a 3 M $NaClO_4$ solution was titrated with a 1.5 M Na_2SO_4 solution, both solutions containing 0.4 μM U(VI). The total U(VI) concentration was lowered compared to that in the experiments at low ionic strength in order to keep unchanged the detector acquisition parameters since the fluorescence of U(VI) in concentrated sulfate solutions is much more intense. A comparison with a series with 2.1 μM U(VI) at 20 °C

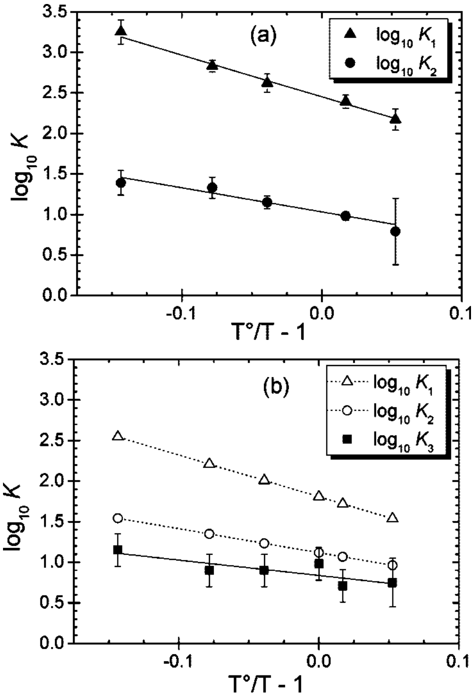

Figure 4. Experimental values of complexation constants as a function of temperature (a) for a 0.1 M Na^+ ionic medium and (b) for a 3 M Na^+ ionic medium, based on K_1 and K_2 estimations (see text).

showed that the fluorescence signals were proportional to the total U(VI) concentrations, as expected. $[H^+]$ was maintained almost constant ($-\log_{10}[H^+] = 2.9$ or 3.8) along the titrations. The fluorescence contribution of UO_2OH^+ was undetectable. It appears that the high ionic strength does not promote the fluorescence of UO_2OH^+, on the contrary to what was observed at low ionic strength. Thus, the uncomplexed uranyl was here fully characterized by the fluorescence of UO_2^{2+}.

The peak maxima were continuously shifted to higher wavelengths as the sulfate concentration increased up to 1.5 M. Attempts to interpret the data as for the previous series of experiments were unsuccessful because the successive formations of the complexes occur for close values of $[SO_4^{2-}]$. It was therefore difficult to accurately determine the spectrum of each complex, and the fitting induced very important correlation between all of the parameters. As a first step, the fitting strategy was based on the measurements at 20 °C. The fluorescence spectra of UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ determined in the 0.1 M Na^+ ionic medium could not correctly fit the experimental spectra in the 3 M Na^+ ionic medium, even for the lowest sulfate concentrations where the speciation should be completely defined by these two complexes. It can be concluded that the individual spectra are affected by the ionic medium and are not transferable from specific ionic conditions to others, as discussed in section 5.1. Consequently, the spectra were treated independently from the results in the 0.1 M ionic medium. At the highest sulfate concentrations (0.3–1.5 M), the total intensity of the measured spectrum varies with $[SO_4^{2-}]$, but the shape of the spectra remains unchanged. The most probable reason for that is a predominance of the spectral contribution of one single complex whose concentration in the solutions varies with $[SO_4^{2-}]$. When this spectrum shape was attributed to $UO_2(SO_4)_2^{2-}$, the fit of the data by adjusting the unknown spectrum of UO_2SO_4 (aq), and the proportion of each species, was unacceptable because the derived complexation constants K_1 and K_2 were unrealistic compared to literature values.[26] Thus, the spectra measured in the 1.5 M Na_2SO_4 solution (Figure 5) were assigned to $UO_2(SO_4)_3^{4-}$. It should be noted that the fluorescence peaks are slightly shifted to the higher wavelengths as the temperature increases. These spectroscopic changes might be related to modifications in the structure of $UO_2(SO_4)_3^{4-}$, and probably to the coordination mode of the three sulfate ligands. When the spectra and the proportions of the other complexes were fitted together on the experimental spectra, all of the parameters were again so correlated that the resulting values were irrelevant. Consequently, the individual spectra of UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ in the 3 M Na^+ ionic medium could not be unambiguously determined. Neither K_1 nor K_2 was determined in the final interpretation of these data. The values of K_1 and K_2 were rather held constant during the fit by using mean values calculated from three independent experimental determinations by Ciavatta et al. for a 3 M $NaClO_4$ medium at 25 °C.[26] The values of K_1 and K_2 at each temperature of interest were calculated by using eq 8 and Δ_rH_1 and Δ_rH_2, which were obtained in the 0.1 M $NaClO_4$ medium (Table 2). The differences of Δ_rH_i between the 0.1 and 3 M $NaClO_4$ media were supposed to be smaller than the uncertainties, which is usually verified for similar systems and is consistent with their theoretical dependence on activity coefficients.[27]

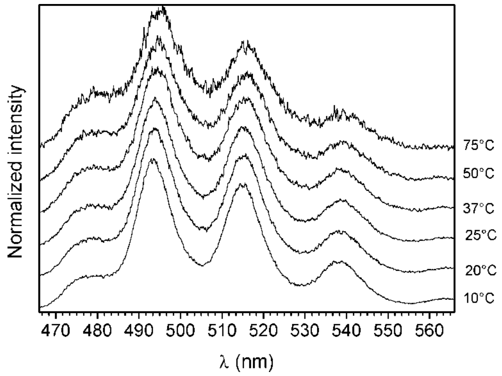

Figure 5. Fluorescence spectra of a 2.1 μM U(VI) solution with 1.5 M Na_2SO_4 ($-\log_{10}[H^+] = 3.0$) measured at different temperatures.

The sensitivity of the model to the experimental data was tested according to eqs 2 and 7 by plotting the fluorescence intensities at 494 nm as a function of the sulfate concentration (Figure 6). Since K_1 and K_2 were fixed, only K_3 and the molar fluorescence intensities F_S^0(494 nm) of the three complexes were adjusted, resulting in a good fit of the data. As a comparison, a poorer fit is presented when omitting the third complex, $UO_2(SO_4)_3^{4-}$ (Figure 6a). The diagram in Figure 6b shows that none of the complexes strongly dominates the speciation, except at the highest sulfate concentrations where

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Table 2. Thermodynamic Parameters for the Stepwise Formation of Sulfate Complexes of U(VI) at 25 °C

$\log_{10} K_i°$	$\log_{10} K_i$	$\Delta_r H_i$ (kJ·mol^{-1})	$\Delta_r S_i{}^a$ (J·mol^{-1}·K^{-1})	exptl. medium (mol·L^{-1})	method	ref.
			$UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4$ (aq)			
		20.79 ± 0.29	122	dilute H_2SO_4	calorimetry	9
		26.99 ± 1.84^b	151 ± 6^b			p.w.
		29.96 ± 2.38^c	163 ± 8^c			p.w.
		18.23 ± 0.17		1 $NaClO_4$	calorimetry	8
		19.6 ± 0.7	127 ± 2	~0.01 Na_2SO_4, pH 2–3	calorimetry	10
3.29 ± 0.10	2.45 ± 0.05	29.1 ± 4.0	145 ± 13	0.1 $NaClO_4$, pH 3–4	TRLFS	p.w.
3.14 ± 0.03		21 ± 2	130 ± 5	0.01–0.15 NH_4ClO_4, pH ~ 5	Donnan membrane	11
3.15 ± 0.02		19.5 ± 1.6	125.7 ± 5.4		review	14
			$UO_2SO_4 (aq) + SO_4^{2-} \rightleftharpoons UO_2(SO_4)_2^{2-}$			
		16.88 ± 0.36		1 $NaClO_4$	calorimetry	8
		18.2 ± 2.1	84 ± 2	0.01 Na_2SO_4, pH 2–3	calorimetry	10
1.04 ± 0.10	1.03 ± 0.04	16.6 ± 4.5	77 ± 15	0.1 $NaClO_4$, pH 3–4	TRLFS	p.w.
1.06 ± 0.13		8 ± 5	47 ± 12	0.01–0.15 NH_4ClO_4, pH ~ 5	Donnan membrane	11
0.99 ± 0.05		15.6 ± 1.3	71.3 ± 4.6		review	14
			$UO_2(SO_4)_2^{2-} + SO_4^{2-} \rightleftharpoons UO_2(SO_4)_3^{4-}$			
	0.76 ± 0.20	11 ± 8	25 ± 27	3 $NaClO_4$, pH 3–4	TRLFS	p.w.

[a] Calculated from $\Delta_r G = \Delta_r H - T\Delta_r S$ and $\Delta_r G = -RT \ln K$. [b] Value obtained from ref 9, using $\log_{10} K_1 = 3.15$ (NEA). [c] Value obtained from ref 9, using $\log_{10} K_1 = 3.29$ (p.w.).

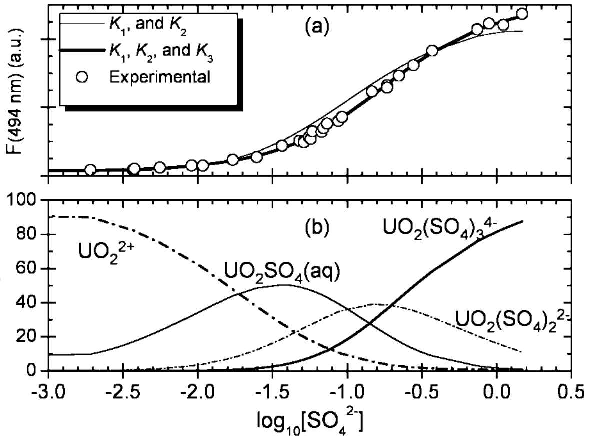

Figure 6. (a) Fluorescence intensities measured at 494 nm as a function of the sulfate concentration for 0.4 μM U(VI) in $Na_2SO_4/NaClO_4$ solutions ($[Na^+]$ = 3 M, $-\log_{10} [H^+] = 3.8$) at 20 °C. Theoretical curves are fitted to the data using K_1 and K_2 values from Ciavatta et al.[26] for a two-complex model and for a three-complex model (fitting K_3). (b) Speciation diagram corresponding to the three-complex model.

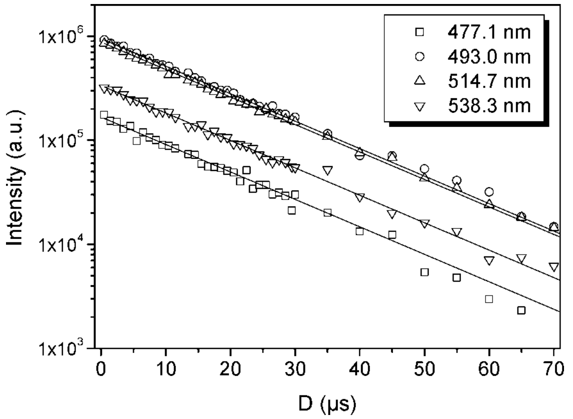

Figure 7. Typical fluorescence decays at the main wavelengths of emission of a 4.2 μM U(VI) solution with 0.05 M Na_2SO_4 ($-\log_{10} [H^+] = 3.1$) and at 10 °C. The data are fitted with linear functions and a single lifetime value (16.9 ± 0.1 μs) for all of the wavelengths (—).

$UO_2(SO_4)_3^{4-}$ represents more than 80% of the total U(VI) concentration. This explains why we failed at obtaining the individual spectra of UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ by fitting all the parameters simultaneously. The same analysis was carried out for the other temperatures. The temperature dependence of the experimental values of K_3 in the 3 M Na^+ ionic medium is shown in Figure 4b. The thermodynamic parameters were determined by a weighed fit of the data using eq 8: $\log_{10} K_3(25\ °C) = 0.76 \pm 0.20$ and $\Delta_r H_3 = 11 \pm 8$ kJ·mol^{-1}. A constant enthalpy approach was found to be relevant to explain this data set, so $\Delta_r C_{p,3}$ was not determined.

4.3. Fluorescence Lifetimes of U(VI) in Aqueous Sulfate Solutions. The decays of fluorescence could be fitted with monoexponential functions for each sulfate concentration and at each temperature. As an example, the fluorescence decays measured at four different wavelengths are shown for a sulfate solution of U(VI) where the expected speciation is 7% UO_2^{2+}, 54% UO_2SO_4 (aq), 26% $UO_2(SO_4)_2^{2-}$, and 13% $UO_2(SO_4)_3^{4-}$ at 10 °C (Figure 7). Simultaneous fitting with eq 1 and a single τ_S value of 16.9 ± 0.1 μs was successful, while one may have expected at most four decay components (if all species would have been detectable). At a given temperature, the measured fluorescence lifetimes of U(VI) increased with increasing sulfate concentration. Moreover, at a given sulfate concentration, $\ln(\tau_S)$ decreased linearly with $1/T$ (not shown) while different U(VI) species distributions are expected. According to the Arrhenius relationship, which often describes the temperature dependence of reaction kinetics,[23] the activation energy (E_a) of temperature quenching of U(VI) fluorescence was determined by linear regression analysis for different sulfate concentrations: $E_a = 49.6 \pm 0.3$, 47.8 ± 0.3, and 48.0 ± 0.3 kJ·mol^{-1} for 0.05, 0.15, and 1.5 M Na_2SO_4 solutions, respectively. These values are of the same order of magnitude as those obtained for $Na_2SO_4/NaClO_4$ solutions,[28] as well as for sulfuric acid solutions,[29] and for phosphate and fluoride solutions.[23] It should be noted that, at 20 °C and low sulfate concentrations where the molar

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fraction of UO_2^{2+} is more important, a biexponential decay is observed with one short-life component (2.3 μs) in consistency with the UO_2^{2+} lifetime and a longer-life component that could rather correspond to an apparent lifetime of the sulfate complexes.

The monoexponential decay curves can be explained by either photochemical processes or by the small differences of fluorescence lifetimes between the sulfate complexes, which would then be hardly discriminated. Monoexponential decays were also observed in another study at sulfate concentrations where at least two sulfate complexes of U(VI) were expected to form,[30] whereas formation constants were determined from multiexponential decays of the fluorescence of U(VI) in sulfate solutions.[15] Such inconsistencies for the uranyl−sulfate aqueous system have already been pointed out, but no definite conclusion has been drawn.[21,31,32] It was proposed that photochemical processes may interfere in the determination of equilibrium constants by using TRLFS when the formation/dissociation of complexes in their excited states is rapid as compared to the rate of relaxation of the excited complexes by fluorescence emission;[32] it was also concluded that this should not be the case for the uranyl−sulfate system. Then, it is more likely that the lifetimes of the sulfate complexes of U(VI) are very close, and accurate determination of them is difficult. Therefore, only the value 18.1 ± 0.8 μs was assigned to the fluorescence lifetime of $UO_2(SO_4)_3^{4-}$ at 20 °C because this complex is highly predominant in the 1.5 M Na_2SO_4 solution.

5. Discussion

5.1. Coordination of Sulfate in the Complexes. The fluorescence spectrum of the sulfate complex of U(VI) was sensitive to the 0.1 and 3 M Na^+ ionic media, suggesting a change in the local geometry of UO_2^{2+} in the complexes. Extended X-ray absorbance fine structure (EXAFS) analysis of uranyl in sulfate solutions showed bidentate coordination of the sulfate ligand in UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$, according to the U−S distances at about 3.12 Å, which is a characteristic distance for bidentate SO_4^{2-} in solid-state structures.[33] The concentrations of the uranyl ion and complexes in the test solutions were estimated by Moll et al.[33] from thermodynamic speciation, which was revised by Vallet and Grenthe due to incorrect estimations of ion activity coefficients.[34] Conversely, U−S distances at about 3.67 Å, indicating monodentate coordination, were determined by high-energy X-ray scattering on a UO_2SO_4 (aq) solution,[35] for which an accurate calculation of the speciation is difficult due to the high total uranium concentrations.[34] Both experimental techniques provide reliable distances, while the observed difference is likely due to differences in the compositions of the test solutions. Recently, Hennig et al. reported EXAFS data for several $H_2SO_4/(NH_4)_2SO_4$ solutions of U(VI).[36] The bidentate sulfate coordination was deduced from the U−S distances of 3.07–3.12 Å in most of the test solutions, and also monodentate sulfate coordination in two of them with U–S distances of 3.56–3.57 Å. The average numbers of S atoms in the first coordination sphere of UO_2^{2+} were fitted to the data to assess the complexes' stoichiometries and were compared to the expected speciation of U(VI). The high ionic strengths required the choice of a model for the calculation of ion activity coefficients.[37] Hennig et al. have considered that, although the simple Davies equation is not valid in the present range of ionic strength (the Davies equation usually applies well at ionic strengths lower than 0.1 $mol \cdot kg^{-1}$), it could estimate the ion activity coefficient without introducing larger errors than the errors obtained when applying either the SIT or Pitzer model with undetermined parameters.[36] Similarly to the ionic medium correction performed in the present work using the SIT formula, we re-evaluated the speciation in the test solutions of Hennig et al., by using reported ion interaction coefficients[7,34] and values for ion interaction with NH_4^+ by analogy to Na^+ as a first approximation. The calculation of the free sulfate concentration also accounted for the degree of association between NH_4^+ and SO_4^{2-}, but the ionic medium effect on the corresponding association constant may be misestimated under these conditions. This speciation evaluation required an iterative procedure because the calculated ionic strength and the free sulfate concentration were correlated parameters. The final results were obtained within only a few steps. Except for one sample, the calculated ionic strength was higher than 0.6 $mol \cdot L^{-1}$ and was between 2.4 and 6.8 $mol \cdot L^{-1}$ for most of the solutions. The speciation was very different from that proposed by Hennig et al.[36] Particularly, the $UO_2(SO_4)_3^{4-}$ complex was found to be predominant in most of the samples (namely, C, D, E, and F[36]). We believe that the speciation calculation with the SIT formula is more correct despite the propagation of errors due to estimated parameters. From our estimations of the species concentrations, average numbers of S atoms coordinated to UO_2^{2+} are expected to range between 2.6 and 3.0. The values derived from the EXAFS spectra were one unit lower while the Debye–Waller factor was fixed during the EXAFS fit procedure.[36] This latter constraint and the possible effect of double-electron excitation[36] should contribute to an increase in the reported error of ±15% in coordination numbers. Then, while monodentate and bidentate coordination was clearly evidenced in these solutions, the final interpretation of the stoichiometries based on the average S coordination numbers is ambiguous.

From the structural studies, it appears that either mono- or bidentate coordination can be stabilized depending on the sulfate concentration, uranium concentration, pH, or ionic

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medium. The geometry of different isomers of UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ has been calculated by quantum chemistry.[34,36] Several isomers would have nearly the same energy and could exist in solution. Moreover, the equilibrium between the bidentate and the monodentate isomers of UO_2SO_4 (aq) mostly depends on the water activity because the change of coordination is necessarily accompanied by a removal of at least one water molecule in the first coordination sphere of UO_2^{2+}. Thus, the isomers of a complex are at equilibrium concentrations when the water activity is constant.

We have concluded from our data treatment that the fluorescence spectra assigned to UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ in the 0.1 M Na^+ medium (Figure 2) are necessarily different from those in the 3 M Na^+ medium (not determined). Hence, the average environment of UO_2^{2+} in each complex probably changes when the ionic composition of the solution changes. Furthermore, in the range 10–75 °C, the fluorescence spectra of UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ in the 0.1 M Na^+ medium do not show significant changes, except for the spectrum of UO_2SO_4 (aq) at 75 °C, which has different relative peak intensities (Figure 2). Conversely, a batochromic shift of the spectrum of $UO_2(SO_4)_3^{4-}$ measured in the 3 M Na^+ medium is observed as the temperature increases (Figure 5). These spectral changes could indicate a modification of the equilibrium between isomers for UO_2SO_4 (aq) and $UO_2(SO_4)_3^{4-}$ that would be originated in changes of water solvating properties when increasing the temperature and either stronger or weaker bonding for the third ligand. No spectral change is detected at 75 °C for $UO_2(SO_4)_2^{2-}$, suggesting that one isomer would predominate at all temperatures. The more probable isomers are five-coordinated complexes at ambient temperature.[34] Thus, $UO_2(SO_4)_3^{4-}$ would have at least one monodentate sulfate group because three bidentate sulfate groups would lead to a six coordination. However, there is no reported U−S distance of about 3.6 Å in solutions where this complex would predominate.[36]

5.2. Thermodynamic Data. The values of $\log_{10} K_1$ and $\log_{10} K_2$ determined in the 0.1 M Na^+ medium were extrapolated to $I = 0$ using the SIT formula. The values at 25 °C compare well to the values selected by the NEA[14] despite a slightly higher value for $\log_{10} K_1°$ (Table 2). For the formation of $UO_2(SO_4)_3^{4-}$, Geipel et al. proposed $\log_{10} \beta_3 = 3.20 \pm 0.25$ from their analysis of the changes of the fluorescence lifetime of U(VI) in a 1 M ionic medium at 25 °C.[15] This value was selected by the NEA as the only available one.[7] Extrapolation to $I = 0$ with the SIT formula was performed by the NEA, using $\Delta\epsilon = -0.11$ instead of the -0.34 originally used by Geipel et al., leading to $\log_{10} \beta_3° = 3.02 \pm 0.38$. In the present work, $\log_{10} \beta_3 = 3.68 \pm 0.24$ was determined in a 3 M Na^+ medium at 25 °C. This value cannot be extrapolated from such a high-ionic-strength medium to $I = 0$ by using the SIT formula with a single $\Delta\epsilon$ parameter. Indeed, in their study performed in a 3 M $NaClO_4$ medium, Ciavatta et al. rather calculated the activity coefficients of the UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ complexes by using empirical rules.[26] The resulting values of $\beta_1°$ and $\beta_2°$ were considered by the NEA to be consistent with their selections, although the parameters used for the calculations of activity coefficients were different from those recommended by the NEA. Hence, no value is proposed at $I = 0$ from our determination in the 3 M Na^+ medium because such ionic medium correction may induce a large uncertainty.

The enthalpies and entropies of the stepwise formation reactions were both found to be positive, which is usually observed for the complex formation of actinide and lanthanide ions with inorganic ligands. In this case, the entropic stabilization drives the complexation reaction. The stepwise formation reactions are endothermic, which suggests that the main contribution to the enthalpy is the dehydration energy of the reactants, which is less and less unfavorable as the number of sulfate ligands increases. While $\Delta_rH_2 = 16.6 \pm 4.5$ kJ·mol^{-1} is in agreement with calorimetric determinations,[8,10] $\Delta_rH_1 = 29.1 \pm 4.0$ kJ·mol^{-1} is significantly higher than published values by a few kilojoules per mole (Table 2). Since a single thermodynamic data set should be consistent with all experimental data, a closer examination of previous calorimetric results seemed necessary.

$\Delta_rH_1°$ and $\Delta_rS_1°$ have been determined by Bailey and Larson from measured heats of solution and calculated heats of dissociation of salts (i.e., excess enthalpy changes due to the nonideality of the solutions), and assuming the value $\log_{10} K_1° = 2.72$.[9] Although this is a very careful work, the chosen value of $K_1°$ is too low. We have therefore recalculated $\Delta_rH_1°$ using different $K_1°$ values. In order to verify that our numerical treatment was consistent with Bailey and Larson's results, the calculation was first performed using the same assumptions as in the original work: we obtained $\Delta_rH_1° = 21.00 \pm 0.33$ kJ·mol^{-1}, which compares to $\Delta_rH_1° = 20.84 \pm 0.42$ kJ·mol^{-1} as reported by Bailey and Larson. It should be noticed that the calculated term due to nonideality is quite small because of the low ionic strength of the solutions, and neglecting it led to $\Delta_rH_1° = 21.42 \pm 0.33$ kJ·mol^{-1}. The $\Delta_rH_1°$ values were markedly increased when using the $K_1°$ value either recommended by the NEA ($\log_{10} K_1° = 3.15$)[7] or obtained at 25 °C in the present TRLFS investigation ($\log_{10} K_1° = 3.29$), leading to 26.99 ± 1.84 and 29.96 ± 2.38 kJ·mol^{-1}, respectively. These values of the enthalpy of reaction better compare to the values obtained in the present work, $\Delta_rH_1° = 29.1 \pm 4.0$ kJ·mol^{-1}, while the uncertainties, calculated as the standard deviation in the four experimental sets, increased significantly. The authors have also determined $\Delta_rH_1°$ by using a different experimental path, which consisted of measuring the heat of dilution of $UO_2(NO_3)_2 \cdot 6H_2O$ in K_2SO_4 solutions. Whereas their results seemed to confirm their previous determination, we did not manage to arrive at the same result according to the given equations and data, and we suspect an error in the reported data or results. We rather calculated 31.55 ± 1.46, 23.51 ± 0.67, and 22.22 ± 0.50 kJ·mol^{-1} for $\Delta_rH_1°$ using $\log_{10} K_1° = 2.72$ (original value), $\log_{10} K_1° = 3.15$ (NEA), and $\log_{10} K_1° = 3.29$ (this work), respectively. The value of $\Delta_rH_1°$ decreased with increasing $\log_{10} K_1°$, but it is unclear whether these determinations are reliable.

The calorimetric measurements by Ahrland and Kullberg were carried out under acidic conditions and at $I = 1$ M, with uranyl concentrations ranging between 0.01 and 0.03 M. They obtained $\Delta_r H_1 = 18.23 \pm 0.17$ kJ·mol^{-1}, which is lower than the one obtained from our TRLFS results, but we could not find a reason for such a discrepancy. The value $\Delta_r H_2 = 16.88 \pm 0.36$ kJ·mol^{-1} is in much better agreement with our determination.

The microcalorimetric study by Ullman and Schreiner was performed by titrating U(VI) solutions with Na_2SO_4 solutions at pH 2.1 and 2.7.[10] The ionic strength of the solutions was not noticed, but we calculated that it should range between 0.2 and 1.2 M according to the amounts of $UO_2(NO_3)_2$ and Na_2SO_4 introduced in the test solutions. A calculation of the expected speciation at $I = 0.25$ M (average value of the experimental ionic strengths) using data selected by the NEA shows that the hydrolysis species $(UO_2)_2OH^{3+}$ and $(UO_2)_2(OH)_2^{2+}$ may have significantly formed (more than 10%) in the initial uranyl solutions at pH 2.7, and to a minor extent at pH 2.1, while only UO_2^{2+}, UO_2SO_4 (aq), and $UO_2(SO_4)_2^{2-}$ were accounted for in the interpretation of the data. Even small amounts of hydrolysis species can significantly alter the calorimetric results since, for instance, the corresponding enthalpy of dissociation of $(UO_2)_2(OH)_2^{2+}$ is about −48 kJ·mol^{-1}.[22] Furthermore, ternary hydroxo-sulfate complexes were evidenced more recently,[5,7,38] and $(UO_2)_2(OH)_2(SO_4)_2^{2-}$ could be stable at a significant concentration under the reaction conditions. Thus, a possible influence of other formation or dissociation reactions on the measured heats of solution cannot be ruled out.

$\Delta_r H_1$ and $\Delta_r H_2$ in the 0.1 M Na^+ ionic medium and $\Delta_r H_3$ in the 3 M Na^+ ionic medium were found to be positive, following the order $\Delta_r H_1 > \Delta_r H_2 > \Delta_r H_3$. Such a trend was also observed for the complexation of U(VI) by acetate,[8,39] which is a moderate oxygen-donor ligand, but stronger than sulfate. The single charged acetate anion (Ac^-) can bind to the uranium ion with two oxygen atoms; bidentate coordination in the UO_2Ac^+ and $UO_2(Ac)_2$ (aq) complexes was evidenced by EXAFS[39] and X-ray absorption[40] spectroscopies, while monodentate acetate coordination in $UO_2(Ac)_3^-$ was supported by EXAFS measurements.[39] In the case of sulfate complexation, both mono- and bidentate coordinations can be expected in UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ depending on the solution composition, as discussed above. $\Delta_r H_3$ is low for $UO_2(Ac)_3^-$ (∼−2 kJ·mol^{-1})[39] and highly negative for $UO_2(CO_3)_3^{4-}$ (∼−55 kJ·mol^{-1}),[41] because the dehydration energy is probably low in the third complex and can be overcome by the bond formations. Comparison of the $\Delta_r H_3$ values suggests that the sulfate anions could act as monodentate and bidentate ligands toward UO_2^{2+} in the third complex, as in the case of $UO_2(Ac)_3^-$.

6. Conclusion

Three uranyl sulfate complexes, UO_2SO_4 (aq), $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$, were identified by TRLFS in aqueous solutions in the temperature range 10–75 °C. $UO_2(SO_4)_3^{4-}$ was only detected at high sulfate concentrations in a 3 M Na^+ ionic medium. A set of thermodynamic formation data was determined. Though the value of $\Delta_r H_1$ was significantly higher than those from calorimetric studies, it compares well with reinterpreted results from one of the calorimetric studies. The value of $\Delta_r H_2$ was found to be in good agreement with calorimetric results. A value of $\Delta_r H_3$ was determined for the first time. The fluorescence spectra measured in low- and high-ionic-strength media were interpreted as being indicative of the presence of different isomers of UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$, in accordance with structural data that shows the existence of both bidentate and monodentate chelation of sulfate in UO_2SO_4 (aq) and $UO_2(SO_4)_2^{2-}$ depending on the solution composition.

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Supporting Information Available: Experimental values of the stepwise formation constants of UO_2SO_4 (aq), $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$. Fluorescence spectra of UO_2OH^+ at variable temperatures. Fluorescence spectra of U(VI) in $Na_2SO_4/NaClO_4$ media with $[Na^+] = 3$ M at 20 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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