

Effect of Temperature on the Complexation of Uranium(VI) with Fluoride in Aqueous Solutions

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Complexation of U(VI) with fluoride at elevated temperatures in aqueous solutions was studied by spectrophotometry. Four successive complexes, UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$, were identified, and the stability constants at 25, 40, 55, and 70 °C were calculated. The stability of the complexes increased as the temperature was elevated. The enthalpies of complexation at 25 °C were determined by microcalorimetry. Thermodynamic parameters indicate that the complexation of U(VI) with fluoride in aqueous solutions at 25 to 70 °C is slightly endothermic and entropy-driven. The Specific Ion Interaction (SIT) approach was used to obtain the thermodynamic parameters of complexation at infinite dilution. Structural information on the U(VI)/fluoride complexes was obtained by extended X-ray absorption fine structure spectroscopy.

1. Introduction

One of the strategies for the safe management of nuclear wastes is to store the high-level nuclear wastes (HLW) in underground geological repositories. Because of the high radiation energy released from the HLW, the postclosure repository is expected to remain at elevated temperatures for thousands of years.¹ If the waste package is breached and becomes in contact with groundwater, the radioactive materials in the HLW will be in aqueous solutions at elevated temperatures. As a result, the interactions of radionuclides with the chemical components in the groundwater at elevated temperatures could determine the migration behavior of radionuclides in the repository.

According to the radionuclide inventory for the HLW to be disposed of in the underground repository, uranium is the most abundant radionuclide in the waste forms (including commercial and DOE spent nuclear fuels and the HLW glass logs).¹ Under oxidizing conditions, uranium is most likely to be in the hexavalent state. Therefore, the migration of U(VI) in the postclosure environment of the repository is a great concern to long-term repository performance. To predict the migration behavior of uranium, it is necessary to have sufficient and reliable thermodynamic data on its complexation with the ligands (e.g., OH^- , F^- , SO_4^{2-} , PO_4^{3-} and CO_3^{2-}) that are present in the groundwater of the repository at elevated temperatures. Among the ligands, fluoride (F^-) is known to form fairly strong complexes with U(VI) at or near 25 °C so that complexation of U(VI) with fluoride could play

a significant role in determining the speciation and migration behavior of U(VI) in the repository. There are about 20 papers in the literature where the stability constants of U(VI)/fluoride complexes at or near 20–25 °C are reported.^{2,3} In contrast, few data on the complexation of U(VI) with fluoride at elevated temperatures are available, and there is only one study where the enthalpy of complexation was determined by calorimetry.⁴ There are a few studies in which luminescence properties (e.g., lifetime) of the U(VI)/fluoride system at variable temperatures were observed, but no stability constants were measured.^{5,6} The lack of stability constants at elevated temperatures and the scarcity of enthalpy data make it difficult to predict the migration behavior of U(VI) in the repository at elevated temperatures. To provide reliable thermodynamic data on the complexation of U(VI) with fluoride at elevated temperatures, we have studied the complexation of U(VI) with fluoride at variable temperatures. Stability constants of U(VI)/fluoride complexes at 25, 40, 55, and 70 °C were determined by spectrophotometry, and the enthalpy of complexation at 25 °C was determined by microcalorimetry. Extended X-ray Absorption Fine

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Structure (EXAFS) spectroscopy was used to obtain structural information on the U(VI)/fluoride complexes in aqueous solution.

2. Experimental Section

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.⁷ Gran's potentiometric method⁸ was used to determine the concentration of free acid in the U(VI) stock solution. Solutions of fluoride were prepared by dissolving solid NaF in water. The ionic strength of all working solutions in this study was maintained at $1.0 \text{ mol}\cdot\text{dm}^{-3}$ (25°C) by adding appropriate amounts of sodium perchlorate as the background electrolyte.

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 Peltier controller. Ten millimeter quartz cuvettes were used. Before being inserted into the sample holders, the sealed cuvettes were immersed in an external constant-temperature water bath for 30–40 min to be pre-equilibrated at the required temperature. This procedure successfully prevented condensation of water on the top of the cuvettes during the spectrophotometric measurements at high temperatures. The sample holders are also equipped with magnetic stirrers so that thorough mixing of the titrant was achieved while the cuvettes were sealed to minimize water evaporation during the titration. Multiple titrations with different concentrations of U(VI) and acid were performed. In each titration, appropriate aliquots of the titrant ($0.900 \text{ mol}\cdot\text{dm}^{-3}$ NaF/ $0.100 \text{ mol}\cdot\text{dm}^{-3}$ HF) were added into the cuvette and mixed thoroughly before the absorption spectrum was collected. Usually 25–30 additions were made, thus generating a set of 25–30 spectra in each titration. The stability constants of the U(VI)/fluoride complexes (on the molarity scale) were calculated by non-linear least-squares regression using the Hyperquad program.⁹

2.3. Microcalorimetry. The enthalpies of complexation of U(VI) with fluoride at 25°C were determined by microcalorimetric titrations conducted on an isothermal microcalorimeter (Model ITC 4200, Calorimetry Science Corp.). The performance of the calorimeter has been tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The result was $-(47.7 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}$ at 25°C , in excellent agreement with the value in the literature. Details of the microcalorimeter are provided elsewhere.¹⁰

In the titrations of the complexation of U(VI) with fluoride, a U(VI) solution of 0.90 cm^3 (at 25°C) was placed in the titration vessel and titrated with a solution of $0.300 \text{ mol}\cdot\text{dm}^{-3}$ NaF/ $0.0333 \text{ mol}\cdot\text{dm}^{-3}$ HF in increments of $5 \mu\text{L}$. Multiple titrations were conducted at each temperature. For each titration, n additions were made (usually $n = 40\text{--}50$), 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: $Q_{\text{r},j} = Q_{\text{ex},j} - Q_{\text{dil},j}$. Multiple titrations were conducted using solutions of different concentrations of U(VI) and acid. The program Letagrop¹¹ was used to analyze the data and calculate the thermodynamic parameters.

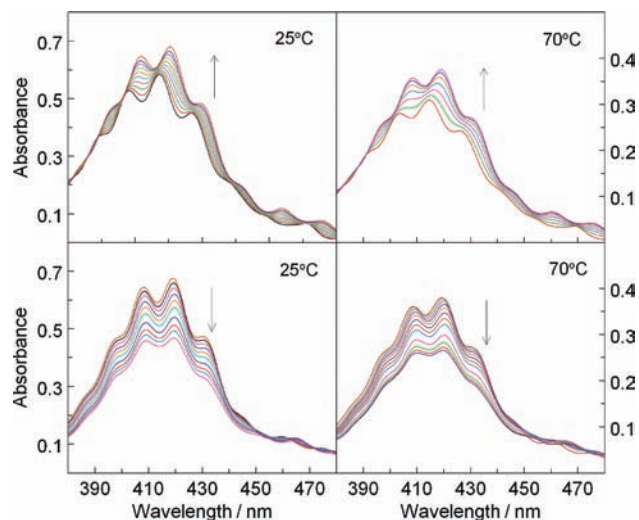


Figure 1. Representative spectrophotometric titrations of U(VI)/fluoride complexation. $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$ Na(ClO₄/F). Upper figures - the first phase of the titrations where the absorbance increased as the concentration of fluoride was increased. Lower figures - the second phase of the titrations where the absorbance decreased as the concentration of fluoride was increased. Cuvette solutions: $V^0 = 2.50 \text{ mL}$; left Figures (25°C), $C_{\text{U}}^0/C_{\text{H}}^0 = 0.0708/0.1242 \text{ mol}\cdot\text{dm}^{-3}$; right Figures (70°C), $C_{\text{U}}^0/C_{\text{H}}^0 = 0.0354/0.08184 \text{ mol}\cdot\text{dm}^{-3}$. Titrant: $C_{\text{F}}/C_{\text{H}} = 1.00/0.100 \text{ mol}\cdot\text{dm}^{-3}$. The spectra are normalized for the total concentration of U(VI). The arrows indicate the progress of the titrations.

2.4. Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS). Uranium L_{II}-edge EXAFS spectra of five solution samples were collected at $t = 22^\circ\text{C}$ at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamline 11-2. The conditions of the samples were such that the dominant U(VI) species in the solutions are UO_2^{2+} , UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- and $\text{UO}_2\text{F}_4^{2-}$, respectively. Approximately 1 mL of the solution was sealed in a polyethylene tube (5 mm i.d.). The polyethylene tubes were mounted on an aluminum sample positioner with Scotch tape for the experiments. Data were collected up to $k_{\text{max}} \sim 16 \text{ \AA}^{-1}$ in both transmission and fluorescence modes. Three to six scans were performed for each sample. Energy calibrations were based on assigning the first inflection point of absorption edge for uranium dioxide to 17166 eV. The EXAFS data were analyzed with the program WinXAS Version 3.1,¹² using parametrized phase and amplitude functions generated by FEFF8¹³ with the crystal structure of bis(tetramethylammonium) aquotetrafluorodioxouranate (VI) dihydrate.¹⁴ Single scattering interactions of $\text{U}=\text{O}_{\text{axial}}$ (axial oxygen), $\text{U}-\text{O}_{\text{eq}}$ (equatorial oxygen), and $\text{U}-\text{F}$ were included.

3. Results and Discussion

3.1. Stability Constants of U(VI)/Fluoride Complexes at Elevated Temperatures. Figure 1 shows the absorption spectra of two representative spectrophotometric titrations at 25 and 70°C . As the titrant was added, the position and intensity of the absorption bands changed. The changes can be discussed in two phases. In the first phase of the titration (two upper figures), the absorption bands were red-shifted, and the intensity increased as the concentration of fluoride was increased. In contrast, in the second phase of the titration (two lower figures), little change in the position of the absorption bands occurred,

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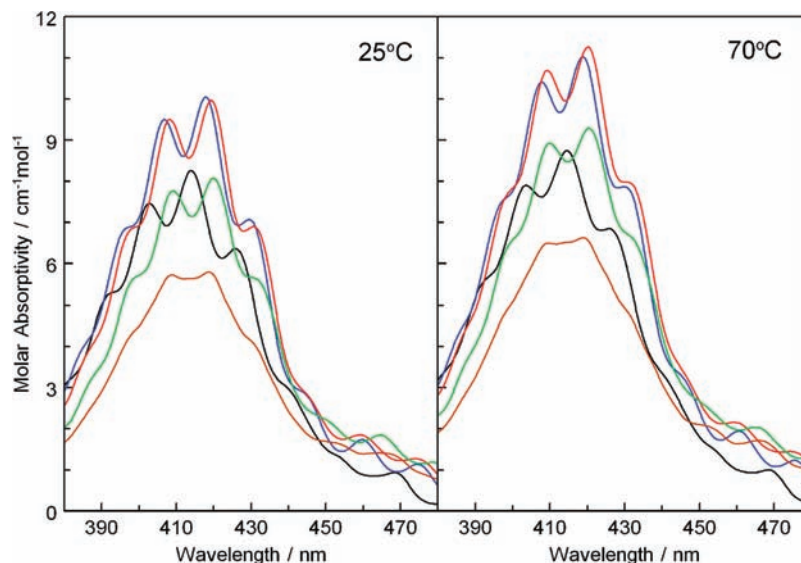
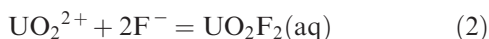
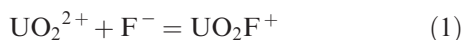


Figure 2. Calculated molar absorptivity of U(VI)/fluoride complexes. $I = 1.0 \text{ mol} \cdot \text{dm}^{-3} \text{ Na}(\text{ClO}_4/\text{F})$. Black, UO_2^{2+} ; blue, UO_2F^+ ; magenta, $\text{UO}_2\text{F}_2(\text{aq})$; green, UO_2F_3^- ; brown, $\text{UO}_2\text{F}_4^{2-}$.

and the intensity decreased as the fluoride concentration was increased. The spectra of the titrations at 40 and 55 °C are not shown, but similar changes in the position and intensity of the absorption bands are observed during the titrations.

Factor analysis of the absorption spectra with the Hyperquad program indicated that there were five absorbing species of U(VI), and the spectra were best-fitted with successive formation of four U(VI)/fluoride complexes (UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$), represented by eqs 1–4.



The molar absorptivities of UO_2^{2+} and the four complexes at 25, 40, 55, and 70 °C are calculated by the Hyperquad program, though only those at 25 and 70 °C are shown in Figure 2. To compare the spectral features at different temperatures, the wavelength of maximum absorption (λ_{max}) and the molar absorptivity at the wavelength (ϵ_{max}) are plotted for all U(VI) species at 25, 40, 55, and 70 °C in Figure 3. Two trends are observed: (1) For all U(VI) species, $\lambda_{\text{max}}(25^\circ\text{C}) < \lambda_{\text{max}}(40^\circ\text{C}) < \lambda_{\text{max}}(55^\circ\text{C}) < \lambda_{\text{max}}(70^\circ\text{C})$, and $\epsilon_{\text{max}}(25^\circ\text{C}) < \epsilon_{\text{max}}(40^\circ\text{C}) < \epsilon_{\text{max}}(55^\circ\text{C}) < \epsilon_{\text{max}}(70^\circ\text{C})$. In other words, the absorption bands are red-shifted and intensified as the temperature is increased. The shift in the wavelength and the increase in the intensity are generally larger for the U(VI)/fluoride complexes (except for the λ_{max} of $\text{UO}_2\text{F}_4^{2-}$) than those

for the free UO_2^{2+} ion (Figure 3). Such observations, also obtained for several other U(VI) complexation systems,^{15–17} imply that the complexation of U(VI) by fluoride is enhanced at elevated temperatures. (2) At each temperature, the λ_{max} and ϵ_{max} do not increase monotonically from the free UO_2^{2+} ion to successively higher complexes (UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$). In fact, $\lambda_{\text{max}}(\text{UO}_2\text{F}_4^{2-}) < \lambda_{\text{max}}(\text{UO}_2\text{F}_3^-)$, and $\epsilon_{\text{max}}(\text{UO}_2\text{F}_4^{2-}) < \epsilon_{\text{max}}(\text{UO}_2\text{F}_3^-) < \epsilon_{\text{max}}(\text{UO}_2\text{F}_2(\text{aq}))$. This trend in λ_{max} for the U(VI)/fluoride complexes differs from the monotonic trend observed for many other complexation systems where higher complexes usually absorb at longer wavelengths.^{15,17}

The stability constants of the four complexes at 25, 40, 55, and 70 °C have been calculated with the Hyperquad program and shown in Table 1. In the calculation, the protonation constants of fluoride at different temperatures in the literature¹⁷ were used. Data in Table 1 indicate that the complexation of U(VI) with fluoride is fairly strong and becomes stronger at higher temperatures. When the temperature is increased from 25 to 70 °C, the stability constants of UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$ are increased by about 2, 3, 8, and 11-fold, respectively.

The stability constants of UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$ are plotted as a function of $1/T$ in Figure 4. The curvature of the plots indicates that the enthalpies of complexation are not constant in the temperature range, and the heat capacities of complexation for the complexes are not zero. This observation could be rationalized by the contributions of the electrostatic interactions between the ionic species and the solvent. In an “isocoulombic” reaction in which the magnitude of the electric charge of each individual ionic species is balanced between the reactants and products, the contributions of electrostatic interactions between the ionic species and the solvent to the temperature dependence of the enthalpy will balance out and the heat capacity of

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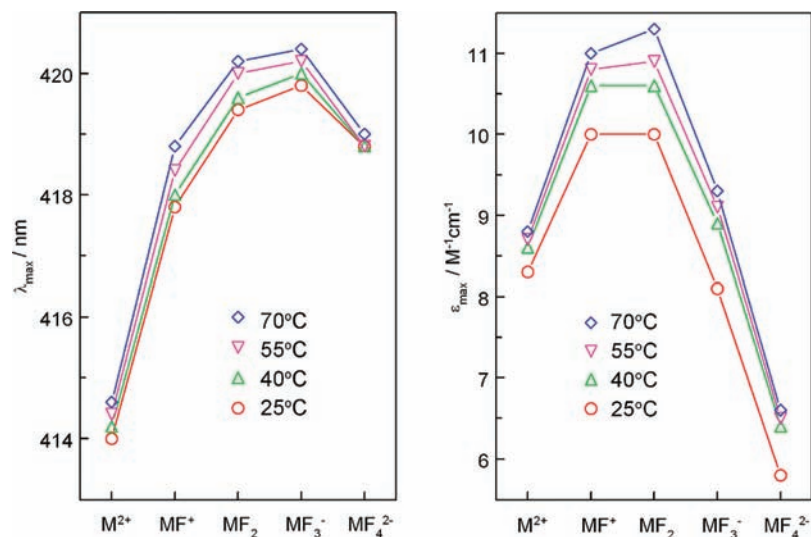


Figure 3. Wavelength for maximum absorption (λ_{\max}) and the molar absorptivity at λ_{\max} (ϵ_{\max}) for the U(VI) species. M^{2+} , MF^+ , MF_2 , MF_3^- , and MF_4^{2-} stands for UO_2^{2+} , UO_2F^+ , UO_2F_2 , $UO_2F_3^-$, and $UO_2F_4^{2-}$.

Table 1. Thermodynamic Parameters for the Complexation U(VI) with Fluoride^a

reaction	t , °C	method	$\log \beta$, $I = 1.0 \text{ mol} \cdot \text{dm}^{-3}$ Na(ClO ₄ /F)	$\log \beta^0$, $I = 0$	ΔH , $\text{kJ} \cdot \text{mol}^{-1}$	ΔS , $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	ref.
$UO_2^{2+} + F^- = UO_2F^+$	25	sp, cal	4.60 ± 0.02	5.20 ± 0.07 5.16 ± 0.06	2.8 ± 0.4 1.70 ± 0.08	97 ± 2	p.w. 3,4
	40	sp	4.62 ± 0.02	5.25 ± 0.07			p.w.
	55	sp	4.67 ± 0.04	5.32 ± 0.07			p.w.
	70	sp	4.80 ± 0.02	5.45 ± 0.07			p.w.
	25	sp, cal	8.07 ± 0.04	8.74 ± 0.07 8.83 ± 0.08	5.2 ± 0.8 2.10 ± 0.19	171 ± 3	p.w. 3,4
$UO_2^{2+} + 2F^- = UO_2F_2(\text{aq})$	40	sp	8.21 ± 0.04	8.91 ± 0.07			p.w.
	55	sp	8.32 ± 0.06	9.06 ± 0.08			p.w.
	70	sp	8.52 ± 0.02	9.31 ± 0.06			p.w.
	25	sp, cal	10.62 ± 0.04	11.25 ± 0.09 10.9 ± 0.1	3.4 ± 1.1 2.35 ± 0.31	213 ± 4	p.w. 3,4
$UO_2^{2+} + 3F^- = UO_2F_3^-$	40	sp	10.78 ± 0.04	11.44 ± 0.09			p.w.
	55	sp	11.21 ± 0.06	11.91 ± 0.10			p.w.
	70	sp	11.55 ± 0.02	12.29 ± 0.09			p.w.
	25	sp, cal	11.92 ± 0.14	12.01 ± 0.18 11.84 ± 0.11	0.2 ± 3.3 0.29 ± 0.47	227 ± 11	p.w. 3,4
$UO_2^{2+} + 4F^- = UO_2F_4^{2-}$	40	sp	12.27 ± 0.02	12.38 ± 0.11			p.w.
	55	sp	12.59 ± 0.06	12.73 ± 0.12			p.w.
	70	sp	12.95 ± 0.04	13.12 ± 0.11			p.w.

^asp, spectrophotometry; cal, calorimetry; sx, solvent extraction; p.w., present work. The uncertainties represent 3σ .

isocoulombic reactions is usually near zero.¹⁸ None of the reactions 1–4 is isocoulombic. Therefore, it is not surprising that the enthalpies of complexation are not constant, and the heat capacities of complexation are not zero.

3.2. Enthalpy and Entropy of Complexation. Data of three calorimetric titrations at 25 °C are shown in Figure 5. The observed reaction heat (total Q) is a function of a number of parameters, including the concentrations of reactants (U(VI), F^- , and proton), the stability constants, and the enthalpy of complexation of the U(VI)/ F^- complexes that form in the titration, as well as the protonation constant and enthalpy of protonation of fluoride. Using the stoichiometric concentrations

of the reactants, the stability constants of U(VI)/fluoride complexes determined by spectrophotometry in this work, and the protonation constant and enthalpy of fluoride previously reported,¹⁹ the enthalpies of complexation for UO_2F^+ , $UO_2F_2(\text{aq})$, $UO_2F_3^-$, and $UO_2F_4^{2-}$ at 25 °C are calculated from the calorimetric titration data. The values of enthalpy at 25 °C from this work are in good agreement with those in the literature.^{2,4} In conjunction with the stability constants, the entropies of complexation are also calculated (Table 1).

The enthalpy and entropy data in Table 1 indicate that the complexation of U(VI) with fluoride is slightly endothermic. The positive entropy of complexation is the

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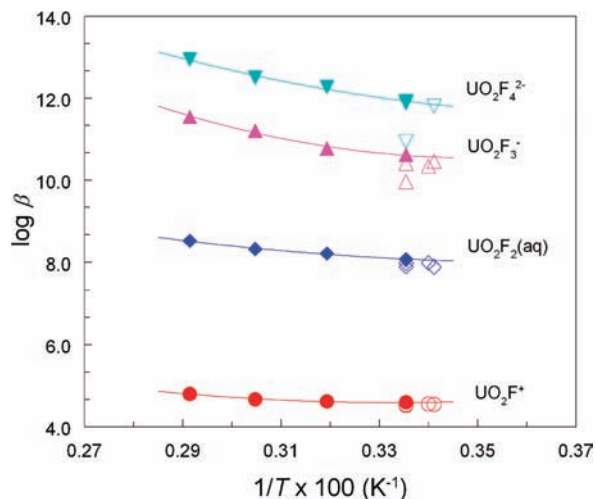


Figure 4. $\log \beta$ vs $1/T$ for the complexation of U(VI) with fluoride. $I = 1.0 \text{ mol} \cdot \text{dm}^{-3} \text{ Na}(\text{ClO}_4/\text{F})$. Solid symbols: data from this work; open symbols: data at $I = 1.0 \text{ mol} \cdot \text{dm}^{-3} \text{ NaClO}_4$ from the literature.³

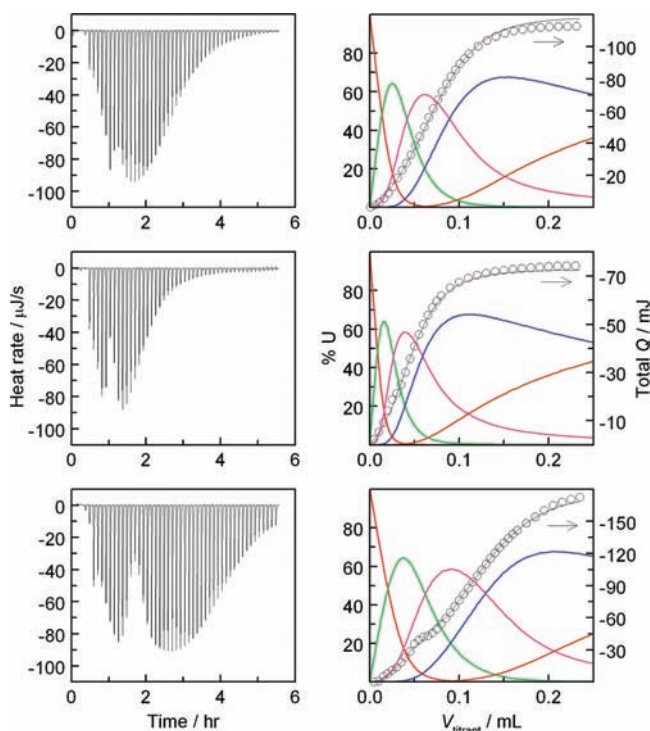


Figure 5. Calorimetric titration of U(VI) fluoride complexation. $I = 1.0 \text{ mol} \cdot \text{dm}^{-3} \text{ Na}(\text{ClO}_4/\text{F})$, $t = 25 \text{ }^\circ\text{C}$. Left column: thermograms of the titrations; right column: total heat (O, exp; solid line, calcd) and the speciation of U(VI) (red, UO_2^{2+} ; green, UO_2F^+ ; magenta, $\text{UO}_2\text{F}_2(\text{aq})$; blue, UO_2F_3^- ; brown, $\text{UO}_2\text{F}_4^{2-}$) as a function of the titrant volume. Cup solutions: 0.900 mL, $C_{\text{U}}/C_{\text{H}}$ ($\text{mmol} \cdot \text{dm}^{-3}$) = 7.87/9.80 (top), 4.92/6.10 (center), 11.80/14.70 (bottom). Titrant: $C_{\text{F}}/C_{\text{H}}$ ($\text{mmol} \cdot \text{dm}^{-3}$) = 300/33.3, 5 $\mu\text{L}/\text{addition}$.

thermodynamic driving force for the formation of U(VI)/fluoride complexes. Release of water molecules from the hydration spheres of both UO_2^{2+} and F^- to the bulk water contributes to the overall entropy of complexation.

3.3. Coordination Modes. The results of EXAFS experiments are shown in Figure 6 and Table 2. In Figure 6, the radial distribution plots (FT magnitude vs R) of all five solutions show a prominent peak representing two oxygen atoms at 1.76–1.80 Å, which can be assigned to

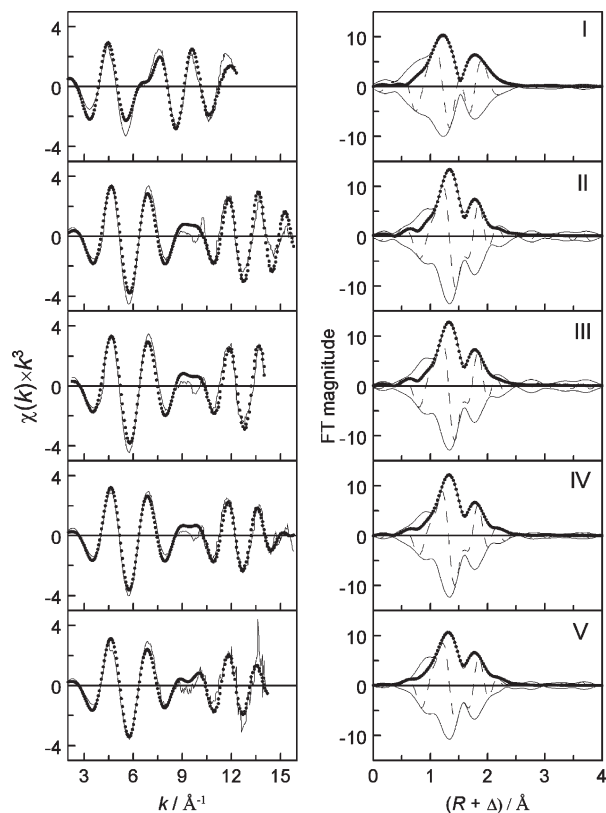


Figure 6. EXAFS spectra (left) and FT magnitude (right) for U(VI)/fluoride systems (Solutions I–V, $t = 22 \text{ }^\circ\text{C}$). Solid lines, experimental; dotted lines, fitted.

the “axial” oxygen in the UO_2^{2+} cation. Beyond this oxygen shell, the features in the radial distribution plots are assigned to coordinating atoms (oxygen and fluorine) in the equatorial plane of the UO_2^{2+} cation. The FT magnitude of Solution I was best-fitted with five oxygen atoms at 2.42 Å, suggesting that the dominant species in this solution is $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$. For Solutions II–V, the EXAFS data were best-fitted with two equatorial coordination shells: one at 2.26–2.29 Å assigned to the fluoride ion, the other at 2.41–2.52 Å assigned to oxygen atoms from water molecules. For all five samples, the total coordination number (including O and F) in the equatorial plane of UO_2^{2+} remains 5. From Solution II to V, the average number of fluoride per uranium increased from 1.2 to 3.8 while the average number of equatorial oxygen per uranium decreased from 4.4 to 1.5. These results show the successive formation of four U(VI)/fluoride complexes: UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$. As shown in Table 2, the average numbers of fluoride observed by EXAFS are in good agreement with those obtained by speciation calculation using the thermodynamic constants measured by spectrophotometry in the present work.

It should be noted that the only significant deviation between the experimental data and the fits in the EXAFS spectra occurs at about $k = 10 \text{ } \text{Å}^{-1}$ (Figure 6). Such deviation, as pointed out by an anonymous reviewer, could be the result of a 2p4f double-excitation in the L_3 EXAFS spectra of actinides²⁰ which becomes visible because of the damped

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Table 2. Fitting Parameters for Uranium L3-Edge EXAFS

no.	sample description			EXAFS data				
	composition (mol·dm ⁻³)	dominant species	CN (F) ^a	shell	R, ^b Å	N ^c	σ ² , ^d Å ²	ΔE ₀ , eV
I	0.045 C _U	UO ₂ ²⁺	0	U–O _{ax}	1.76	2.0	0.00202	–12.49
	0.053 C _H			U–O _{eq}	2.42	5.1	0.00700	–12.49
II	0.045 C _U	UO ₂ F ⁺	1.06	U–O _{ax}	1.80	2.0	0.00229	–8.19
	0.053 C _H			U–F	2.26	1.2	0.00080	–8.19
	0.050 C _F			U–O _{eq}	2.41	4.4	0.0138	–8.19
III	0.045 C _U	UO ₂ F ₂ (aq)	1.90	U–O _{ax}	1.80	2.0	0.00229	–9.63
	0.053 C _H			U–F	2.26	2.1	0.00103	–9.63
	0.100 C _F			U–O _{eq}	2.43	3.2	0.00104	–9.63
	0.045 C _U			U–O _{ax}	1.80	2.0	0.00283	–10.45
IV	0.053 C _H	UO ₂ F ₃ ⁻	3.10	U–F	2.29	3.4	0.00393	–10.45
	0.200 C _F			U–O _{eq}	2.50	1.8	0.00410	–10.45
	0.045 C _U			U–O _{ax}	1.79	2.0	0.00384	–11.75
V	0.053 C _H	UO ₂ F ₄ ²⁻	3.90	U–F	2.29	3.8	0.00499	–11.75
	0.670 C _F			U–O _{eq}	2.52	1.5	0.00280	–11.75

^a The average coordination number of fluoride per uranium obtained by speciation calculation using the stability constants at 25 °C from the present work (Table 1). ^b The 95% confidence limits for the bond lengths (*R*) and coordination numbers (*N*) for each shell are U–O_{ax}, 0.01 Å and ±15%, U–O_{eq}, 0.02 Å and ±25%, respectively. ^c The number of axial oxygen atoms is fixed at 2.0. The amplitude reduction factor (*S*₀²) is restrained to be 0.9. ^d σ² is the EXAFS Debye–Waller term which accounts for the effects of thermal and static disorder through damping of the EXAFS oscillations by the factor exp(–2*k*²σ²).

EXAFS amplitude in this *k* range. The double-excitation is expected to have some effect on the calculated coordination number, but little effect on the calculated bond distance. We believe that the uncertainties assigned to the coordination numbers (15%–25%) in this work are sufficiently large to cover the deviations caused by the double-excitation effect.

Data from the present work on the coordination modes of UO₂F₃⁻ and UO₂F₄²⁻ complexes are in good agreement with the EXAFS data in the literature that have shown the UO₂F₃⁻ and UO₂F₄²⁻ complexes (identified as UO₂F₃(H₂O)₂⁻ and UO₂F₄(H₂O)₂²⁻) have pentagonal bipyramid geometry with U–F and U–H₂O distances equal to 2.26 and 2.48 Å.²¹ A weak UO₂F₅³⁻ complex was identified by ¹⁹F NMR,^{22,23} and the stepwise stability constant (UO₂F₄²⁻ + F⁻ = UO₂F₅³⁻) was calculated to be (0.60 ± 0.05) (mol·dm⁻³)⁻¹ at 25 °C. Obviously such weak complex forms only in very concentrated fluoride solutions. The results of spectrophotometry and EXAFS indicate that the UO₂F₅³⁻ complex can be neglected under the experimental conditions in the present work.

3.4. Calculation of Stability Constants at Variable Temperatures to Infinitely Dilute Solutions: Analysis by the Specific Ion Interaction Approach (SIT). Before using the Specific Ion Interaction (SIT) approach to analyze the data, the stability constants of U(VI)/fluoride complexes in molarity should be converted to the constants in molality using eq 5 described in the literature.²⁴

$$\log K_m = \log K_M + \sum_r \nu_r \log \vartheta \quad (5)$$

where *K*_m and *K*_M are the equilibrium constants in molality and molarity, respectively. ∑_rν_r is the stoichiometric coefficient of the reaction (ν_r is positive for products and negative for reactants) and is equal to –*i* for the formation of the ML_{*i*} complex (M + *i*L = ML_{*i*}). ϑ is the ratio of the values of molality to molarity for the specific ionic medium and varies for different media and concentrations. For 1.0 mol·dm⁻³ NaClO₄, log ϑ is about 0.02.²⁴

The SIT approach originated from the Brønsted–Guggenheim–Scatchard model^{25–27} is used to calculate the equilibrium constants at zero ionic strength.^{23,24} For reactions 1–4, the equilibrium constants at *I* = 0 (log β⁰) are related to log β at other ionic strengths by the following equation:

$$\log \beta - \Delta Z^2 \times D = \log \beta^0 - \Delta \varepsilon I_m \quad (6)$$

where Δ*Z*² = {∑(*Z*_{products}²) – ∑(*Z*_{reactants}²)}, and equals –4, –6, –6, and –4 for reaction 1, 2, 3, and 4, respectively. *D* is the Debye–Hückel term used in the SIT method and *D* = *A**I*_m^{1/2}/(1 + 1.5*I*_m^{1/2}), *I*_m is the ionic strength in molality, and ε is the ion interaction parameter used in the SIT method.^{23,24} The ion interaction parameters (25 °C, kg mol⁻¹) involved in reactions 1–4 include the following: ε(UO₂²⁺, ClO₄⁻), ε(UO₂F⁺, ClO₄⁻), ε(Na⁺, F⁻), ε(Na⁺, UO₂F₃⁻), and ε(Na⁺, UO₂F₄²⁻). The values of Δε at 25 °C are –(0.19 ± 0.06), –(0.50 ± 0.05), –(0.52 ± 0.08), and –(0.62 ± 0.10) for reactions 1–4, respectively.² For the calculation of log β⁰ at temperatures other than 25 °C, we have adopted the following approaches: (1) using the values of *A* at different temperatures tabulated in the literature²⁴; and (2) using the value of Δε at 25 °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 (∂ε/∂*T*)_p are usually ≤ 0.005 kg·mol⁻¹·K⁻¹ for temperatures below 200 °C.²⁴

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Besides, the values of $(\partial\epsilon/\partial T)_p$ for the reactants and products may balance out each other so that $\Delta\epsilon$ for many reactions remains approximately constant up to 100 °C.^{28,29} 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 $\log K_M$ and the uncertainties in $\Delta\epsilon$ at 25 °C). The values of $\log \beta^0$ for all four U(VI)/fluoride complexes at 25 °C are in good agreement with those selected by the NEA review within the error limits.²

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4. Summary

Four successive $\text{UO}_2\text{F}_i^{(2-i)+}$ ($i = 1, 2, 3, 4$) complexes have been identified in aqueous solutions in the temperature range of 25–70 °C. The complexation is entropy driven and is enhanced at elevated temperatures. The stability constants of UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$ increase by about 2-, 3-, 8- and 11-times, respectively, as the temperature is increased from 25 to 70 °C.

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