Uranium(VI) Speciation at Elevated Temperatures and Pressures by Time-resolved Laser-induced Fluorescence Spectroscopy

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A few experimental studies on uranium(VI) hydrolysis and complexation at elevated temperatures and pressures performed to date are obviously quite insufficient to depict a comprehensive picture of the species and the behavior in a wide variety of hydrothermal conditions in the geosphere. In this study, an optical cell system for spectroscopic speciation of metal ions in hydrothermal solutions was developed and combined with time-resolved laser-induced fluorescence spectroscopy for uranium(VI) speciation.

Emission spectra and lifetimes of 1×10^4 M(=mol dm⁻³) uranium(VI) in NaClO₄ solutions in the presence and absence of sulfate or fluoride ion were measured as a function of pH, ligand concentration, temperature (25-200 °C), or pressure (0.1 or 40 MPa). The results were compared with speciation calculations at various conditions on the basis of thermodynamic model and data in the literature. The emission intensities and lifetimes of uranium(VI) decreased rapidly with increasing temperature. The pressure effect on the fluorescence properties could not be neglected, but it was rather small relative to the temperature effect. The temperature dependence of the lifetimes obeyed well the Arrhenius law, and the activation energy was characterized for uranyl(VI) ion and the hydroxide and fluoride complexes.

KEYWORDS: uranium(VI), speciation, hydrolysis, sulfate complexation, fluoride complexation, lifetime, timeresolved laser-induced fluorescence spectroscopy

I. Introduction

The solution chemistry of uranium has been extensively investigated in connection with the chemistry of the nuclear fuel cycle and of migration behavior related to nuclear waste disposal and the tailings of uranium mining.^{1,2)} However, only a few experimental studies to date have been performed for uranium(VI) hydrolysis and complexation at temperature outside the ranges of 20 to 30 °C,¹⁾ which is obviously quite insufficient to depict a comprehensive picture of uranium species and the behavior in a wide variety of hydrothermal conditions in the geosphere. In general, metal species and the behavior in hydrothermal solutions must be strongly dependent on the conditions, since the properties of water, e.g., density,³⁾ dielectric constant,⁴⁾ ion product,⁵⁾ viscosity,⁶⁾ etc., vary remarkably with increasing temperature and Instead of overcoming the difficulty of pressure. experimental works at elevated temperatures and pressures, theoretical studies of uranium under hydrothermal conditions have also been conducted,⁷⁻⁹⁾ however those predictions do not cover all aspects of the behavior in hydrothermal solutions and should be validated by comparing with precise experimental results. For a better understanding of the hydrothermal geochemistry and migration behavior of uranium, the following studies should be necessary as future works; development of in-situ speciation technology, elucidation of temperature and/or pressure dependence of chemical reactions, validation of thermodynamic model and data, etc.

A number of spectroscopic techniques have been employed for speciation study of uranium, *e.g.*, Raman¹⁰ and NMR¹¹ spectroscopy, UV-Vis spectrophotometry,¹² X-ray absorption spectroscopy,^{13,14} and so on. Time-resolved laser-induced fluorescence spectroscopy (TRLFS) is a well-

*Corresponding author, Tel: +81-29-282-5493, Fax: +81-29-282-5935, E-mail: kimura@analchem.tokai.jaeri.go.jp known sensitive and versatile technique not only for uranium(VI) but also for several lanthanides(III) and actinides(III). The fluorescence properties of the uranyl(VI) ion, UO_2^{2+} , have been extensively studied in acidic solutions and in various complexing media using TRLFS at ambient temperature (e.g., Refs. 15-27). Recently, TRLFS was also applied to the hydrolysis study of U(VI) in the temperature range of 10-60 °C.²⁸⁾ On the other hand, X-ray absorption fine structure and Raman studies of metal ions in subcritical and supercritical water have been reported using an autoclave having optical windows.^{29,30)} The combination of this kind of optical cell and TRLFS makes it possible to perform *in-situ* speciation of U(VI) under hydrothermal conditions at higher than 100 °C and 0.1 MPa.

In the present work, an optical cell system was developed for spectroscopic speciation of metal species under hydrothermal conditions and it was combined with TRLFS for U(VI) speciation. The fluorescence properties of U(VI) in NaClO₄ solutions with and without sulfate or fluoride ion were measured in the temperature range of 25 to 200 °C at a pressure 0.1 or 40 MPa.

II. Experimental

1. Sample preparation

Sample solutions of 1×10^{-4} M U(VI) were prepared from a stock solution of 2×10^{-2} M uranyl(VI) perchlorate in 1.0 M HClO₄. The stock solution was prepared by dissolving Na₂U₂O₇ in HClO₄. Na₂U₂O₇ was precipitated from uranyl(VI) nitrate solution by adding 1 M NaOH. The precipitate was filtered, washed three times with doubly distilled deionized water, and redissolved with HClO₄. This process was repeated two times. The U(VI)

concentration was determined by potentiometric titration using $K_2Cr_2O_7$ after the reduction of U(VI) to U(IV) by Fe(II) in phosphoric acid solution. The sample solutions were adjusted to ionic strength I=0.5 and appropriate pH by the addition of NaClO₄, HClO₄ and/or NaOH and the solution pH was checked before and after the fluorescence measurements. All other chemicals such as NaF and Na₂SO₄ were of analytical reagent grade.

2. Optical cell system for spectroscopic speciation at elevated temperatures and pressures

The optical cell system consists of a HPLC pump (JASCO, PU-1586), a pre-heating tube (1/16-in. I.D.), an optical cell with three sapphire windows, an electric furnace, a cooling tube (1/16-in. I.D.), a back pressure regulator (JASCO, SCF-Bpg), etc. To avoid the dilution of the sample solution by water during the fluorescence measurements, the optical cell and a water flowing line were connected using a T-type joint. The optical cell used has the body fabricated by Hastelloy C-276 and has an internal volume of 10.5 cm³. Excitation of the sample by a laser beam and emission light collection were carried out by way of three sapphire windows which were sealed to the cell using gold-plated metal foil. The cell was fixed horizontally in the electric furnace with three quartz windows and the temperature was controlled in the range of ambient temperature to 200 °C. The sample temperature determined with a sheathed Chromel-Alumel was thermocouple at the point of 12 mm from the center of the Doubly distilled water was loaded into the water cell flowing line using the HPLC pump, and pressure control up to 40 MPa within ±0.1 MPa was achieved by the back pressure regulator.

3. Time-resolved laser-induced fluorescence measurements

U(VI) in the sample solutions was excited by 266 nm (fourth harmonic) laser beam that was obtained directly from a pulsed (5 Hz) output of a Nd:YAG laser (Spectron Laser Systems Ltd., SL-803). The pulse power was typically 3 mJ per pulse and the pulse width was about 15 ns. For measurements of the fluorescence spectra, the emission light was focused on a polychromator (HR-320, ISA Jobin-Yvon) using an optical fiber and detected by a gated multichannel diode array (DIDA-512, Princeton Instruments, Inc.) with appropriate delay and gate times. The spectral resolution was 0.5 nm and the spectral range was 256 nm. Α Spectrometric Multichannel Analyzer system (SMA, Tokyo Instruments, Inc.) installed on a personal computer controlled the spectrometer. For measurements of the fluorescence lifetimes, the emission light was collected at 90° into an Oriel 77257 monochromator using another optical fiber and detected by a Hamamatsu R3896 photomultiplier tube. The signal was fed into a Hewlett Packard 54510A digitizing oscilloscope that was connected to the personal computer through a GP-IB interface.

III. Results and discussion

1. Corrections of equilibrium constants for speciation calculation

In order to compare and interpret the experimental results, species distribution was calculated for U(VI) at various conditions on the basis of thermodynamic model and data. Prior to the calculations, temperature and ionic strength corrections of stability constants were made, respectively, by using the DQUANT equation³¹⁾ as an example of approximation methods³²⁾ and the SIT (specific ions interaction theory) method¹⁾ where the ionic interaction coefficients were considered to be temperature independent.

Assuming that the temperature dependence of the heat capacity of a dissociation reaction is proportional to the temperature dependence of the electrostatic contribution, Helgeson³¹⁾ obtained the DQUANT equation:

$$\log_{10} K^{0}(T) = \frac{\Delta_{r} S_{m}^{0}(T_{0})}{\ln(10)RT}$$

$$x \left\{ T_{0} - \frac{\theta}{\omega} \left[1 - \exp\left(\exp\left(b + aT\right) - c + \frac{T - T_{0}}{\theta}\right) \right] \right\}$$

$$- \frac{\Delta_{r} H_{m}^{0}(T_{0})}{\ln(10)RT}, \qquad (1)$$

where R is the molar gas constant; θ =219 K; a=0.01875 K⁻¹; b=-12.741; c=exp(b+aT_0)=7.84x10⁻⁴; ω =(1+ac θ)=1.00322; T₀ is the reference temperature (298.15 K); $\Delta_r S_m^0(T_0)$ and $\Delta_r H_m^{-0}(T_0)$ are the molar entropy and enthalpy, respectively, of the dissociation reaction at T₀. The equilibrium constants for the following reactions:

$$mUO_{2}^{2+} + nH_{2}O = (UO_{2})_{m}(OH)_{n}^{(2m-n)+} + nH^{+}, \qquad (2)$$

$$UO_2^{2+} + nSO_4^{2-} = UO_2(SO_4)_n^{(2-2n)+},$$
 (3)

$$UO_2^{2+} + nF^- = UO_2F_n^{(2-n)+},$$
 (4)

at zero ionic strength in the temperature range of 25 to 200 °C were calculated from thermodynamic data, $\Delta_r S_m^{0}(T_0)$ and $\Delta_r H_m^{0}(T_0)$, reported in the literature.^{1,28)} Six hydroxide species, $(UO_2)_m(OH)_n^{(2m-n)+}$, (mn)=(11), (12), (13), (22), (35), (37); two sulfate species, $UO_2(SO_4)_n^{(2-2n)+}$ (n=1,2); and four fluoride species, $UO_2F_n^{(2-n)+}$ (n=1-4), were taken into account in the speciation calculations. After the ionic strength correction to I=0.5, speciation diagrams of UO_2^{2+} and its complexes were calculated as a function of pH or ligand concentration, as shown in the later part of the paper.

2. Analyses of U(VI) fluorescence data

Fluorescence intensity at a given wavelength λ in the presence of multiple emitting species can be described as:

$$F(\lambda, t) = \sum_{i} F_{i}(\lambda, 0) \exp\left(-\frac{t}{\tau_{i}}\right)$$

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$$= (kI_0 d) \sum_i (\varepsilon_i \phi_i C_i) \exp\left(-\frac{t}{\tau_i}\right), \qquad (5)$$

where $F_i(\lambda,0)$ is the initial fluorescence intensity of the *i*th species which consists of k the apparatus factor, I₀ the laser intensity, d the optical pathlength, ε_i the molar absorption coefficient, ϕ_i the fluorescence quantum yield, τ_i the fluorescence lifetime and C_i the concentration of the *i*th For quantitative analyses of C_i of multiple species. emitting species from a series of emission spectra, the ε_i , ϕ_i , and τ_i for each species have to be known in advance even only at ambient temperature. Furthermore, both the $F_i(\lambda, 0)$ and τ_i should have a specific temperature dependence for various species. Therefore, the temperature dependence of τ_i independent of $F_i(\lambda,0)$ was studied as a first step for hydroxide, sulfate, and fluoride complexation of U(VI). When several fluorescent species coexist in the sample and the ligand exchange rates among those species are lower than their fluorescence decay rates, the fluorescence decay curves observed at a given temperature can be described by using a multi-exponential function.

The Arrhenius law that is known as an exponential relationship among the rate constant k, the temperature T, and the activation energy E_a of the reaction considered often express the temperature dependence of reaction kinetics. For a fluorescence decay process, the rate constant k corresponds to the de-excitation constant k_{obs} of the fluorescent species, defined as the reciprocal of the lifetime τ_{obs} , *i.e.*,

$$k_{obs} = \frac{1}{\tau_{obs}} = A \exp\left(-\frac{E_a}{RT}\right),$$
(6)

where A and E_a are characteristic constants of the species.

3. Hydroxide complexation of U(VI)

Figure 1 shows speciation diagrams of UO_2^{2+} and the hydroxide complexes at different temperatures. The carbonate complexes; *i.e.*, $UO_2(CO_3)_n^{(2-2n)+}$ (n=1-3), in equilibrium with atmosphere $(0.03 \% CO_2 \text{ partial pressure})$ were also taken into account in these calculations, however those were not contributed in the pH range of less than 7. Figure 1 indicates that the hydrolysis of U(VI) is promoted with an increase of temperature and that relative concentrations of mononuclear complexes such as UO₂OH⁺ and UO2(OH)3 increase, while those of polynuclear complexes such as $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^{+}$, and $(UO_2)_3(OH)_7$ decrease with increasing temperature. These effects could be correlated with the decrease in the dielectric constant of the solvent water with increasing temperature. From the maximum peaks in the emission spectra of U(VI) in 0.5 M NaClO₄ at 25 °C in the range of pH 2.0-6.0, emission wavelength to measure the lifetimes was fixed at 510 nm.

The k_{obs} of U(VI) observed in 0.5 M NaClO₄ at pH 2.0-6.0 as a function of temperature are summarized in Figs. 2(a)



Fig. 1 Speciation diagrams of uranyl(VI) ion and the hydroxide-complexes at different temperatures; [U(VI)]=1x10⁴ M; I=0.5 (NaClO₄); (a) T=25 °C, (b) T=50 °C, (c) T=100 °C, (d) T=150 °C: (mn)=(UO₂)_m(OH)_n^{(2m-n)+}.

and (b) as the Arrhenius plots. At pH 2.0-3.5, only one component of the k_{obs} was observed in the temperature range of 25.0-100 °C as plot 1 in Fig. 2(a), indicating that the plot 1 corresponds to UO₂²⁺ as shown in Figs. 1(a)-(c). The small deviation from the plot 1 observed at above *ca*. 75 °C and pH 3.0 would be due to the formation of UO₂OH⁺ or (UO₂)₂(OH)₂²⁺. The activation energy and lifetime at 20 °C and 0.1 MPa that calculated from the plot 1 at pH 2.0 were (44.9±1.2) kJ·mol⁻¹ and (2.0±0.4) µs, respectively.

At pH 4.0 and 4.5, two or three components (plots 1-3 in Fig. 2(a)) of the k_{obs} depending on the temperature ranges were analyzed and found in the fluorescence decay curves by using double- or triple-exponential function without any fixation in the statistical analysis. The plot 1 measured at



Fig. 2 Arrhenius plots of the temperature dependence of the decay constants of U(VI) species; [U(VI)]=1x10⁴ M; I=0.5 (NaClO₄); (a) pH 2.0-4.5, (b) pH 5.0-6.0; open symbols, 0.1 MPa; closed symbols, 40 MPa.

pH 4.0 or 4.5 in the temperature range of 25-87.5 °C agreed well with those at pH 2.0-3.5, corresponding to UO_2^{2+} . The plot 2 was observed in the temperature range of 25-200 °C at both pH 4.0 and 4.5, however those slopes changed slightly at the temperature ca. 125 °C. From the plot 2 (T=25-100 °C) at pH 4.5, the activation energy and lifetime at 20 °C and 0.1 MPa were calculated to be (39.3 ± 1.2) kJ·mol⁻¹ and (13.9 ± 2.9) µs, respectively. The plot 3 was detected at the temperature above 112.5 °C (pH 4.0) or 50 °C (pH 4.5), respectively, and the fluorescence intensities increased with increasing temperature. The plot 3 (T=50-100 °C) gave (10.6 \pm 0.7) kJ·mol⁻¹ and (33.9 \pm 3.9) μ s as the activation energy and lifetime at 20 °C and 0.1 MPa, respectively. The speciation diagrams (Fig. 1) indicate the coexistence of UO_2^{2+} , UO_2OH^+ , $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ in the pH range 4.0-4.5 with different temperature dependence of the concentrations. From the comparison of the calculated

lifetime (13.9 \pm 2.9) μ s and that in the literature,²⁸⁾ the plot 2 can be assigned to $(UO_2)_2(OH)_2^{2^+}$ and the slope at higher temperature may be influenced by UO_2OH^+ or $(UO_2)_3(OH)_5^+$. The temperature dependence of the fluorescence intensity of the plot 3 indicates that this component is due to UO_2OH^+ .

At pH 5.0-6.0, one component of the k_{obs} (plot 4 in Fig. 2(b)) was observed in the temperature range of 25-200 °C, which those slopes varied gradually with pH. Additionally, another component (plot 5) was found in the temperature range of 125-200 °C at pH 6.0, corresponding to UO₂OH⁺ (plot 3 in fig. 2(a)). From the speciation diagrams (Fig. 1), the plot 4 can be assigned to $(UO_2)_3(OH)_5^+$, but the slopes at pH 5.0 and 5.5 would be influenced by $(UO_2)_2(OH)_2^{2+}$, especially at lower temperature. From the plot 4 (T=25-100 °C) at pH 6.0, the activation energy and lifetime at 20 °C and 0.1 MPa were calculated to be (37.8 ± 0.7) kJ·mol⁻¹ and (35.7±4.3) µs, respectively. Figure 1 indicated the large contribution of $UO_2(OH)_3^-$ and $(UO_2)_3(OH)_7^-$ at higher pH and temperature and their lifetimes at 20 °C and 0.1 MPa have been reported to be 0.8 ± 0.1 µs and 230 ± 20 µs, respectively.²⁶⁾ However, those components were not observed in the fluorescence decay curves. This suggests that relative fluorescence intensity of $(UO_2)_3(OH)_5^+$ is much stronger than those of $UO_2(OH)_3^-$ and $(UO_2)_3(OH)_7^-$ or that the temperature and ionic strength corrections of the stability constants for the speciation calculation at higher temperature have some problems in the thermodynamic model (Eq. (1)) or the data of $\Delta_r S_m^{0}(T_0)$ and $\Delta_r H_m^{0}(T_0)$ used.

The pressure dependence of the physicochemical properties of the solvent water is considerably small in contrast to their temperature dependence in the experimental conditions.³⁻⁶⁾ As expected from the fact, the difference of the lifetimes between 0.1 MPa and 40 MPa was not observed for UO₂OH⁺ or $(UO_2)_3(OH)_5^+$, while small differences were found for UO₂²⁺ and $(UO_2)_2(OH)_2^{2+}$, as shown in Fig. 2

4. Sulfate complexation of U(VI)

The speciation diagrams of UO_2^{2+} and the sulfate complexes at different temperatures are shown in Fig. 3. The pH 3.0 for the experiments was selected from two reasons that hydroxide and carbonate complexes are not formed and relative concentrations of the species are insensitive to this pH range at 25 °C. Figure 3 indicates that the sulfate complexation of U(VI) increases with increasing temperature at a constant concentration of sulfate ion, according to the increases of the stability constants. To determine the emission wavelength for measurements of the lifetimes, the emission spectra of U(VI) in Na₂SO₄+NaClO₄ solutions were measured at 25 °C. The intensities of the spectra increased remarkably with increasing sulfate ion The emission peaks were also shifted concentration. gradually to longer wavelength and the lifetimes were measured for each 1 nm rise in the wavelength range of 510-515 nm for the samples of $[SO_4^{2-}] = 3x10^{-4}-1x10^{-1}$ M, respectively.

Figure 4 shows the temperature dependence of the k_{obs} of U(VI) samples at 0.1 MPa or 40 MPa as the Arrhenius plots.



Fig. 3 Speciation diagrams of uranyl(VI) ion and the sulfatecomplexes at different temperatures; [U(VI)]=1x10⁴ M; I=0.5 (Na₂SO₄+NaCIO₄); pH 3.0; (a) T=25 °C, (b) T=50 °C, (c) T=100 °C, (d) T=150 °C.

All the fluorescence decay curves measured in this system were fitted by using single-exponential function, *i.e.*, only one component of the k_{obs} was observed in each sample at each condition. According to the speciation diagrams of Fig. 3, different concentrations of UO_2^{2+} and the sulfate complexes have to be contained in each sample at a given condition. This indicates that the ligand (SO_4^{2-}) exchange rates among the species are much higher than their fluorescence decay rates or that the lifetimes of these species are similar with each other. Therefore, each data points in Fig. 4 provide only the averaged k_{obs} of the mixed species and direct speciation of the sulfate complexes is difficult from the Arrhenius plots. From plots 1-6 in Fig. 4, the activation energy and lifetime ranges at 25 °C and 0.1 MPa



Fig. 4 Arrhenius plots of the temperature dependence of the decay constants of U(VI) species; [U(VI)]=1x10⁻⁴ M; I=0.5 (Na₂SO₄+NaCIO₄); pH 3.0; [SO₄⁻²]=3x10⁻⁴-1x10⁻¹ M; open symbols, 0.1 MPa; closed symbols, 40 MPa.

were calculated to be (45.1-39.6) kJ mol⁻¹ and (1.50-7.11) μ s, respectively. The pressure effect between 0.1 MPa and 40 MPa was small but observed for all the samples.

5. Fluoride complexation of U(VI)

Figure 5 shows speciation diagrams of UO_2^{2+} and the fluoride complexes at different temperatures. The pH 3.0 for the experiments was selected from the similar reasons mentioned in the sulfate system. Figure 5 indicates that the fluoride complexation of U(VI) is suppressed with an increase of temperature at a constant concentration of fluoride ion, in spite of the increases of the stability constants. This means that the formation of HF and HF_2 competes with the fluoride complexation of U(VI) and surpasses in the fluoride system at higher temperature. As described subsequently, experimental results showed the formation of UO₂OH⁻ at lower concentration of fluoride ion and at higher temperature (>100 °C). The speciation diagrams including UO₂OH⁻ are also shown in Fig. 5 with dashed lines. In a similar manner with the sulfate system, the emission spectra of U(VI) in NaF+NaClO₄ solutions were measured at 25 °C. The intensities of the spectra remarkably with increasing fluoride ion increased concentration. The emission peaks were also shifted gradually to longer wavelength and the lifetimes were measured for each 1 nm rise in the wavelength range of 515-520 nm for the samples of $[F^-]=3x10^{-5}-1x10^{-2}$ M, respectively.

Figures 6(a) and (b) show the temperature dependence of the k_{obs} of U(VI) samples at 0.1 MPa or 40 MPa as the Arrhenius plots. At [F]= $3x10^{-5}$ and $1x10^{-4}$ M, two or three components (plots 1-3 in Fig. 6(a)) of the k_{obs} depending on the temperature ranges were analyzed in the fluorescence decay curves by using double- or triple-exponential function



Fig. 5 Speciation diagrams of uranyl(VI) ion and the fluoridecomplexes at different temperatures; [U(VI)]=1x10⁴ M; I= 0.5 (NaF+NaClO₄); pH 3.0; (a) T= 25 °C, (b) T= 50 °C, (c) T= 100 °C, (d) T= 150 °C.

without any fixation in the statistical analysis. The plots 1(T=25-100 °C) and 3(T=100-200 °C) are in fair agreement with the plots 1 and 3 of Fig. 2(a) in the hydroxide system, corresponding to UO_2^{2+} and UO_2OH^+ , respectively. The plot 2 can be assigned obviously to UO_2F^+ from the speciation diagrams (Fig. 5). In Fig. 6(b), three components (plots 4-6) were also analyzed at $[F] = 3x10^{-4} M$, indicating UO₂OH⁺ (plot 6, T=175-200 °C) and UO₂F⁺ (plot 4), and the other one (plot 5) appeared. These results indicate that the formation of UO₂OH⁺ cannot be neglected at higher temperature, even in strong complexing media. At $[F^-] = 1 \times 10^{-3}$ M, UO₂OH⁺ disappeared and plot 4(UO₂F⁺) and plot 5 were observed. From the plots 2 and 4 observed at $[F^{-}] = 3x10^{-5} - 1x10^{-3}$ M, the activation energy and lifetime



Fig. 6 Arrhenius plots of the temperature dependence of the decay constants of U(VI) species; $[U(VI)]=1x10^4$ M; I=0.5 (NaF+NaClO₄); pH 3.0; (a) $[F^-]= 3x10^5-1x10^4$ M, (b) $[F^-]= 3x10^4-1x10^{-2}$ M; open symbols, 0.1 MPa; closed symbols, 40 MPa.

at 20 °C and 0.1 MPa of UO_2F^+ were calculated to be (37.0 ± 1.0) kJ·mol⁻¹ and (43.4 ± 7.4) µs, respectively. At higher concentration of fluoride ion ([F]= $3x10^{-3}$ and $1x10^{-2}$ M), only one component (plot 5) remained. This indicates that fluorescence intensities of the plot 5 are much stronger than that of UO_2F^+ . From Fig. 5, the plot 5 observed at $[F] = 3x10^4 - 1x10^2$ M is associated with UO₂F₂ and UO₂F₃ and the plot 5 at different concentration of fluoride ion can be described by using double function of Eq. (6). However, it was difficult to assign the calculated activation energies to UO_2F_2 and UO_2F_3 directly, since those varied with fluoride ion concentration (see Fig. 6(b)). Further study is necessary to identify those species. The pressure effect between 0.1 MPa and 40 MPa was small but found for UO_2F^+ and $UO_2F_2+UO_2F_3^-$.

Species	$\tau_{obs}~(\mu s,20~{}^{o}C)^{a)}$	Ref.	E _a (kJ·mol⁻¹) ^{a)}	Ref.
UO2 ²⁺	1.7 ± 0.3 2 0 + 0 4	22 ± 0.5^{b} 2 ± 0.1^{c} 1.75^{d}	44.0 ± 1.1 44.9 ± 1.2	$41.5 + 1.7^{b}$ $44.3 + 1.5^{d}$
$\rm UO_2OH^+$	33.8 ± 2.0	2.2 ± 0.3 , 2 ± 0.1 , 1.75	10.3 ± 0.4	+1.5 <u>+</u> 1.7 , ++ .5 <u>+</u> 1.5
(UO) (OH) ²⁺	33.9 ± 3.9	$39.3 \pm 4.4^{\text{b}}, 80 \pm 5^{\text{c}}$	10.6 ± 0.7	24.6 ± 1.6^{b}
$(00_2)_2(011)_2$	13.9 ± 2.9	$13.4 \pm 2.4^{\text{b}}, 9 \pm 1^{\text{c}}$	37.8 ± 0.0 39.3 ± 1.2	35.1 ± 2.7^{b}
(UO ₂) ₃ (OH) ₅ ⁺	35.9 ± 4.1		38.9 ± 0.9	н.
	35.7 ± 4.3	$25.3 \pm 3.6^{\text{b}}, 23 \pm 3^{\text{c}}$	37.8 ± 0.7	22.9 ± 2.1^{b}
UO ₂ F	37.7 ± 5.8 43.4 ± 7.4	50 ^{d)}	37.6 ± 1.2 37.0 ± 1.0	29.4 ± 0.6^{d}

Table 1 Fluorescence lifetimes τ_{obs} and activation energies E_a for uranyl(VI) ion and the hydroxide and fluoride complexes

^{a)} I=0.5 at 40 MPa (upper) and 0.1 MPa (lower), ^{b)}I=0.5 at 20 °C²⁸, ^{c)}I=0.1 at 20 °C²⁶, ^{d)}I=1 at 25 °C²⁵

IV. Conclusion

We have developed the optical cell system for spectroscopic speciation of metal species in hydrothermal solutions and demonstrated the performance in the speciation study of hydroxide, sulfate, and fluoride complexation of U(VI) by combining with TRLFS. Several U(VI) species were identified directly by the Arrhenius plots of the \boldsymbol{k}_{obs} that were determined from the fluorescence decay curves by using a multi-exponential function. To compare with the literature data, the lifetimes at 20 °C and activation energies of the U(VI) species are summarized in Table 1, indicating large discrepancies except for UO_2^{2+} . This suggests obviously the necessity for further investigations of not only hydrolysis and complexation but also redox reaction, precipitation, and so on to elucidate the hydrothermal geochemistry of U(VI). These are in progress and the results will be presented in forthcoming papers.

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