

SPECIATION OF ACTINIDES IN AQUEOUS SOLUTION BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY (TRLFS)

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Time-resolved laser-induced fluorescence spectroscopy (TRLFS) as a sensitive and selective method has been applied to the speciation of actinides in aqueous solution. Studies on hydrolysis and carbonate complexation of U(VI) and on determination of hydration number of Cm(III) are reported.

Keywords: Speciation, TRLFS, Emission spectrum, Lifetime, U(VI), Hydrolysis,
Carbonate complexation, Cm(III), Hydration number

1. HYDROLYSIS AND CARBONATE COMPLEXATION OF U(VI)

1.1 INTRODUCTION

The chemical behavior of U(VI) toward hydrolysis and carbonate complexation, which are considered reactions of major importance of actinides in natural aquatic systems[1], was investigated by a great number of studies during the last half decade[2,3]. Despite these efforts, there has been considerable discrepancy within the available data on hydrolysis and carbonate complexation of U(VI). Due to the extensive use of uranium in nuclear reactors all over the world and the necessity of disposing of uranium in deep geological formations, reliable information on the relevant chemical reactions of uranium under natural aquatic system condi-

tions is necessary.

To overcome the difficulties involved in the study and evaluation of data for actinide elements, sensitive spectroscopic techniques have been developed[4,5]. These methods have been shown to provide insight into the behavior of actinides in aqueous solutions[5–9]. Among these techniques, time-resolved laser-induced fluorescence spectroscopy(TRLFS) is especially promising, since an intense laser light source allows detection of low concentrations of metal ions, and the differences in the lifetimes of the excited states of metal species allow a differentiation of individual fluorescence contributions from different species by time resolution of the emission process. On the other hand, sufficiently long lifetimes of excited states can be observed for only a few metal ions in aqueous solutions, among them UO_2^{2+} .

Despite this promising feature, TRLFS has not yet been extensively applied to the speciation of U(VI). The studies available in this area have been summarized recently by Saini et al.[10]. In their own study of U(VI) in aqueous solutions at different pH by UV-Vis and fluorescence spectroscopy, the enhancement of U(VI) luminescence was observed with increasing pH. In their report, the identification of individual species was not described, and the U(VI) solutions investigated were supersaturated with respect to U(VI)[10].

In the present study, samples at different pH were taken from U(VI) solutions in solid-liquid equilibrium with schoepite $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ under 0.03 % CO_2 partial pressure, i.e., air[11]. The present report deals with a demonstration of the applicability of TRLFS for the spectroscopic speciation of U(VI) hydrolysis and carbonate complexes.

1.2 EXPERIMENTAL

Sample solutions were taken from 0.1 M perchlorate solution of pH 3.87 to 7.00 containing 5×10^{-6} M to 2×10^{-2} M U(VI). Phase separation was done with cellulose acetate ultrafilters(200 nm), which had been preequilibrated with the respective solutions to avoid influence of the sorption effect. Quartz cuvettes of a pathlength of 1 cm were used, also after being preequilibrated with the respective solutions. Further details of the solubility study are given elsewhere[11].

The spectrometer consisted of a Nd:YAG laser(Spectron Physics Systems, U.K.) with a pulse duration of 15 ns and a pulse intensity of 1 mJ at an excitation wavelength of 266 nm (fourth harmonic). The fluorescence emission was focused on a polychromator(HR 320, Division Jobin Yvon) and detected by a diode array multichannel analyzer(DIDA-512, Princeton Instruments, Inc.). The spectral reso-

lution was 0.5 nm and the spectral range was 256 nm. A delay generator(Princeton Instruments Co.) was used for time resolution. The spectrometer was controlled by a Spectrometric Multichannel Analyzer System(SMA, Tokyo Instruments Inc.) installed on an NEC-9801/RX personal computer. Spectra deconvolution was made by an algorithm based on the sequential Simplex[12] developed during this work.

1.3 RESULTS AND DISCUSSION

Lifetime τ and the characteristic emission spectrum of a species due to complexation provide two parameters which allow U(VI) speciation. The use of an intense laser beam as excitation light source allows speciation of U(VI) at low concentration. Detection limits of U(VI), which are defined as 3σ of background counts at a peak wavelength of the emission spectrum, are given as: 2×10^{-9} M in 5.0 M H_2SO_4 and 2×10^{-10} M in 4.0 M H_3PO_4 .

TRLFS was applied to the investigation of U(VI) in 0.1 M perchlorate solution under atmospheric CO_2 partial pressure in solubility equilibrium with schoepite. Details on the procedures and evaluation of that study were given elsewhere together with the single-component emission spectra of the species $UO_2^{2+}(aq)$, $(UO_2)_2(OH)_2^{2+}(aq)$, $(UO_2)_3(OH)_5^+(aq)$ and $UO_2CO_3(aq)$ [11]. Figure 1.1 gives the distribution of the species as a function of pH which was obtained from the calculation with the formation constants reported. Shaded areas account for 1σ error limits.

Discussion will be made on the basis of six emission spectra recorded at pH 3.87, 4.06, 4.98, 5.77, 6.02 and 7.00. These spectra are digitally interpreted by the single component spectra given in

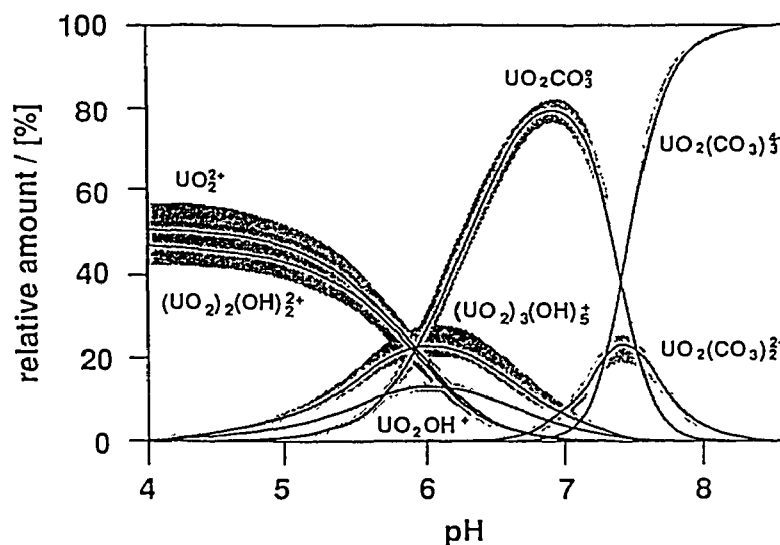


Fig. 1.1. Distribution of U(VI) species in 0.1 M perchlorate solution as a function of pH. Formation constants employed are $\log \beta_{11}=7.70 \pm 0.04$ for UO_2OH^+ [14], $\log \beta_{22}=21.59 \pm 0.06$ for $(UO_2)_2(OH)_2^{2+}$ [13], $\log \beta_{35}=51.78 \pm 0.06$ for $(UO_2)_3(OH)_5^+$ [11], $\log \beta_{101}=9.23 \pm 0.02$ for $UO_2CO_3^0$ [15], $\log \beta_{102}=15.38 \pm 0.17$ for $UO_2(CO_3)_2^{2-}$ [15] and $\log \beta_{103}=21.86 \pm 0.05$ for $UO_2(CO_3)_3^{4-}$ [15].

reference[11]. Lifetimes and emission maxima of the single-component spectra are given in Table 1.1. The spectra give the observed fluorescence emission as a function of the wavelength in the range 450 to 650 nm. Since it turned out to be most convenient, the discussion will be based on emission

Table 1.1. Emission maxima and lifetimes of fluorescence spectra of U(VI) hydrolysis species and $\text{UO}_2\text{CO}_3^\circ$

species	lifetime(μs)	emission maxima(nm)
UO_2^{2+}	τ_{10} 0.9 \pm 0.3	509 488 534 560 473 588
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	τ_{22} 2.9 \pm 0.4	519 499 542 566
$(\text{UO}_2)_3(\text{OH})_5^+$	τ_{35} 7 \pm 1	516 533 500 ^{a)} 554 ^{a)}
$\text{UO}_2\text{CO}_3^\circ$	τ_{101} 35 \pm 5	520

a): shoulder

spectra recorded for 1 μs of time window. Only qualitative discussion will be based on the spectra; the restriction in the time window, therefore, will not affect the results of the discussion.

In Fig. 1.2(a), the emission spectrum observed for sample solution at pH 3.87 is given together with the relative contributions of the single components $\text{UO}_2^{2+}(\text{aq})$, $(\text{UO}_2)_2(\text{OH})_2^{2+}(\text{aq})$ and $(\text{UO}_2)_3(\text{OH})_5^+(\text{aq})$ as a result of the numerical spectrum analysis. The calculated spectrum and the measured spectrum coincided in all cases with marginal differences due to scatter and background effects.

Though the species $\text{UO}_2^{2+}(\text{aq})$ and $(\text{UO}_2)_2(\text{OH})_2^{2+}(\text{aq})$ were found to be of similar concentration in the solution at pH 3.87, the emission from the $(\text{UO}_2)_2(\text{OH})_2^{2+}(\text{aq})$ species shows the dominating contribution. This observation agrees with previous results[13] in a study of the $\text{UO}_2^{2+}/(\text{UO}_2)_2(\text{OH})_2^{2+}$ equilibrium, where the high fluorescence intensity of the dimer was observed. In addition, the weak contribution of the trimer also indicated a high fluorescence intensity of the trimer compared to that of free $\text{UO}_2^{2+}(\text{aq})$, since the calculation in Fig. 1.1 indicates only a rather low relative concentration. It should be noted, however, that Fig. 1.1 gives species contributions. Since the oligomeric species contain several metal ions, the relative concentrations of U(VI) present as dimer or trimer species are much higher than those given by Fig. 1.1.

The lifetime τ_{10} for $\text{UO}_2^{2+}(\text{aq})$ under given conditions was determined previously as 0.9 \pm 0.3 μs [13], while the lifetime τ_{22} for the dimer was obtained as 2.9 \pm 0.9 μs [13], in good agreement with the present result $\tau_{22} = 2.9\pm 0.4$ μs .

The qualitative interpretation of the spectrum for the solution at pH 3.87 is validated by the interpretation of the spectrum at pH 4.06 (Fig. 1.2(b)). Fluorescence contributions of both dimer and free UO_2^{2+} decrease, while the contribution of trimer increases.

At pH 4.98 (Fig. 1.2(c)), no significant contribution of the emission from

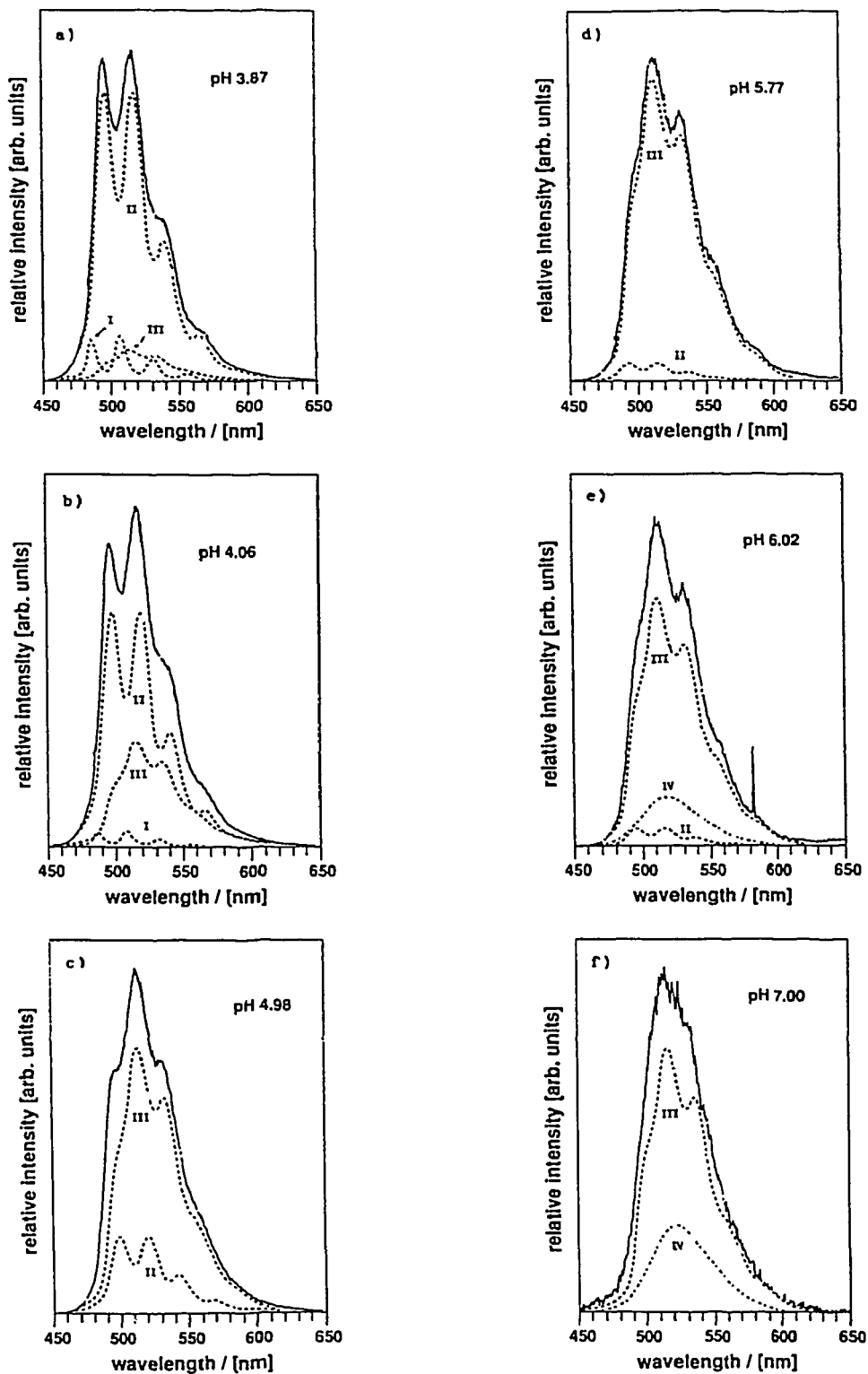


Fig. 1.2. Emission spectra of U(VI) in 0.1 M NaClO_4 solutions of various pH (full line) and calculated emission contributions of the species: I; $\text{UO}_2^{2+}(\text{aq})$, II; $(\text{UO}_2)_2(\text{OH})_2^{2+}(\text{aq})$, III; $(\text{UO}_2)_3(\text{OH})_5^+(\text{aq})$ and IV; $\text{UO}_2\text{CO}_3(\text{aq})$, (calculated contributions are given in dashed lines): $P_{\text{CO}_2}=0.03\%$: pH; (a) 3.87, (b) 4.06, (c) 4.98, (d) 5.77, (e) 6.02 and (f) 7.00.

$\text{UO}_2^{2+}(\text{aq})$ could be found any longer. Here, the emission from trimer is the dominating factor, while the dimer's contribution decreases further. The fluorescence lifetime τ_{35} for the trimer was determined as $7 \pm 1 \mu\text{s}$.

At pH 5.77 (Fig. 1.2(d)), the trimer is almost the single emission component, while a small contribution of the emission of the dimer still could be found.

A decrease in the trimer's contribution is observed at pH 6.02 (Fig. 1.2(e)), which is the result of the ingrowth of a new component with a rather long lifetime, $35 \pm 5 \mu\text{s}$, and a rather low fluorescence intensity. The emission spectrum of this long-living component does not show a fine structure. The emission maximum is at about 520 nm. However, due to its low fluorescence intensity and the low U(VI) total concentration in the pH range 6.3 to 7.0, i.e., ca $5 \times 10^{-6} \text{ M}$, the emission maximum is difficult to allocate. In this connection, spectrum and lifetime are quite similar to spectra observed in a U(VI) solution under 100 % CO_2 atmosphere in equilibrium with rutherfordine $\text{UO}_2\text{CO}_3(\text{s})$ [15] at pH 4.5 to 5.2. Since under those conditions $\text{UO}_2\text{CO}_3(\text{aq})$ is the prevailing species[15], the emission spectrum of the long-living component in Fig. 1.2(d) was assigned to this species in agreement with Fig. 1.1. This interpretation is validated by the numerical analysis of the emission spectrum for the sample at pH 7.00 in Fig. 1.2(f). The fluorescence emission of the monocarbonate complex shows a relative increase, while the dimer's component has disappeared. Further increase in pH resulted in a strong decrease of the observed total fluorescence emission, and fluorescence components due to $\text{UO}_2(\text{CO}_3)_2^{2-}(\text{aq})$ and $\text{UO}_2(\text{CO}_3)_3^{4-}(\text{aq})$ could not be observed.

The results of an investigation of U(VI) hydrolysis and carbonate complexation by time-resolved laser-induced fluorescence spectroscopy (TRLFS) were reported and discussed in terms of a species distribution calculated on the basis of formation constants [11,13–15]. Numerical evaluation of the emission spectra resulted in the relative contributions of the single-component UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$ and UO_2CO_3 aqueous species to the emission spectra. Significant contributions of other unknown species could not be found. Comparison of the numerically evaluated relative contributions with the calculated species distribution gave satisfactory results and validates the results of the solubility study[11]. Hence, TRLFS has been shown to be a powerful method for chemical speciation of hydrolysis species. High carbonate species, however, could not be detected, which illustrates the limits of TRLFS for the speciation. Nevertheless, since there is considerable discrepancy in the present knowledge on the important basic reactions of U(VI) under conditions of natural aquatic systems, TRLFS may provide further insight into the problems. In the present study, only a qualitative discussion was given to support the solubility

data[11] and to identify the single-component emission spectra. Further work is in progress for the quantitative analysis of aqueous U(VI) chemistry using well-characterized and equilibrated U(VI) solutions together with the more selective excitation capabilities of a dye laser in order to investigate the presence of minor species, e.g. $\text{UO}_2\text{OH}^+(\text{aq})$.

REFERENCES

- 1) Kim J.I.: "Chemical Behavior of Transuranium Elements in Natural Aquatic Systems", in: *Handbook on the Physics and Chemistry of the Actinides* ed. Freeman A.J and Keller C., Elsevier Science Publishers, Amsterdam (1986).
- 2) Fuger J., Khodakovskiy I.L., Sergeeva E.I. and Navratil J.D.: "The Chemical Thermodynamic of Actinide Elements and Compounds – Part 12. The Actinide Inorganic Complexes", IAEA, Wien (1990).
- 3) Grenthe I., Fuger J., Konings R.J.M., Lemire R.I., Muller A.B., Nguyen-Trung C. and Wanner H.: *The Chemical Thermodynamics of Uranium*, NEA/OECD, Paris (1991).
- 4) Kim J.I., Stumpe R. and Klenze R.: "Laser-induced Photoacoustic Spectroscopy for the Speciation of Transuranium Elements in Natural Aquatic Systems", in: *Topics in Current Chemistry*, 157, 129 (1990).
- 5) Beitz J.V., Bowers D.L., Doxtader M.M., Maroni V.A. and Reed D.T.: *Radiochim. Acta*, 44/45, 87 (1988).
- 6) Stadler S. and Kim J.I.: *Radiochim. Acta*, 44/45, 39 (1988).
- 7) Meinrath G. and Kim J.I.: *Radiochim. Acta*, 52/53, 29 (1991).
- 8) Wimmer H., Klenze R. and Kim J.I.: *Radiochim. Acta*, 56, 79 (1992).
- 9) Moulin C., Decambox P., Mauchien P., Moulin V. and Theyssier M.: *Radiochim. Acta*, 52/53, 119 (1991).
- 10) Saini R.D., Bhattacharyya P.K. and Iyer R.M.: *J. Photochem. Photobiol. A*, 47, 65 (1989).
- 11) Meinrath G., Kato Y. and Yoshida Z.: "A Study of Solid Liquid Equilibria of U(VI) under Atmospheric CO_2 Partial Pressure", to be published.
- 12) Nelder J.R. and Mead R.: *Comput. J.*, 8, 308 (1965).
- 13) Meinrath G., Kato Y. and Yoshida Z.: "A Spectroscopic Study of the Dimeric Uranyl(VI) Hydrolysis Species $(\text{UO}_2)_2(\text{OH})_2^{2+}$ ", *J. Radioanal. Nucl. Chem.*, in press.
- 14) Caceci M.S. and Choppin G.R.: *Radiochim. Acta*, 33, 207 (1983).
- 15) Meinrath G. and Kimura T.: "The Carbonate Complexation of the U(VI) Ion", *J. Alloys Comp.*, 202, 89 (1993).

2. DETERMINATION OF HYDRATION NUMBER OF Cm(III)

2.1 INTRODUCTION

The hydration of a metal ion is an important factor in the structural and chemical behavior of complexes. The techniques for studying the size and/or structure of the hydration sphere can be classified as direct or indirect methods. The direct methods include X-ray and neutron diffraction, luminescence decay and NMR(nuclear magnetic resonance) relaxation measurements, while the indirect methods involve compressibility, NMR exchange and absorption spectroscopy measurements. Because of the high sensitivity and selectivity of laser-induced luminescence spectroscopy, the luminescence measurement is the most promising direct method for the hydration study of radioactive actinide ions such as Cm(III) and Am(III).

For Eu(III) and Tb(III), a linear correlation has been found between the reciprocal of the excited-state lifetime (i.e., the decay constant k_{obs}) and the number of water molecules in first coordination sphere, n_{H_2O} , of their complexes[1]. A similar correlation is expected for Cm(III) from the analogy of spectroscopic properties between trivalent lanthanide and actinide ions. Beitz, et al.[2] reported the first study of aqueous Cm^{3+} photophysics, including measurement of the emission spectrum and lifetime of aqueous Cm^{3+} in H_2O and D_2O . Research on the spectroscopic and luminescence studies of Cm(III) in solution has been reviewed recently[3-5]. The lifetimes of various Cm(III) complexes were measured and the number of coordinated water molecules was calculated by Beitz[3]. From the assumption that aqueous Cm^{3+} has 8 or 9 water molecules in the first coordination sphere, he calculated 2.5-2.8 water molecules for Cm^{3+} complexed by carbonate in 1 M Na_2CO_3 , 3.4-3.8 for the Cm-CDTA complex and 1.3-1.5 for the DTPA complex. These values are chemically reasonable but the method remained suspect without validation from studies of crystalline solids of known hydration.

A luminescence study of Cm(III) and of Eu(III)(as a reference ion) has been performed to assess the relationship between the lifetime and the hydration number of Cm(III) in liquid and solid phases. The lifetime of Cm^{3+} in D_2O/H_2O mixtures and in crystalline lanthanum compounds were measured for the calibration of k_{obs} vs. n_{H_2O} . As an application of the relationship obtained, the hydration state of Cm(III) complexed with polyamino-polycarboxylate ligands was measured.

2.2 EXPERIMENTAL

^{248}Cm ($t_{1/2}=3.4\times 10^5$ y, >96 atom %) was purified by passage through cation exchange resin (Dowex 50wX4) with elution by ethanol-HCl solution [6]. The concentration of the Cm(III) stock solution (0.01 M HClO_4) was determined by liquid scintillation counting (LSC) with discrimination of the spontaneous fission and fission products regions. Eu(III) stock solution was prepared by dissolving an appropriate amount of Eu_2O_3 (Aldrich) in perchloric acid. Solutions of the polyaminopolycarboxylate complexes were prepared by mixing stoichiometric amounts of Cm^{3+} or Eu^{3+} and ligand stock solutions of known concentration. The concentrations of Cm(III) and Eu(III) were 10^{-7} – 10^{-6} M and 10^{-2} M, respectively, in the samples.

The Cm(III) in the samples was excited to the F-state ${}^6\text{I}_{17/2,11/2}$ [8] by a pulsed laser beam at 397 ± 1 nm with subsequent emission from the A-state ${}^6(\text{D},\text{P})_{7/2}$ to the groundstate $\text{Z } {}^8\text{S}_{7/2}$ [2], 594–605 nm, which was measured to obtain the luminescence lifetime. The Eu(III) was excited to the lowest excited state ${}^5\text{D}_0$ by a pulsed laser beam at 579 ± 1 nm and the emission from the ${}^5\text{D}_0$ state to the groundstate ${}^7\text{F}$ manifold (${}^7\text{F}_2$), 615 nm, was measured. The laser pulse power was typically 2–3 mJ for 397 nm and 10–15 mJ for 579 nm, and the pulse width was in the nanosecond range.

2.3 RESULTS AND DISCUSSION

The hydration number of Eu(III) and Tb(III) has been obtained by using the difference in the decay rate constants in H_2O and D_2O solutions [1]. In general, $k_{\text{H}_2\text{O}} \gg k_{\text{D}_2\text{O}}$, $k_{\text{D}_2\text{O}} \approx \text{constant}$, and ligands are not as effective in causing nonradiative deexcitation of the excited state. For Eu(III), a relationship has been proposed in which the hydration number is related directly to the decay rate constant in H_2O [7].

The luminescence decay constants k_{obs} (ms^{-1}) of Cm^{3+} and Eu^{3+} were measured in $\text{D}_2\text{O}/\text{H}_2\text{O}$ solutions of various volume percentage, $\chi_{\text{H}_2\text{O}}$, of H_2O . The results are shown in Fig. 2.1, and Eqs. (1) and (2) express the relations obtained for Cm^{3+} and Eu^{3+} .

$$k_{\text{obs}}(\text{Cm}) = 0.147\chi_{\text{H}_2\text{O}} + 0.786, \rho = 0.9999 \quad (1)$$

$$k_{\text{obs}}(\text{Eu}) = 0.0859\chi_{\text{H}_2\text{O}} + 0.430, \rho = 0.9997 \quad (2)$$

where ρ is a correlation coefficient. The results show that the quenching behavior of Cm^{3+} and Eu^{3+} in the $\text{D}_2\text{O}/\text{H}_2\text{O}$ system is similar and is due mainly to energy

transfer from the excited state to OH vibrators of the H₂O molecules bound to the metal. From Eq. (1), the lifetimes of Cm³⁺ in H₂O and D₂O are calculated to be 64.6±0.7 μs and 1,270±20 μs, respectively. Our data in H₂O agreed with those of Beitz et al. (65±2 μs[2], 68±3 μs[9]) and Wimmer et al. (65±2 μs[10]). However, our data in D₂O is appreciably longer than that of Beitz et al. (940±20 μs[2]) and is close to the computed radiative lifetime, 1,300 μs, by Carnall et al.[11]. The lifetimes of Eu³⁺ in H₂O and D₂O are calculated to be 111±2 μs and 2,330±40 μs, respectively, from Eq. (2), in agreement with the literature[12,13].

The electron configuration of Cm³⁺, [Rn]5f⁷, and that of Gd³⁺, [Xe]4f⁷, are similar. However, the emissive properties of Cm³⁺ are quite different with those of Gd³⁺ and are more similar to those of Eu³⁺ and Tb³⁺. This is due to the energy gap of Cm³⁺ (1.68x10³ cm⁻¹) (defined as energy difference between the lowest emissive level and the highest level of the ground-state manifold) is smaller than that of Gd³⁺ (3.2x10³ cm⁻¹) but close to those of Eu³⁺ (1.215x10³ cm⁻¹) and Tb³⁺ (1.48x10³ cm⁻¹)[14].

The hydration number of Eu³⁺ in H₂O has been reported to be between 9.0 and 9.6 from luminescence studies of perchlorate [1,7], while it is 8.3 (from X-ray studies) in 3.23 M chloride solution[15]. The luminescence studies have an inherent uncertainty of about ±0.5 water molecules. We have measured the k_{obs} of Cm(III) and Eu(III) doped

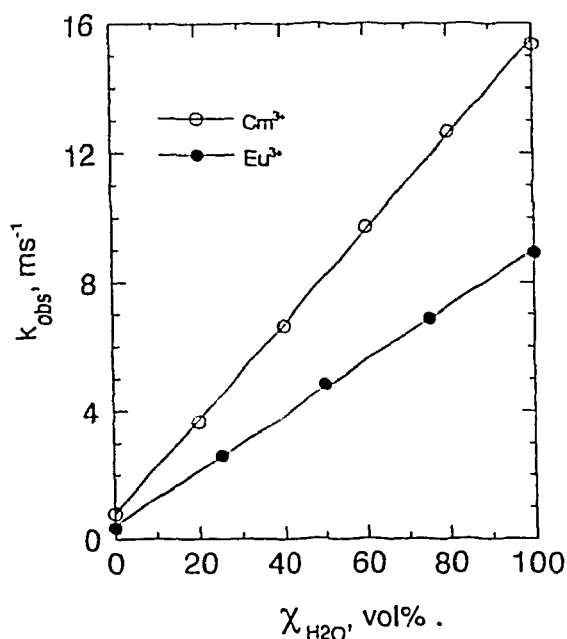


Fig. 2.1. Luminescence decay constants for Cm³⁺ and Eu³⁺ as a function of volume percentage, $\chi_{\text{H}_2\text{O}}$, of H₂O in D₂O/H₂O solutions: o, 3.0x10⁻⁷ M Cm³⁺; ●, 1.0x10⁻² M Eu³⁺.

Table 2.1. Calibration data for Cm(III) or Eu(III) doped lanthanum compounds with H₂O hydration

anion	$n_{\text{H}_2\text{O}}^a$	Decay constant k_{obs} (ms ⁻¹)			
		La(Cm) ^b	La(Eu) ^c	Eu[ref 1]	Eu[ref 7]
dipicolinate	0	2.11	0.64	0.77	0.73
nicotinate	2	3.76	2.31	2.49	2.40
oxalate	3	6.16	3.03	3.53	3.58
thiodiacetate	4	7.03	4.98	5.35	4.42
bromate	9	15.41	8.80	8.69	8.83

^aNumber of H₂O molecules in the primary coordination sphere of La(III) and Eu(III). ^bCm:La=1:6.9x10³. ^cEu:La=1:50.

lanthanum compounds with the results summarized in Table 2.1. For each compound of the La(Cm) and La(Eu) systems, at least two different samples were prepared. The errors of the k_{obs} measured were estimated to be within ± 0.1 for each compound. Although the chemical structure of the compounds was not analyzed by X-ray diffraction, the compounds prepared were indicated to be the expected composition from the k_{obs} of the La(Eu) compounds which was very similar to that of the Eu(III) compounds in the literature[1,7]. The following correlations were derived for the hydration numbers of Cm(III) and Eu(III) under our experimental conditions.

$$n_{\text{H}_2\text{O}} = 0.65k_{\text{obs}}(\text{Cm}) - 0.88, \text{ with } \rho = 0.9938 \quad (3)$$

$$n_{\text{H}_2\text{O}} = 1.07k_{\text{obs}}(\text{Eu}) - 0.62, \text{ with } \rho = 0.9921 \quad (4)$$

If there is no contribution from the ligand to the deexcitation of the luminescent excited state, the hydration of Cm(III) and Eu(III) in the different complexes can be obtained directly from the values of k_{obs} measured in H_2O . Equation (4) for Eu(III) agrees with that reported by Barthelemy et al.[7] and should give results consistent with those obtained by the procedure of Horrocks et al.[1] within the uncertainty of the luminescence method. By using Eqs. (1)–(4), the $n_{\text{H}_2\text{O}}$ of Cm^{3+} and Eu^{3+} in H_2O were calculated to be 9.2 ± 0.5 and 9.0 ± 0.5 , respectively.

The residual hydration of lanthanide complexes of polyaminopolycarboxylate ligands have been determined by luminescence measurements as a function of the pH for Eu(III) and Tb(III) by Brittain, et al.[16–18] Table 2.2 shows the results of our measurements of k_{obs} for Cm(III) and Eu(III) for a number of such complexes. The solution pH was kept constant at 4.6 by acetate buffer for Cm(III) and at 5.5, without buffer, for Eu(III). For the Eu(III) complexes, the calculated hydration numbers

Table 2.2. Hydration states of Cm(III) and Eu(III) complexes of polyaminopolycarboxylate ligands

ligand	Cm ^a		Eu ^b		
	$k_{\text{obs}}(\text{ms}^{-1})$	$n_{\text{H}_2\text{O}}^{\text{c}}$	$k_{\text{obs}}(\text{ms}^{-1})$	$n_{\text{H}_2\text{O}}^{\text{d}}$	$n_{\text{H}_2\text{O}}[\text{ref}]$
NTA	11.01 ± 0.14	6.28	4.78 ± 0.04	4.49	4.5[16]
HEDTA	7.78 ± 0.10	4.18	3.56 ± 0.13	3.19	3.1[17]
EDTA	7.09 ± 0.03	3.73	3.06 ± 0.10	2.65	2.6[17]
CDTA	7.20 ± 0.23	3.80	2.90 ± 0.07	2.48	2.3[17]
DTPA	3.89 ± 0.02	1.65	1.47 ± 0.02	0.95	1.1[17]
TTHA	2.25 ± 0.02	0.58	0.74 ± 0.01	0.17	0.2[18]

^a[Cm(III)]= 5.3×10^{-6} M, [ligand]= 5.7×10^{-6} M, [acetate]= 3.6×10^{-2} M, pH 4.6. ^b[Eu(III)]= 1.0×10^{-2} M, [ligand]= 1.0×10^{-2} M, pH 5.5.

^cCalculated by using Eq.(3). ^dCalculated by using Eq.(4).

agreed well with the literature values[16–18], within ± 0.2 water molecules. This suggests that Eq. (4) is reliable for the determination of the hydration number of Eu(III) in the complexes and, presumably, Eq. (3) for Cm(III). The residual hydration number of Cm(III) is consistently larger than that of Eu(III) for the same complex, despite the similar thermodynamic parameters of complexation for both the complexes[19]. To clarify the differences of the $n_{\text{H}_2\text{O}}$ between the Cm(III) and Eu(III) complexes, [ligand]/[Cm(III)] ratio and pH dependencies of the hydration state in the Cm(III)–polyaminopolycarboxylate complexes were then studied.

The decay constants k_{obs} of the Cm(III) complexes were measured by varying [ligand]/[Cm(III)] ratio, R, at pH 4.6 using acetate buffer. Figure 2.2 shows the results of hydration number calculated from the k_{obs} vs. R. The hydration numbers for R were almost independent of R, except for the Cm+NTA complex. This is consistent with formation of the 1:1 complex with HEDTA, EDTA, CDTA, DTPA and TTHA under those conditions which agreed with speciation calculations using stability constants[20]. In the case of NTA complexation, the speciation calculation was consistent with a decrease in net hydration number as formation of $\text{Cm}(\text{NTA})_2$ increased.

The pH dependence of the hydration of Cm(III) in the presence of these ligands was studied over the pH range of 1–13 in 0.1 M NaClO_4 solution without buffer. The results are shown in Fig. 2.3 and are similar to the pH dependence of the hydration of the Eu(III) and Tb(III)

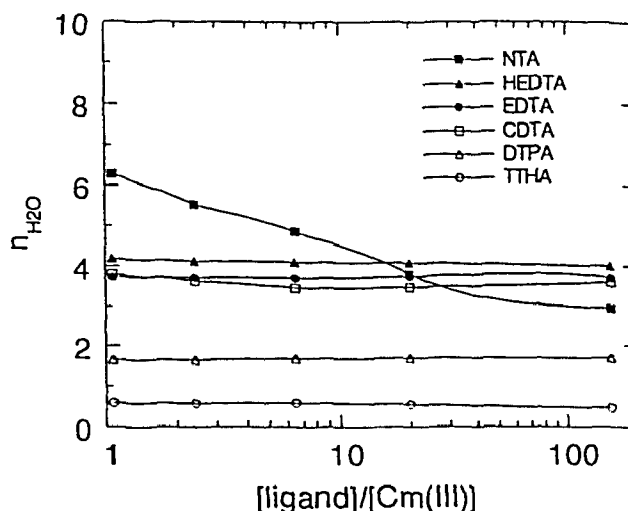


Fig. 2.2. [ligand]/[Cm(III)] ratio dependence of hydration state in Cm(III) complexes of polyaminopolycarboxylate ligands: [Cm(III)]= 5.3×10^{-6} M, [acetate]= 3.6×10^{-2} M, pH 4.6.

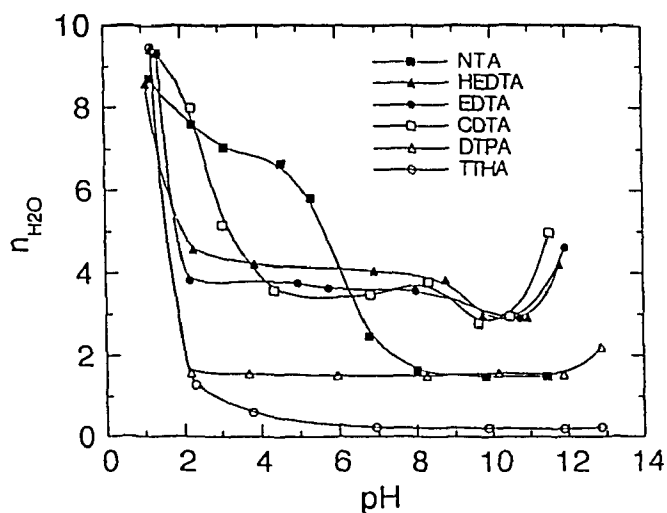


Fig. 2.3. pH dependence of hydration state in Cm(III) complexes of polyaminopolycarboxylate ligands: $l=0.1$ M NaClO_4 , [Cm(III)]= 7.3×10^{-6} M, [ligand]= 8.0×10^{-6} M.

complexes[16,17]. There are three buffer regions; the first at low pH in which the hydration number of the cations is equivalent to that of the free ions; a second in the pH range of 4–8 in which the hydration number is that of the metal ion in the 1:1 complex; and a third at high pH(ca. 9–12) associated with the formation of ternary hydroxo complexes. This pattern is not followed by the NTA system. The speciation calculation shows that a first plateau in pH 2.5–5.0 is caused by the formation of Cm(NTA) complex and that a second plateau in pH 7.5–11.5 is due to the formation of Cm(NTA)₂ and Cm(OH)₂⁺ complexes.

In all these systems, the total coordination number, i.e. the sum of the number of ligand donor groups and the number of primary water molecules, was 8.8±0.5 for Eu(III) and 8.5±0.5 for Tb(III) complexes[16–18], where n(NTA)=4, n(HEDTA)=5.5, n(EDTA)=n(CDTA)=6, n(DTPA)=7.5 and n(TTHA)=8.5[21] were used as the numbers of the ligand donor groups. If the value for the Cm(NTA) complex is omitted, the total coordination number of the Cm(III) complexes is calculated to be 9.3±0.4, which is consistent with the value 9.2±0.5 in H₂O.

In summary, our results indicate that the total coordination number of Cm(III) is possibly 0.5 larger than that of Eu(III) in polyaminopolycarboxylate complexes.

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REFERENCES

- 1) Horrocks Jr. W.D. and Sudnick D.R.: J. Am. Chem. Soc., 101, 334 (1979).
- 2) Beitz J.V. and Hessler J.P.: Nucl. Technol., 51, 169 (1980).
- 3) Beitz J.V.: Radiochim. Acta, 52/53, 35 (1991).
- 4) Kim J.I., Klenze R. and Wimmer H.: Eur. J. Solid State Inorg. Chem., 28, 347 (1991).
- 5) Yusov A.B.: Radiokhimiya, 35, 3 (1993).
- 6) Thompson S.G., Harvey B.G., Choppin G.R. and Seaborg G.T.: J. Am. Chem. Soc., 76, 6229 (1954).
- 7) Barthelemy P.P. and Choppin G.R.: Inorg. Chem., 28, 3354 (1989).
- 8) Carnall W.T. and Rajnak K.: J. Chem. Phys., 63, 3510 (1975).
- 9) Beitz J.V., Bowers D.L., Doxtader M.M., Maroni V.A. and Reed D.T.: Radiochim. Acta, 44/45, 87 (1988).
- 10) Wimmer H., Kim J.I. and Klenze R.: Radiochim. Acta, 58/59, 165 (1992).
- 11) Carnall W.T. and Crosswhite H.M.: Report ANL–84–90 (1985).
- 12) Kropp J.I. and Windsor M.W.: J. Chem. Phys., 42, 1599 (1965).
- 13) Tanaka F. and Yamashita S.: Inorg. Chem., 23, 2044 (1984).

- 14) Stein G. and Würzberg E.: J. Chem. Phys., 62, 208 (1975).
- 15) A. Habenschuss and F.H. Spedding, J. Chem. Phys., 73, 442 (1980).
- 16) Brittain H.G. and Jasinski J.P.: J. Coord. Chem., 18, 279 (1988).
- 17) Brittain H.G., Choppin G.R. and Barthelemy P.P.: J. Coord. Chem., 26, 143 (1992).
- 18) Chang C.A., Brittain H.G., Telser J. and Tweedle M.F.: Inorg. Chem., 29, 4468 (1990).
- 19) Choppin G.R., Rizkalla E.N. and Sullivan J.C.: Inorg. Chem., 26, 2318 (1987).
- 20) Martell A.E. and Smith R.M.: *Critical Stability Constants*, Plenum Press, New York (1974).
- 21) Choppin G.R.: J. Alloys Comp., 192, 256 (1993).