

Curium(III) Complexation with Desferrioxamine B (DFO) Investigated Using Fluorescence Spectroscopy

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Hydroxamate-type siderophores like desferrioxamine B (DFO) are the most common siderophores ubiquitously found in the environment. These naturally occurring chelating substances have the potential to enhance the solubility and mobility of actinides by forming soluble complexes. The unknown interaction between curium(III) and aqueous DFO species is the subject of this paper. The reactions between soluble species of curium(III) and DFO were studied at trace curium(III) concentrations (3×10^{-7} M) in 0.1 M $NaClO_4$ using time-resolved laser-induced fluorescence spectroscopy (TRLFS). Three Cm^{3+}–DFO species, $M_pH_qL_r$, could be identified from the luminescence spectra, CmH_2DFO^{2+}, $CmHDFO^{+}$, and CmDFO, having emission maxima at 599, 611, and 614 nm, respectively. The large formation constants, $\log \beta_{121} = 31.62 \pm 0.23$, $\log \beta_{111} = 25.70 \pm 0.17$, and $\log \beta_{101} = 16.80 \pm 0.40$, compared to those of other chelating agents illustrate the unique complexation properties of hydroxamate-type siderophores. An indirect excitation mechanism for the curium(III) luminescence was observed in the presence of the DFO molecules.

Actinides have been and will be introduced into shallow and deep groundwater environments via various human activities. The process of interaction between naturally occurring chelating substances and metals may influence the migration behavior of hazardous actinides in the environment once they have been released. Siderophores are chelating substances produced by microorganisms under iron-deficient conditions. For example, Powell et al. demonstrated the occurrence of hydroxamate siderophores produced by microorganisms in concentrations ranging from 10^{-7} to 10^{-8} M in a variety of soils.[1] Previous studies showed that catechol and hydroxamate groups in siderophores are the main functional groups involved in binding with actinides.[2–4] Desferrioxamine B (DFO) is a microbial produced trihydroxamate ligand (see Figure 1) which is commercially available and occurs naturally in soils. In 1960 DFO was identified as a metabolite of *Actinomyceten* which are major constituents of the soil micro flora.[5] Recently Essen et al. demonstrated the production of desferrioxamine siderophores by *Pseudomonas stutzeri* (CCUG 36651) which had been isolated at the Äspö Hard Rock Laboratory.[6] *Pseudomonas* species are ubiquitous soil and groundwater bacteria. Structures of DFO complexes with actinides, their stability constants and dissolution experiments of solids in the presence of DFO are reported mainly for Pu^{IV} [7–9] but also for Th^{IV} [10] and U^{VI}.[11,12] Brainard et al. discussed also the speciation of lanthanides (e.g., Yb^{III}, Eu^{III}, and La^{III}) in the presence of aqueous DFO species.[11] As a result, the existence of one relatively stable 1:1 complex of the type MLH^{n-2} with these lanthanides was reported. However, no information about the spectroscopic properties of the identified lanthanide–DFO species is given to provide a basis for comparison. A further interesting point to study the speciation of actinides with DFO is the bioavailability of those species for microbes. John et al. suggested an accumulation of Pu^{IV} as a Pu^{IV}–DFO complex by metabolically active cells of *Microbacterium flavescens* (JG-9).[13] In contrast to this, Yoshida et al. and Ozaki et al. reported a dissociation of a Eu^{III}–DFO complex in the presence of *Pseudomonas fluorescens* cells and the uptake of Eu^{III} as a free ion by bacteria.[14,15]

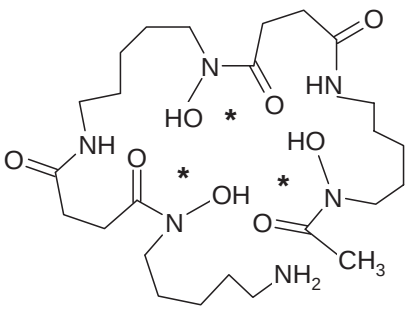

Figure 1. Structural model of the desferrioxamine B (DFO) molecule. Asterisks indicate the complexation sites.

The observed mobilization effects of DFO molecules on radionuclides probably due to the formation of strong soluble species motivated detailed investigation of their complexation characteristics, using a radionuclide suitable for spectroscopic methods. Therefore, this present work focuses on how curium(III) interacts with DFO in aqueous solution. To the best of our knowledge, the characteristics of the complexation of DFO species with trivalent actinides (e.g. curium) are unknown. To address this lack, we thus present findings regarding the complexation of curium(III) with aqueous DFO species, obtained using time-resolved laser-induced fluorescence spectroscopy (TRLFS). The speciation experiments were performed at trace concentrations of curium(III) (3×10^{-7} M) in 0.1 M $NaClO_4$ by varying the DFO concentration and pH of the test solutions. The different curium(III) DFO complex species could be distinguished on the basis of their individual luminescence spectra. The obtained stability constants were

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compared to those of pyoverdins.[4] Pyoverdins are bacterial siderophores produced under iron-deficient conditions by fluorescent *Pseudomonas* species. The functional groups that participate in the metal binding are the catechol group of the chromophore and two ligand sites in the peptide chain, i.e. one or two hydroxamate groups and one or two α-hydroxy acid moieties. The results of this study increase our understanding of the mobilization of actinides by naturally occurring chelating substances containing hydroxamate groups secreted by resident bacteria in a natural environment.

Experimental

Preparation of Curium(III) DFO Solutions. Desferrioxamine B mesylate was purchased from SIGMA-ALDRICH. The stock solutions were prepared freshly for each experiment. A stock solution of the long-lived curium isotope ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ years) was used. This solution had the following composition: 97.3% ^{248}Cm, 2.6% ^{246}Cm, 0.04% ^{245}Cm, 0.02% ^{247}Cm, and 0.009% ^{244}Cm in 1.0 M $HClO_4$. The experiments were performed in a glove box under N_2 atmosphere at 25 °C. As a background electrolyte, analytical grade 0.1 M $NaClO_4$ (Merck, Darmstadt, Germany) was used. To prevent the carbonate complexation of curium(III), carbonate-free water and a NaOH solution were used. The curium(III) concentration was fixed at 3×10^{-7} M in all TRLFS measurements. The pH was measured using an InLab 427 combination pH puncture electrode (Mettler-Toledo, Giessen, Germany). The electrode was calibrated with standard buffers and by using solutions of known [H^+] concentrations. The pH was changed by adding analytical grade NaOH or $HClO_4$ with an accuracy of $\pm$0.02 units. Four series of experiments were performed to explore the complexation behavior of curium(III) with DFO. In the first and second run, the DFO concentrations were kept constant at 7.6×10^{-5} and 1.5×10^{-4} M, respectively, while varying the pH between 1.6 and 11.0; in the third run, the DFO concentration was varied between 3×10^{-5} and 6×10^{-4} M at a fixed pH of 5 and in the fourth run, the DFO concentration again was kept constant at 6×10^{-4} M, while varying the pH between 5.0 and 9.8.

Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS): Experimental Setup. The time-resolved luminescence spectra were recorded at 25 °C using a pulsed flash lamp pumped Nd:YAG-OPO laser system (Powerlite Precision II 9020 laser equipped with a Green PANTHER EX OPO from Continuum, Santa Clara, CA, USA). Further details about the laser system can be found online.[4] The laser pulse energy, in the range of 2–3 mJ, was monitored using a photodiode. The luminescence spectra were detected using an optical multi-channel analyzer-system, consisting of an Oriel MS 257 monochromator and spectrograph with a 300 or 1200 line mm^{-1} grating and an Andor iStar ICCD camera (Lot-Oriel Group, Darmstadt, Germany). The curium(III) emission spectra were recorded in the 500–700 (300 line mm^{-1} grating) and 570–650 nm (1200 line mm^{-1} grating) ranges. A constant time window of 1 ms was applied, and an excitation wavelength of 395 nm was used. Selected samples were measured by applying two excitation wavelengths, 360 and 395 nm. For time-dependent emission decay measurements, the delay time between laser pulse and camera grating was scanned with time intervals between 10 and 20 µs. The TRLFS spectra were measured after an equilibration time of 10 min.

Evaluation of the Luminescence Spectra. The spectra were base-line corrected and normalized using the ORIGIN 6.1G (OriginLab Corporation, USA) code. Then, the factor analysis technique was used to further evaluate the luminescence data. Factor analysis of spectroscopic data is a powerful tool for the determination of the number of independent absorbing/emitting species in a series of mixtures. The approach of the factor analysis program SPECFIT[16] to analyze, e.g., TRLFS spectra, is a quantitative decomposition of the spectra of mixtures into different spectral components/constituents. Due to the spectroscopic properties of each individual chemical species, the measured spectra showed variations depending on the physicochemical parameter (e.g., pH and ligand concentration) varied. These spectral variations are used in SPECFIT to determine the spectra of the single components, their concentration distribution and their equilibrium constants. As a consequence, the single component spectra derived from SPECFIT can be attributed to the formed species. In the past we could demonstrate the successful application of SPECFIT to describe the complexation of Cm^{3+} with a variety of ligands by luminescence data.[4,17–19] The following model assumptions were made in order to estimate Cm^{3+}–DFO stability constants. According to the structural schema shown in Figure 1, the DFO molecule exhibits three hydroxamate groups and one amine group. It follows that the DFO molecule can release four protons, three from the hydroxamate sites which are most likely responsible for metal coordination, and one from the free amine site. Those pK values were determined using absorption spectroscopy at a fixed [DFO] concentration of 1×10^{-4} M while varying the pH between 2 and 11 in 0.1 M $NaClO_4$. The SPECFIT evaluation of the wavelength range 190 to 290 nm of the pH-dependent absorption spectra resulted in the following pK-values: $pK_1 = 8.36 \pm 0.11$, $pK_2 = 8.94 \pm 0.02$, $pK_3 = 9.60 \pm 0.14$, and $pK_4 = 11.18 \pm 0.39$. Our DFO deprotonation constants are in good agreement with those published in the literature.[10] Input parameters for the data fitting were the known and calculated total concentrations of Cm^{3+}, DFO, the pH of each sample, and the protonation constants of the DFO molecule. All data-sets, i.e. 34 individual spectra, and the known luminescence spectrum of the Cm^{3+} aquo ion were used in the SPECFIT calculations.

Results and Discussion

Luminescence Spectra Using Direct Excitation and Stability Constants. Due to the unique luminescence properties of curium(III), TRLFS is an established experimental technique for characterizing those complexes with inorganic and organic ligands. The evaluation of those luminescence sum spectra is based on a quantification of the curium(III) species by deconvoluting the total emission spectra. The emission bands of inner-sphere complexes of curium(III) with organic ligands in aqueous solution are generally red-shifted compared to the Cm^{3+} aquo ion. An overview of the emission spectra of 3×10^{-7} M curium(III) in 0.1 M $NaClO_4$ measured in the DFO system is presented in Figure 2. The spectral variations depicted in Figure 2; (a) as a function of the DFO concentration at pH 5 and (b) as a function of pH at a fixed DFO concentration; are clear indications for a strong interaction with aqueous DFO species and Cm^{3+}. The emission maximum of Cm^{3+} at 593.8 nm decreased with: (a) increasing DFO amounts at fixed pH and (b) increasing pH at fixed [DFO]. No influence of the Cm^{3+} aquo ion could be detected in the measured sum TRLFS spectra at pH $\geq$6.2. At the same time, the amount of a first Cm^{III}–DFO species increased having an emission maximum at approximately 600 nm. The formation of the second

Cm^{III}–DFO species is shown by the strong changes in the emission spectra between pH 5.8 and 6.2 (see Figure 2). Then, the spectra are independent from pH until pH 8.7. The again red-shifted emission maximum at pH 9.8 indicates the increased influence of the third Cm^{III}–DFO complex.

The spectral changes detected were used in the SPECFIT factor analysis program[16] to describe the complex formation reactions occurring in the Cm^{3+}–DFO system. In light of relevant complexation studies of DFO with metals,[10–12] and taking into consideration the deprotonation of the DFO molecule, possible curium(III)–DFO species of the $M_pH_qL_r$ type were introduced into the data analysis procedure. As a result, we were able to develop a chemical model describing the complexation reactions in the Cm^{3+}–DFO system. The variations observed in the emission data (see Figure 2) could be described by the following equilibria:

$$Cm^{3+} + DFO^{3-} + 2H^+ \rightleftharpoons CmH_2DFO^{2+} \quad (1)$$

$$Cm^{3+} + DFO^{3-} + H^+ \rightleftharpoons CmHDFO^+ \quad (2)$$

$$Cm^{3+} + DFO^{3-} \rightleftharpoons CmDFO \quad (3)$$

Formation constants for reactions 1 to 3 were calculated to be $\log \beta_{121} = 31.62 \pm 0.23$, $\log \beta_{111} = 25.73 \pm 0.17$, and $\log \beta_{101} = 16.80 \pm 0.40$, respectively (see Table 1). These results indicate that DFO forms strong 1:1 complexes with curium(III). No published data exist for curium(III) to provide a basis for comparison. The corresponding single-component spectra of the individual species are summarized in Figure 3. The spectrum of the 1:2:1 species shows a complex structure with a maximum at 599 nm and two shoulders at 595 and 607 nm. Such a structured emission spectrum was not observed in our previous studies in a variety of organic systems.[4,17–19] Therefore, this might be a special feature of the first Cm^{III}–DFO complex which was identified in all runs. The two other species, $CmHDFO^+$ and CmDFO, are characterized by single

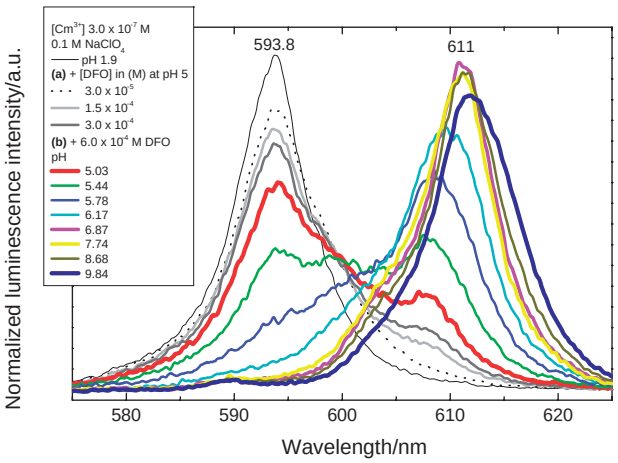

Figure 2. Luminescence spectra of 3×10^{-7} M curium(III) in 0.1 M $NaClO_4$ measured as a function of the DFO concentration at pH 5.0 (not all data shown) and at a fixed DFO concentration of 6×10^{-4} M as a function of pH (not all data shown). The spectra are scaled to the same peak area.

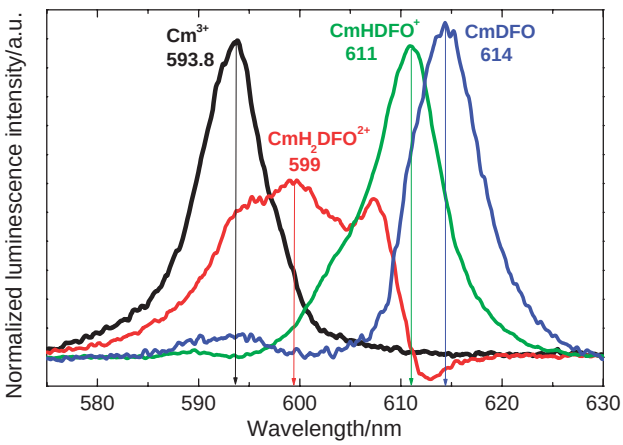

Figure 3. Luminescence spectra of the single components in the Cm^{3+}–DFO system, as derived by peak deconvolution using SPECFIT. The spectra are scaled to the same peak area.

Table 1. Summary of Emission Maxima, Lifetimes, Complex Stability Constants $\log \beta$ and $\log K$ of the Cm^{III}–DFO Species Compared to Cm^{III}–*P. fluorescens* Pyoverdin Species and to Relevant Literature Data

Ligand	$M_pH_qL_r$	Complex species	$\lambda_{emission}$/nm	Lifetime/μs	Ionic strength /M	$\log \beta$	$\log K$	Reference
Fe^{III}–DFO	111	$FeHDFO^+$			0.1		30.00[a]	12
Eu^{III}–DFO	111	$EuHDFO^+$			0.1		15.00[b]	12
Cm^{3+}	100		593.8	68 ± 1	0.1 ($NaClO_4$)			
DFO	121	CmH_2DFO^{2+}	599	85 ± 8	0.1 ($NaClO_4$)	31.62 ± 0.23	10.84[c]	This work
	111	$CmHDFO^+$	611	123 ± 16		25.73 ± 0.17	14.55[d]	
	101	CmDFO	614	320 ± 76		16.80 ± 0.40	16.80	
Pyoverdin	121	CmH_2L^+	602	86 ± 2 (80%) 198 ± 10 (20%)	0.1 ($NaClO_4$)	32.50 ± 0.06	9.83[e,g]	4
	111	CmHL	608	83 ± 2 (64%) 229 ± 5 (36%)		27.40 ± 0.11	15.20[f,g]	
	101	CmL^-	611	100 ± 5 (71%) 330 ± 10 (29%)		19.30 ± 0.17	19.30[g]	

a) $Fe^{3+} + HDFO^{2-} \rightleftharpoons FeHDFO^+$. b) $Eu^{3+} + HDFO^{2-} \rightleftharpoons EuHDFO^+$. c) $Cm^{3+} + H_2DFO^- \rightleftharpoons CmH_2DFO^{2+}$. d) $Cm^{3+} + HDFO^{2-} \rightleftharpoons CmHDFO^+$. e) $Cm^{3+} + LH_2^{2-} \rightleftharpoons CmH_2L^+$. f) $Cm^{3+} + LH^{3-} \rightleftharpoons CmHL$. g) Recalculated in this study.

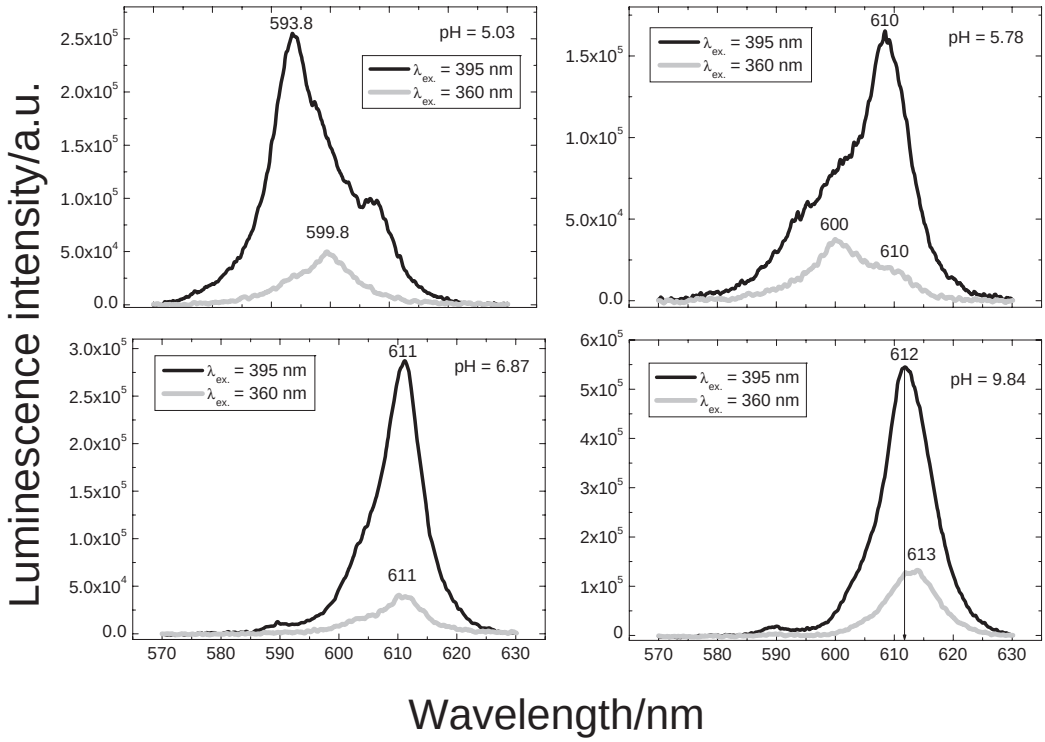

Figure 4. Comparison of luminescence spectra of curium(III) in aqueous DFO solutions measured at excitation wavelengths of 360 (indirect excitation mode) and 395 nm (direct excitation mode); $[Cm^{3+}] = 3 \times 10^{-7}$ M, [DFO] $= 6 \times 10^{-4}$ M, 0.1 M $NaClO_4$.

emission peaks at 611 and 614 nm, respectively. The single component spectrum of the CmDFO species shows in addition a small and broad maximum at 594 nm. This feature is rather a result of the SPECFIT analysis than a contribution of the uncomplexed Cm^{3+} aquo ion, because no free Cm^{III} exists under the experimental conditions (e.g., DFO concentration and pH) where CmDFO is formed. This explanation is supported by our experiments applying the indirect excitation mode of the Cm^{III} luminescence (Figure 4).

Luminescence Spectra Using Indirect Excitation. Previous studies[4,20–23] have shown that the luminescence of Cm^{III} complexes with organic ligands like pyoverdins and humic acids can be generated either by direct excitation of the Cm^{III} luminescence or by excitation of the ligand followed by an energy transfer from the ligand molecule to the Cm^{III} ion (indirect excitation). Hence, a luminescence spectrum of Cm^{III} with sufficient intensity can only be observed via an energy transfer from the coordinated ligand at an excitation wavelength of 360 nm (indirect excitation). Therefore, the indirect excitation mode can be applied for a direct determination of the complexed Cm^{III} in the presence of uncomplexed Cm^{III}. So, the luminescence properties of the Cm^{III}–DFO complex species can be as well determined using an excitation at 360 nm via the discussed energy transfer from the DFO molecule to the Cm^{III}. Figure 4 shows the spectroscopic speciation of Cm^{III} in the DFO system measured by excitation at 360 and 395 nm as a function of pH. In all samples the emission intensity from indirect excitation is on average 20% of the value from direct excitation. This can be explained by (a) the absorption of laser energy due to the free DFO molecules and (b) a lower energy-transfer efficiency of the ligand at 360 nm because the DFO absorptivity is higher in the wavelength range between 220 and 280 nm. At pH 5.03 the emission spectrum at 395 nm reveals the emission band of Cm^{3+} (aq) besides the contribution of the CmH_2DFO^{2+} complex. In contrast the luminescence spectrum at 360 nm is dominated by a single emission band at 599.8 nm corresponding to the 1:2:1 Cm^{III}–DFO species. The emission spectrum measured by indirect excitation at pH 5.03 can be used as further argument for the assignment of the complex single component spectrum shown in Figure 3 which was attributed to one single species namely the CmH_2DFO^{2+} complex. At pH 5.78 the emission spectra obtained using both excitation wavelengths exhibit the influence of the 1:2:1 and the 1:1:1 Cm^{III}–DFO species. At pH 6.87 mainly the species $CmHDFO^{+}$ contributes to the emission spectra detected with direct and indirect excitation. The influence of the third complex, CmDFO, is more pronounced in the emission spectra measured with indirect excitation at pH 9.84. The spectroscopic speciation determined at 360 and 395 nm is in agreement.

Luminescence Lifetimes. The complexation is accompanied by an increase of the luminescence lifetime. Luminescence lifetime measurements of curium(III) aqueous species can be used to obtain information on the composition of the first coordination sphere and on the kinetics of the complex formation reactions. A linear correlation between the decay rate and the number of H_2O molecules in the first coordination sphere of curium(III) was found by Kimura and Choppin.[24] Our finding of 68 ± 1 μs measured for the Cm^{3+} aquo ion corresponds to nine water molecules, while the value of 1370 μs measured in D_2O[25] corresponds to zero water molecules in the first coordination sphere of curium(III). This linear relationship can be used for an approximate insight into the structure of the formed Cm^{III}–DFO species. In all samples in which

the Cm^{3+} aquo ion and the first DFO complex, CmH_2DFO^{2+}, are present, a mono-exponential decay was measured with an average lifetime of 85 µs; this lifetime could correspond to the CmH_2DFO^{2+} species. Between pH 6 and 8.5, again a mono-exponential decay with an average lifetime of 123 µs was observed. This lifetime can be attributed to the $CmHDFO^{+}$ species. At pH values greater than 8.5, a bi-exponential decay was measured with lifetimes of 124 and 319 µs. The latter might correspond to the third Cm^{III}–DFO species, CmDFO. The bi-exponential decay suggests a low ligand-exchange rate for the DFO complexes, compared to the luminescence decay rate of the excited Cm^{3+} aquo ion. The increasing lifetimes of the Cm^{III}–DFO species reflect the exclusion of water molecules from the first coordination sphere of curium(III), due to the identified complex formation reactions. The average number of water molecules in the first coordination sphere of CmH_2DFO^{2+}, $CmHDFO^{+}$, and CmDFO, calculated with the determined luminescence lifetimes are 6.8 (5), 4.4 (3), and 1.2 (2), respectively. The numbers of water molecules estimated from the stoichiometry found with SPECFIT are given in parenthesis and were calculated as follows. Due to the lack of information regarding the structure of Cm^{III} complexes with DFO, we postulate a bidentate coordination by the hydroxamate oxygens ([O,O]-mode) according to the 1:1 complex of U^{VI} with salicylhydroxamic acid (=2-hydroxybenzohydroxamic acid).[26] In the CmH_2DFO^{2+} complex two hydroxamate groups of the DFO molecule are deprotonated and coordinated in a bidentate fashion via their oxygen atoms to the Cm^{III} center. This results in a release of four water molecules from the first coordination sphere of Cm^{III}. Hence, the CmH_2DFO^{2+} complex contains five water molecules. A bidentate coordination of three deprotonated hydroxamate groups of DFO results in three remaining water molecules in the $CmHDFO^{+}$ complex. Two remaining water molecules in the CmDFO complex can be explained by a bidentate coordination of the three deprotonated hydroxamate groups and an additional interaction of Cm^{III} with the amine group of the DFO molecule (Figure 1). The measured lifetimes represent sum values of all luminescence emitting species present in the individual test solutions. Due to the overlapping area of existence of all Cm^{III} species in the DFO system (Figure 5), the preparation of samples with only one Cm^{III} species is hampered. This might explain the discrepancies in the number of remaining water molecules especially for the 1:2:1 and the 1:1:1 species determined with the Kimura–Choppin relation and with SPECFIT. The lower number of remaining water molecules in the CmDFO species could be explained by an additional interaction with one amide group of the DFO molecule (Figure 1).

Conclusion

Table 1 gives a summary of the determined emission maxima, lifetimes, and complex formation constants of the Cm^{III}–DFO complexes in comparison to those of the Cm^{III}–*P. fluorescens* pyoverdin species and to relevant Eu^{III} and Fe^{III} data. For a better direct comparison of the strength of the formed species the determined $\log\beta$ values were recalculated in $\log K$ values using the involved aqueous ligand species. Since DFO is a chelating agent synthesized by microbes to provide the cells with essential Fe^{III}, it is not surprising that the corresponding formation constants are the largest, as shown in Table 1. Furthermore, Table 1 indicates that DFO is also able to complex elements other than Fe^{III} at a considerably high efficiency. The stability constants and luminescence properties of three Cm^{III}–DFO species, CmH_2DFO^{2+}, $CmHDFO^{+}$, and CmDFO, have been determined. For comparison only one complex having a 1:1:1 stoichiometry was observed for Eu^{III}.[11] A direct comparison between the $\log K$ values of this Eu^{III}–DFO and the corresponding Cm^{III}–DFO species shows a similar tendency of both metals to form complexes with DFO. However, due to the occurrence of two further Cm^{III}–DFO species their stability range as a function of pH is increased by one pH unit compared to the Eu^{III} system. The observed differences might also result in a different bioavailability of Cm^{III}–DFO species to microbes as observed for Eu^{III}.[14,15] More experiments, building on our results, are needed to clarify this point. A direct comparison of the Cm^{III} stability constants determined with the two types of natural bioligands shows slightly stronger species between Cm^{III} and the pyoverdins secreted by *P. fluorescens* (CCUG 32456). This can be explained by the additional participation of the catechol groups of the pyoverdin chromophore in the complex formation. Whereas the unique binding properties provided by the pyoverdin molecule, e.g., structure, might be a further explanation. This is underlined by the larger $\log K$ value of the 1:1:1

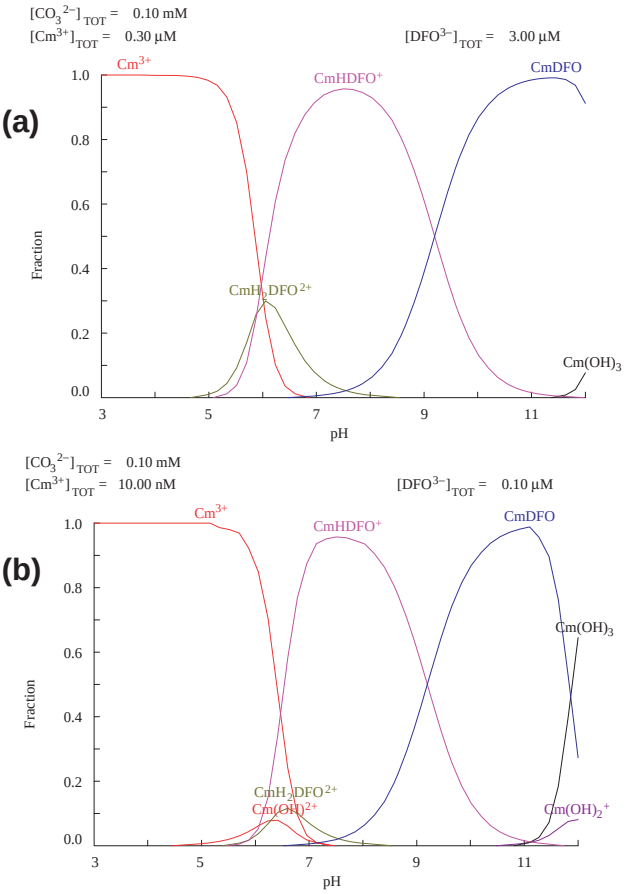

Figure 5. Speciation of curium(III) in aqueous solutions in dependence of the curium and DFO concentration (10^{-4} M carbonate each): (a) 3×10^{-7} M Cm^{III}, 3×10^{-6} M DFO; (b) 1×10^{-8} M Cm^{III}, 1×10^{-7} M DFO.

complex of Fe^{III} with pyoverdins compared to the value for $FeHDFO^{+}$ shown in Table 1. The complexation of curium(III) with DFO is slightly weaker than the complexation with EDTA ($\log \beta_{101} = 18.41$)[27] but stronger than the complexation with hydroxide ($\log \beta_{101} = 6.8 \pm 0.5$),[28] or carbonate ($\log \beta_{101} = 8.1 \pm 0.3$).[28]

In conclusion, use of TRLFS in combination with the SPECFIT factor analysis software provides a sensitive method for investigating the speciation of curium(III) in the aqueous DFO system. Figure 5 shows the speciation of curium(III) in an aqueous solution with tenfold excess of DFO and 10^{-4} M carbonate each. The speciation was done with the program MEDUSA.[29] The curium(III) DFO species dominate over a wide curium concentration and pH range. Hence, strong Cm^{3+} DFO species are formed, indicating the great potential of trihydroxamate siderophores to mobilize curium(III) in the biologically relevant pH range. Three Cm^{3+} DFO complexes, CmH_2DFO^{2+}, $CmHDFO^{+}$, and CmDFO, could be identified by their individual emission spectra (Figure 3). The results of the present work contribute to an improved understanding of the chemistry of curium(III) coordination with natural trihydroxamate siderophores in aqueous solution. Such complexation studies of selected bioligands are essential to explain both the enhanced mobility of actinides in the presence of siderophores and the overall interaction processes of actinides with microbes at a molecular level. The determined stability constants can be used directly in safety calculations to quantify the actinide-mobilizing effect of the bioligands released, for example, in the vicinity of a nuclear waste disposal site.

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