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Complexation of trivalent actinide and lanthanide ions by glycolic acid: a TRLFS study

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Complexation in the Cm(III) and Eu(III) glycolate systems has been studied by time-resolved laser fluorescence spectroscopy (TRLFS). Measurements have been performed at trace Cm(III) and Eu(III) concentrations (about 10^{-7} and 10^{-6} mol L^{-1}, respectively), at different concentrations of glycolic acid and at different pH using $NaClO_4$ as background electrolyte. Measurements at higher Eu(III) concentrations (10^{-3} mol L^{-1}) have also been performed in order to study the influence of metal ion concentration on the complexation reaction. By varying the glycolic acid concentration from 0.1 to 0.5 mol L^{-1} at low pH ($[H^+] = 10^{-3}$ mol L^{-1}) the stepwise formation of glycolate complexes $[Cm(HOCH_2CO_2^-)_n(H_2O)_{9-2n}]^{3-n}$ with n = 1–4 were confirmed spectroscopically. By varying the pH between 4.5 and 12.0 in 1 M glycolate three Cm(III) species were identified from the luminescence emission spectra (i) a hydrated tetraglycolate complex $[Cm(HOCH_2CO_2^-)_4(H_2O)]^-$ (Cm/complex 1) with a peak maximum at 602.3 nm and a luminescence emission lifetime of 206 ± 3 μs, (ii) a mixed hydroxide–glycolate complex $[Cm(HOCH_2CO_2^-)_4(OH)]^{2-}$ (Cm/complex 2) with a peak maximum at 605.6 nm and the same lifetime as Cm/complex 1 and (iii) a chelate complex $[Cm(HOCH_2CO_2^-)_3(^-OCH_2CO_2^-)(OH)]^{3-}$ or $[Cm(HOCH_2CO_2^-)_2(^-OCH_2CO_2^-)_2(H_2O)]^{3-}$ (Cm/complex 3) (peak maximum 611.3 nm) which is generated after deprotonation of one or two of the coordinated α-OH groups of the glycolate with a luminescence emission lifetime of 295 ± 15 μs. In the europium system there is evidence only for the corresponding Eu/complex 1 and 3. The corresponding europium mixed hydroxide–glycolate complex is not detectable spectroscopically. The luminescence decay is different in the Cm and Eu systems in the pH range from 7.8 up to 10.5; a bi-exponential decay behaviour was observed for the Cm system, while the Eu system shows mono-exponential decay. This indicates that the kinetics of the chelating process is much slower for Cm(III) than for Eu(III). The rate of protonation of the coordinated α-O^- group in the Eu/complex 3 is much faster than in the case of Cm/complex 3. Different spectra were observed for Eu(III)/glycolate complexes at europium concentrations of 3×10^{-6} and 1×10^{-3} mol L^{-1} indicating the formation of poly-nuclear Eu(III)/glycolate complexes at high metal ion concentration.

Introduction

It is well-known that the acidity of the OH-group(s) in hydroxy-carboxylates increases strongly when they are coordinated to metal ions[1,2] and that the resulting complexes are so stable that precipitation of hydrous oxides does not take place even at very high pH. As an example, Grenthe[3] reported a solubility of >1 M in the Er(III) glycolate system at pH > 13, presumably as a result of proton dissociation from coordinated hydroxy-acetate, A, and the formation of ternary complexes $M_pH_{-q}A_r$, where p, q, r are stoichiometric coefficients in reactions of the type

$$pM + rA \longrightarrow M_pH_{-q}A_r + qH^+ \qquad (1)$$

In a previous study Toraishi *et al.*[4] investigated the formation of $M_pH_qA_r$ complexes, where M is a lanthanide(III) or Th(IV). The stoichiometry and equilibrium constants have been determined using equilibrium analysis, based on potentiometric and NMR data. An analysis of the structure of the Th-complexes in solution has been made using EXAFS data.

These findings indicate that it is possible to investigate the solution chemistry of lanthanides and actinides at high pH, a region largely unexplored. Information of this type might be used to separate trivalent lanthanides and actinides, processes where α-hydroxycarboxylates are commonly used. We have extended previous studies of the lanthanide glycolate systems by using time-resolved laser fluorescence spectroscopy (TRLFS) on Cm(III) and Eu(III) because this method allows studies to be made at such low metal ion concentrations that the formation of polynuclear complexes and the precipitation of solid phases, $Ln(OH)_3$ (s) or $Ln(HOCH_2CO_2^-)_3 \cdot H_2O$ can be avoided. In addition fluorescence spectroscopy allows deconvolution of individual luminescence spectra and the determination of luminescence decay. In consideration of the luminescence intensity factors the deconvolution of the spectra allows a direct spectroscopic determination of the concentration of different complexes, while the lifetime provides information on the number of coordinated water molecules and OH-groups from the glycolate. There is previous information on structure and bonding and on chemical equilibria in solutions at pH < 5 that may be used as a platform for investigations at higher pH. The study of both Cm(III) and Eu(III) allows us to compare the chemistry of both 4f and 5f elements at trace concentrations. The intensity and positions of the emission

peaks for both Cm(III) and Eu(III) are good indicators of changes in the coordination sphere. The lifetime of the excited states of Cm and Eu provides information on the ligand exchange dynamics and the number of coordinated water and glycolate ligands in the first coordination sphere.[5]

Experimental

TRLFS studies

One set of these studies was made at total concentrations of Eu(III) (3×10^{-6} mol L^{-1}) and Cm(III) (1×10^{-7} mol L^{-1} and 9×10^{-8} mol L^{-1}, determined by ICP-mass spectroscopy), thereby avoiding precipitation of solid phases and the formation of polynuclear complexes. For comparison another TRLFS study was made at a Eu(III) concentration of 1×10^{-3} mol L^{-1}. The long-lived curium isotope Cm-248 ($t_{½} = 3.4 \times 10^5$ years) stock solution had the composition 97.3% Cm-248, 2.6% Cm-246, 0.04% Cm-245, 0.02% Cm-247 and 0.009% Cm-244 in 1.0 M $HClO_4$. The glycolic acid (Aldrich) was of analytical grade. All solutions were prepared with Milli-Q Plus ultra pure water. The studies were performed in $NaClO_4$ media of constant ionic strength. The pH was measured using a glass electrode (type Blue Line 16 pH, Schott) calibrated in H^+ concentration units. All experiments were made at 25 ± 1 °C in a glove box under a nitrogen atmosphere.

TRLFS measurements were performed by using a flash lamp pumped Ti:sapphire laser (Elight, Titania). Details on the experimental set-up are given elsewhere.[6–8] The laser pulse energy, at most 4 mJ, was controlled by a photodiode. The fluorescence emission was detected by an optical multi-channel analyser, which allows simultaneous detection of the whole emission spectrum. The system consists of a monochromator and spectrograph (Oriel; MS 257) with a 300 or 1200 lines mm^{-1} grating and a ICCD camera (Andor). The excitation wavelength was 395 nm and the emission spectra of Cm(III) and Eu(III) were recorded in the 520–680 nm (300 lines mm^{-1} grating) and 580–620 nm (1200 lines mm^{-1} grating) ranges, respectively, using a constant time window of 1 ms. For measuring the time dependent emission decay, the delay time between laser pulse and camera grating was scanned with time intervals between 10 and 15 μs.

Four series of experiments were made; in the first series we investigated the complex formation between Cm^{3+} and glycolate in 0.100 M $NaClO_4$ by varying the total concentration of glycolic acid at constant hydrogen ion concentration. In the other series, performed with Cm(III) and Eu(III), we varied the pH at constant concentration of glycolate equal to 1.00 M and an ionic strength of 3.00 M. After addition of titrant we recorded the emission spectra to ascertain that equilibrium had been attained. Equilibration took several hours in the Cm(III) system, while it was much faster in the Eu(III) system, *c.f.* Results. The standard procedure was to record the spectra one day after adding NaOH to ensure that thermodynamic equilibrium was reached.

Results

TRLFS-studies, Cm(III) data

Luminescence emission spectra of 1×10^{-7} mol L^{-1} Cm(III) with glycolic acid concentrations varied between 0.010 and 0.500 M glycolic acid in 0.1 M $NaClO_4$ solution at pH 3 are shown in Fig. 1. The emission band of the Cm^{3+} aquo ion has a peak maximum at 593.8 nm. When adding glycolic acid there is a pronounced red-shift of the emission as a result of the complex formation accompanied by an increase in the luminescence emission lifetime from 74 to 104 μs according to eqn. (2) for $n = 1$–4.

$$Cm^{3+} + n\text{glyc}^- \longrightarrow Cm(\text{glyc})_n^{3-n} \qquad (2)$$

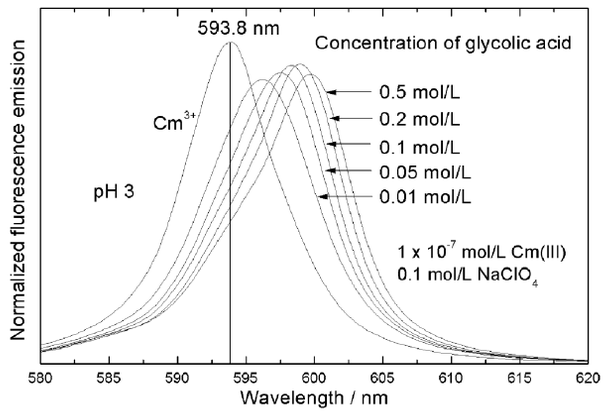

Fig. 1 Luminescence emission spectra of 1×10^{-7} mol L^{-1} Cm(III) in 0.1 mol L^{-1} $NaClO_4$ solution at pH 3 at various concentrations of glycolic acid; the spectra are scaled to the same peak area.

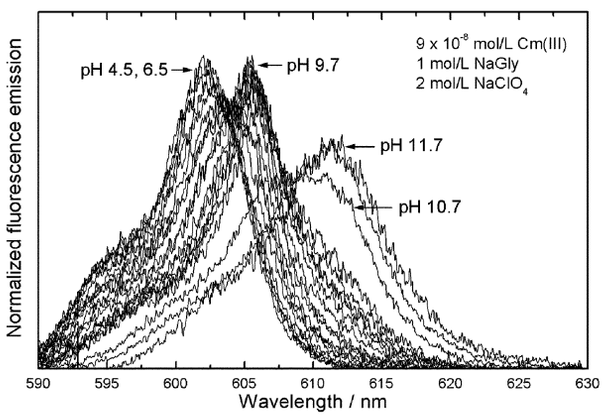

Fig. 2 Luminescence emission spectra of 9×10^{-8} mol L^{-1} Cm(III) in 1.0 mol L^{-1} sodium glycolate solution at various pH; the spectra are scaled to the same peak area.

The luminescence spectra of 9×10^{-8} mol L^{-1} Cm(III) in 1.0 M glycolate as a function of $-\log[H^+]$ are shown in Fig. 2. In the pH range between 4.5 and 6.5 only one Cm(III) peak with a maximum at 602.3 nm is observed. Its intensity decreases at pH > 6.5. In the same pH range a second peak at 605.6 nm appears simultaneously. The latter grows to a maximum at $-\log[H^+] = 9.7$ and then decreases as a third peak with a maximum at 611.3 nm appears. From the measured composite spectra we calculated the contributions of the pure components using an eigenvector analysis.[9] A plot of the experimentally determined speciation based on the deconvoluted spectra (Fig. 3) is shown in Fig. 4. Plots of the ratio log(complex 2/complex 1) and

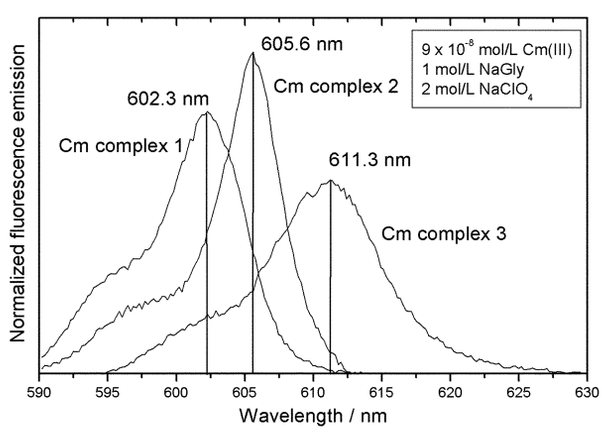

Fig. 3 Luminescence emission spectra of Cm/complex 1, Cm/complex 2 and Cm/complex 3 as derived by peak deconvolution; the spectra are scaled to the same peak area.

Table 1 Spectroscopic characteristics of the Cm(III) glycolate test solutions studied as a function of the total concentration of ligand at pH 3.00 in 0.1 M $NaClO_4$

[Glycolic acid]/M	Peak max./nm	Lifetime/μs	Average number of coordinated glycolates	Number of coordinated waters from eqn. (3)[a]	Calculated coordination number of Cm(III)[b]	Number of coordinated waters[c]	Coordination number of Cm(III)[d]
0	593.8	65	0	9.1	9.1	9.1	9.1
0.010	596.2	74	1.11	7.9	10.1	6.79	9.01
0.050	597.6	81	1.52	7.1	10.1	5.58	8.62
0.100	598.4	87	1.94	6.6	10.5	4.66	8.54
0.200	599.0	98	2.35	5.7	11.4	3.35	8.05
0.500	599.9	104	2.98	5.4	11.4	2.42	8.38

[a] Assumption: only the H_2O molecules in the first coordination sphere quench the excited state. [b] The coordination number is calculated under the assumption that the glycolate ligands occupy two coordination places (bi-dentate chelate *via* the α-OH and carboxylate groups) and the number of water molecules given in column 5. [c] Assumption: water molecules in the first coordination sphere and coordinated α-OH groups of the glycolate ligands quench the excited state. [d] The coordination number is calculated under the assumption that the glycolate ligands occupy two coordination places and the water molecules given in column 7.

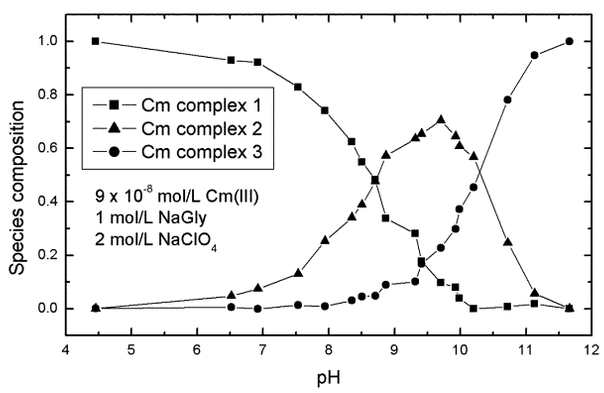

Fig. 4 Experimental species distribution of the Cm(III)–glycolate system as a function of pH.

log(complex 3/complex 2) *vs.* $-\log[H^+]$ give slopes of 0.83 and 1.02, respectively, indicating that $n = 1$ for each of the reactions:

$$\text{Cm complex 1} \rightleftarrows \text{Cm complex 2} + n\text{H}^+$$

and

$$\text{Cm complex 2} \rightleftarrows \text{Cm complex 3} + n\text{H}^+$$

Lifetime (luminescence decay) measurements

The luminescence lifetime provides information on the composition of the first coordination sphere. According to the method developed by Horrocks[10] for Eu(III) and later applied to Cm(III) by Kimura and Choppin[11] there is a linear correlation between the decay rate and the number of H_2O molecules in the first coordination sphere

$$k^{(H_2O)} = 1.54n_{H_2O} + 1.35 \quad (3)$$

where $k^{(H_2O)}$ is the contribution of coordinated water to the experimental relaxation rate and n_{H_2O} is the number of coordinated water molecules. $Cm(H_2O)_9^{3+}$ corresponds to a lifetime of 68 ± 3 μs.[12–15] When no water is coordinated the lifetime is 1250 ± 80 μs.[16,17]

In addition to the information about the bonding in the first coordination shell of the metal ion, the time dependence of the luminescence emission contains information about the kinetics of the complex formation reactions.[5] If the rate of ligand exchange is high compared to that of luminescence decay of the different excited Cm(III) or Eu(III) species, we expect to observe an average lifetime of the species and a mono-exponential decay. If the ligand exchange rate is lower than that of luminescence decay, we expect a bi-exponential decay. The emission decay of the test solutions with glycolic acid concentrations varied between 0.010 and 0.500 M glycolic acid studied at pH 3.00 (given in Table 1) is mono-exponential in all cases, indicating fast exchange rates among the different Cm(III) glycolate complexes.

In addition to the spectra of 9×10^{-8} mol L^{-1} Cm(III) in 1.0 M glycolate, we also measured the luminescence emission lifetime as a function of $-\log[H^+]$. In the range $4.5 < -\log[H^+] < 6.5$, where Cm complex 1 is the predominant species, we found mono-exponential luminescence decay with a lifetime of 206 ± 3 μs. The same lifetime is found in the presence of Cm complex 2. In the range 9.5 < pH < 11.0 we observed a bi-exponential decay with the lifetimes 206 and 295 ± 15 μs respectively. The lifetime measurements of Cm/glycolate complexes at pH 8.7 and 10.6 show a change in the emission decay when Cm complex 3 is present. The bi-exponential decay behaviour at pH 10.6 indicates slow exchange between Cm complex 2 and Cm complex 3. At pH > 11 the luminescence decay is again mono-exponential, indicating that one complex is predominating. The slow ligand exchange in the presence of the Cm complex 3 is shown by the slow spectral changes after acidifying a solution containing Cm complex 3. By changing the pH of a Cm/glycolate test solution from 11 to 4.7 the equilibrium pH was attained within minutes, but it took more than one day for the peak of Cm complex 3 to disappear (Fig. 5). This observation indicates that the protonation of

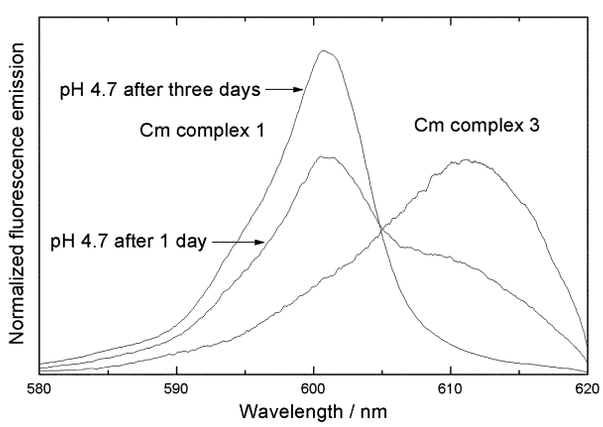

Fig. 5 The change with time of the emission spectra of a Cm–glycolate test solution initially at high pH complexes after acidification. The chemical reaction involves shifting the species distribution from Cm/complex 3 to Cm/complex 1.

Cm glycolate complex 3 is very slow in comparison to the instantaneous attainment of equilibrium of aqueous Cm complexation reactions with other inorganic or organic ligands *e.g.* protonation of Cm hydrolysis species.

TRLFS-studies, Eu(III) data at low metal ion concentration

While the luminescence emission spectra of Cm(III) are very sensitive to changes in the ligand field, the position of the europium luminescence bands is almost independent of the chemical environment of the metal ion. Only the intensity and the peak form of the $^5D_0 \longrightarrow {}^7F_2$ transition changes significantly when Eu(III) complexes are formed, a result of the so-called "hypersensitive" transition.[18–20] The peak form, the ratio of the emission intensity obtained for the $^5D_0 \longrightarrow {}^7F_1$ (λ = 594 nm) and $^5D_0 \longrightarrow {}^7F_2$ (λ = 619 nm) transitions and the lifetime of the luminescence emission provide information on the europium(III) speciation.[21,22]

Luminescence spectra of 3×10^{-6} mol L^{-1} Eu(III) in 1.0 M glycolate as a function of $-\log[H^+]$ are shown in Fig. 6. In

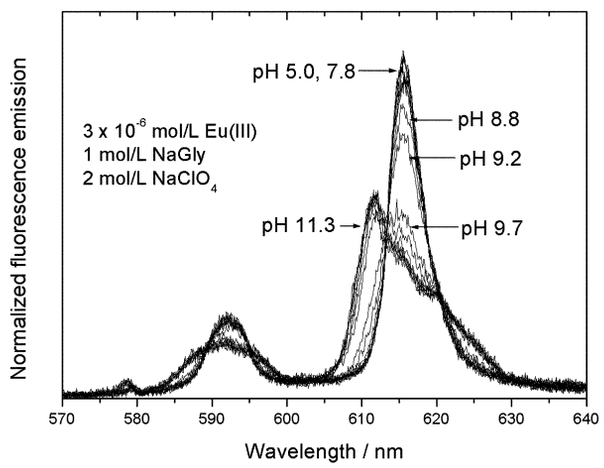

Fig. 6 Luminescence emission spectra of 3×10^{-6} mol L^{-1} Eu(III) in 1.0 mol L^{-1} sodium glycolate solution at various pH; the spectra are scaled to the same peak area.

the pH range from 5.0 to 7.8 both the peak form and the luminescence emission lifetime are approximately constant, indicating that the limiting Eu glycolate complex (complex 1) is formed. Above pH 7.8 the intensity of the Eu(III) luminescence emission decreases slightly and a change in the peak form with increasing pH is observed. A peak deconvolution was carried out to separate the individual species from the composite luminescence emission spectra. Two different Eu/glycolate complexes have been identified. From the spectra of the pure components the species distribution of Eu(III)/glycolate complexes as a function of $-\log[H^+]$ was calculated, *cf.* Fig. 7. The

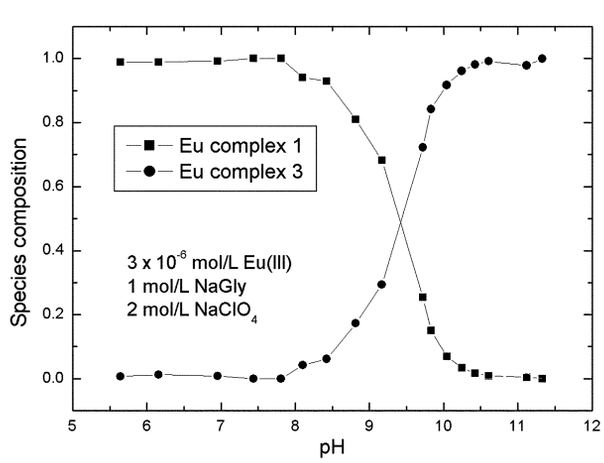

Fig. 7 Species distribution in the Eu(III)–glycolate system as a function of pH.

slope analysis of the reaction Eu complex 1 $\rightleftarrows$ Eu complex $3 + nH^+$ gives $n = 1.1$.

The luminescence emission lifetime in the Eu(III)/glycolate solutions changes from 350 ± 10 μs at pH 6.9 to 430 ± 12 μs at pH 11.8 (the lifetime of the Eu^{3+} aquo ion is 110 μs), indicating the loss of one quenching ligand in the first Eu(III) coordination sphere. In the pH range from 7.8 up to 10.5 where Eu complex 1 and Eu complex 3 are present the decay is mono-exponential. An average lifetime of 370 ± 11 μs was measured at pH 9.5 where the concentrations of Eu complex 1 and 3 are approximately the same. The fast ligand exchange observed when a solution containing Eu complex 3 is acidified, indicates that the protonation kinetic of Eu complex 3 is fast in comparison to the corresponding reaction in the Cm(III) system.

TRLFS-studies, Eu(III) data at high metal ion concentration

Luminescence emission spectra of 1×10^{-3} mol L^{-1} Eu(III) in 1.0 M glycolate were measured as a function of $-\log[H^+]$. The peak evolution at increasing pH is similar to that observed at low europium concentration. The spectra for the different complexes derived by peak deconvolution shown in Fig. 8 for two

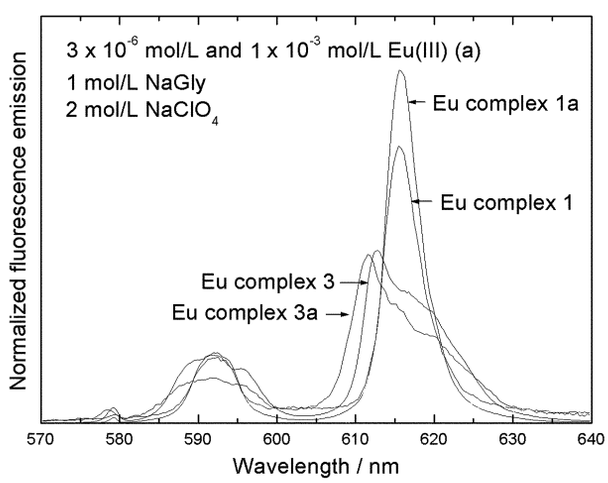

Fig. 8 Individual emission spectra of the Eu/glycolate complexes derived by peak deconvolution at Eu(III) concentrations of 3×10^{-6} and 1×10^{-3} mol L^{-1} (a).

different concentrations (3×10^{-6} and 1×10^{-3} M) are almost identical. The calculated species distribution as a function of $-\log[H^+]$ is shown in Fig. 9 and is compared with the species

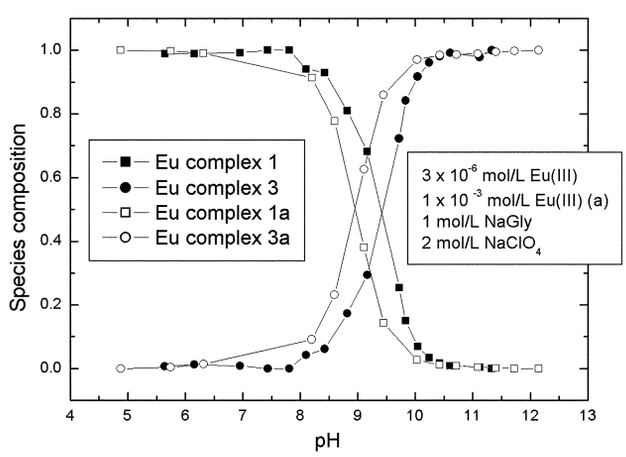

Fig. 9 Species distribution in the Eu(III)–glycolate system at europium concentrations of 3×10^{-6} and 1×10^{-3} mol L^{-1} (a) as a function of pH.

distribution found for the Eu(III)/glycolate system at trace metal ion concentration (3×10^{-6} mol L^{-1}). The formation of the limiting Eu/glycolate complex at high $-\log[H^+]$ takes place at a hydrogen ion concentration that is 0.6 log units lower at high

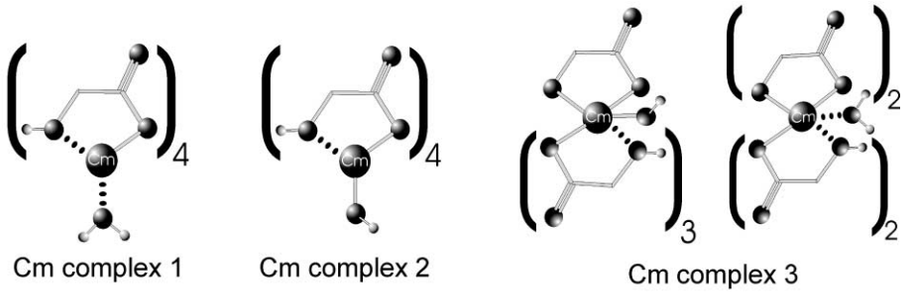

Fig. 10 Schematic structure models of the Cm(III)/glycolate complexes in 1.0 mol L^{-1} sodium glycolate solution.

europium concentration than at low concentration. A plot of the ratio log(complex 3a/complex 1a) *vs.* $-\log[H^+]$ has a slope of 1.43, indicating that the test solutions contain more than two different complexes.

Discussion

The average number of coordinated glycolates has been calculated using $\log K = 3.650$ for the protonation of glycolate and the equilibrium constants, $\log\beta_1 = 2.826$, $\log\beta_2 = 4.75$, $\log\beta_3 = 6.00$, for the formation of Cm(III)/glycolate complexes[23] and $\log\beta_4 = 6.7$ estimated from the corresponding Gd complex.[24] The results are shown in Table 1 column 4. An estimation of the coordination number of Cm(III) in glycolate complexes at low pH, based on the assumption that only H_2O molecules quench the Cm(III) luminescence emission lifetime and that glycolate is bi-dentate coordinated, is given in Table 1 column 6. This results in a coordination number increasing from 9 to 11.4, which is in disagreement with the well known nine coordination of curium in aqueous solution. This indicates that not only the coordinated water molecules, but also the α-OH-groups of the glycolate ligands, quench the exited state. We have tested this assumption using the data at $-\log[H^+] = 3$, where the predominant species are the species $Cm(glycolate)_n^{3-n}$, $n = 0$–4, and where the glycolate forms a five membered chelate ring. The calculated Cm(III) coordination number based on this assumption is shown in column 8. The estimated coordination numbers of the Cm(III) between 8 and 9 agrees fairly well with the expected value of 9, considering the uncertainty in the measured lifetime and the equilibrium constants used to calculate the speciation, ±0.5 quencher and ±0.05 units in $\log\beta_n$, respectively. Additional uncertainty may be caused by different quenching rates of the OH groups of the coordinated water and of the α-OH-groups.

Cm complex 1 and 2 have the same luminescence emission lifetime implying that the number of quenching ligands in the first Cm(III) coordination sphere remains unchanged. A possible explanation for this observation is the formation of ternary hydrolysed glycolate species at higher pH values, where OH^- has similar quenching as H_2O.[12] The equilibrium analysis of the reaction: Cm complex 1 $\rightleftarrows$ Cm complex 2 + nH$^+$ indicates the release of one proton and supports the assumption that a ternary hydroxo/glycolate/Cm complex is formed. The larger red-shift from 605.6 nm (Cm complex 2) to 611.3 nm (Cm complex 3) in the Cm/glycolate system at high pH (>9.7) is the result of a stronger change in the ligand field of the Cm(III) ion during the reaction: Cm complex 2 $\rightleftarrows$ Cm complex 3. Similar large red-shifts have been observed with ligands like EDTA.[25] This red-shift is much larger than that found for Cm hydroxide complexes,[26] indicating that it is due to the formation of strong complexes with oxyacetate, obtained by deprotonation of the coordinated α-OH group in glycolate. The experimental lifetime measurements give strong support to this interpretation. Further evidence for the formation of complexes containing coordinated oxyacetate is provided by the slow ligand exchange reactions, in contrast to the fast ligand exchange reactions of aqueous Cm(III) complexes with other inorganic or organic ligands. We conclude that Cm(III) forms nine-fold coordinated complexes with the stoichiometry: Cm complex 1 $[Cm(HOCH_2CO_2^-)_4(H_2O)]^-$ and Cm complex 2 $[Cm(HOCH_2CO_2^-)_4(OH)]^{2-}$. The strong red-shift for the reaction Cm complex 2 $\longrightarrow$ Cm complex 3 and the result of the slope analysis for this reaction could be explained either by the formation of $[Cm(^-OCH_2CO_2^-)(HOCH_2CO_2^-)_3(OH)]^{3-}$ or $[Cm(HOCH_2CO_2^-)_2(^-OCH_2CO_2^-)_2(H_2O)]^{3-}$. The formation of the latter is not very likely as the formation of this structural unit is accompanied by the release of one proton and the rearangement of a second proton from the α-OH group of the glycolate to the coordinated OH group in one step. However, studies at higher total metal concentrations have shown that tetranuclear complexes that contain approximately two oxyacetates per metal[4] are formed.

The Cm(III)/glycolate complexes are illustrated schematically in Fig. 10. In the europium system only the corresponding Eu/glycolate complex 1 and 3 are formed under the conditions used in the present study. The europium mixed hydroxo glycolate complex has not been detected spectroscopically. If a ternary europium hydroxo glycolate complex exists as an intermediate species one would expect an exchange of two protons by the reaction: Eu complex 1 $\rightleftarrows$ Eu complex 3 + nH$^+$. However, the slope analysis gives a slope of 1.1 indicating the exchange of only one proton. The differences in the kinetics and the emission decay behaviour of the third complex between Eu(III) and Cm(III) indicate relatively large differences in the chemical properties of the lanthanides and actinides at high pH. A fact that can be exploited in group-separation schemes; studies of this type are under way.

The differences in the spectra of the pure components observed for Eu(III)/glycolate complexes at europium concentrations of 3×10^{-6} and 1×10^{-3} mol L^{-1} can be explained by the formation of poly-nuclear Eu(III)/glycolate complexes at high metal ion concentration, such complexes have been identified by Toraishi *et al.*[4] The slope of 1.43 obtained for the reaction: Eu complex 1a $\rightleftarrows$ Eu complex 3a + nH$^+$ at high Eu(III) concentration provides additional evidence for this suggestion. The deprotonation of the coordinated α-OH group of the glycolate indicated by the large change in the Eu(III) luminescence emission spectrum occurs at lower pH in the solution with high metal ion concentration in comparison to solutions with trace Eu(III) concentrations. This observation is in good agreement with the observations by Toraishi *et al.*[4] and bridges to investigations done in the milli-molar concentration range.

Acknowledgements

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