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Ternary complex formation of Eu(III) and Am(III) with pyridine-2,6-dicarboxylate in aqueous solutions

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Abstract

Ternary hydroxo complex formation of Eu(III) with pyridine-2,6-dicarboxylate (PDA) was investigated by potentiometry and fluorescence spectrophotometry. Curves of equilibrium pH versus amount of OH^- added showed that the pH for the precipitation of Eu(III) was decreased due to the formation of ternary hydroxo complex, EuOHL(s) (L = PDA), which was confirmed by the enhancement of fluorescence intensity of Eu(III) in precipitate with PDA excitation wavelength. The ternary hydroxo complex species was also confirmed by the analysis of concentrations of the Eu(III), OH^- and PDA in the precipitate. Solubility products of EuOHL(s) and $Eu(OH)_3$ were determined as $pK^0_{sp} = 19.2 \pm 0.2$ and 24.5 ± 0.1, respectively. Similar behavior for the ternary hydroxo complex formation was observed for trace ^{241}Am(III) added to Eu(III).

Keywords: Ternary complex; Precipitation; Europium; Pyridine-2,6-dicarboxylate; Fluorescence

1. Introduction

The ternary complex formation of metal ions with ligands in aquatic solution has been of interest in various research fields such as synergistic extraction [1], spectrophotometry, spectrofluorometry [2], light conversion molecular devices increasing Ln(III) luminescence [3], solubility [4,5], and sorption [6,7] of radionuclides in the environment. The migration of actinide elements in hydrogeological systems is strongly related to their complexation with ligands, since it may affect the chemical behavior (such as soluble species formation, sorption, etc.) which control their distribution between the mobile and stationary phases in natural aquatic systems. Many studies on the complexation of radionuclides in the environment have focused on binary complex formation. Recently, ternary complex formation has attracted attention in the studies on radionuclides' migration in the environment. There are various ligands in near-neutral groundwater which can form stable ternary actinide complexes such as hydroxocarbonate. There is also a possibility to form the ternary complex containing hydroxide or carbonate together with natural organic matters, such as humic and fulvic acids in natural aquatic systems. It was reported that the ternary lanthanide complexes with some organic ligands were more stable than corresponding binary lanthanide complexes due to the extra stability by exothermic enthalpy changes [8]. For this reason, the prediction of radionuclide migration obtained from modeling without considering ternary complex formation may have a large uncertainty concerning natural phenomena.

The aim of this work is to study the reaction of pyridine-2,6-dicarboxylate (PDA) with Eu(III) ions, especially for the formation of ternary hydroxo complexes. Since PDA has two carboxylic functional groups and a nitrogen atom with non-bonding electrons to form stable complexes with metal ions, it is used as a model compound of natural organic matter to form stable complexes. Because PDA has two negatively charged $-COO^-$ groups when completely dissociated, the ternary hydroxo complex of Eu(III)–OH–PDA will be electrically neutral and will eventually decrease the solubility of Eu(III) ions.

The ternary complex formation was confirmed by potentiometric titration which showed the pH of precipitation started at a lower pH value for the Eu(III)–OH–PDA system than that for the Eu(III)–OH system, and by fluorescence intensity of Eu(III) ion enhanced with the wavelength of PDA ligand excitation due to

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the energy transfer from PDA to Eu(III) in the complexes. In this Eu(III)–OH–PDA system, the fluorescence intensity of Eu(III) can be enhanced by excitation of PDA through various species such as EuL^+, $EuL_2{}^-$, $EuL_3{}^{3-}$ and precipitated EuOHL(s). Thus removal of the precipitate will reduce the fluorescence intensities. The ternary complex composition was also confirmed by the measurement of the amounts of Eu(III), OH^-, and PDA included in the precipitate.

2. Experimental

2.1. Reagents

All solutions were prepared using deionized water from the Milli-Q system. Stock solutions of Eu(III) perchlorate were prepared by dissolving Eu_2O_3 (99.99%) in excess $HClO_4$ (analytical grade). The concentration of Eu(III) was measured by ICP-AES (ULTIMA2C, Jobin Yvon). The concentration of perchlorate was determined by acid–base titration after Eu^{3+} was completely replaced with H^+ by cation exchange (AG 50W-X6, 200–400 mesh). Pyridine-2,6-dicarboxylic acid (99%) was dissolved in water and the concentration was determined by potentiometric titration (DL77, Mettler) with a glass combination pH electrode. The sodium perchlorate solution was prepared by dissolving $NaClO_4{\cdot}H_2O$ (analytical grade) and used to adjust ionic strengths. ^{241}Am(III) in 0.1 M HCl (4.17 kBq/ml) was purified by (1) adsorbing onto a cation exchange resin column (AG 50WX8, 200–400 mesh), (2) washing with 0.1 M HCl to remove ^{237}Np, and (3) eluting with 7 M HCl. The eluate was evaporated to dryness, the residue dissolved in $HClO_4$, the procedure repeated several times, and finally dissolved in $HClO_4$ solution to make the concentration 0.01 M $HClO_4$. The ^{241}Am(III) solution was confirmed to be free of ^{237}Np by γ-spectrometry.

2.2. Procedures

A ternary complex was prepared in the pH range of 7–10 at 0.1 M ($NaClO_4$) ionic strength for Eu(III), and 0.01 M ($NaClO_4$) ionic strength for Eu(III) with a trace of ^{241}Am(III). The concentration of Eu(III) was 0.10 mM and that of PDA was varied from 0 to 0.15 mM. The weighed amount of Eu(III) and PDA solution were added into the reaction system since the weight measurement is more accurate than volume measurement. To adjust the pH of the solution, a 0.1 M standard NaOH solution (semiconductor grade, 99.99%, $Na_2CO_3 < 1\%$) was added to a Eu(III)–PDA solution using a titrator. The pH electrode was calibrated using pH buffer solutions (Mettler Toledo). All experiments were done under Ar gas flow and the temperature was kept constant at 25 °C. For the calculation of the quantity of OH^- in the Eu(III) precipitation, free protons associated with both perchloric acid in Eu(III) solution and pyridine-2,6-dicarboxylic acid (H_2PDA) were removed by adding NaOH, and the Eu(III)–PDA solution was equilibrated at pH 7.0 ± 0.3. Carbonate was removed by stirring acidic Eu(III)–PDA solution with Ar gas before the NaOH addition. To bring the pH of the solution up to 10, an adequate amount of NaOH was added repeatedly to increase about 0.2 pH unit at each step. When the pH of solution was stable, the solution was allowed to equilibrate for 30 min. At a given pH, 5 ml of the solution was taken out and filtered using a membrane filter with 0.1 μm pore size. The concentration of Eu(III) and PDA in the aqueous phase were determined.

For the Am(III)–OH–PDA system, a trace amount of ^{241}Am was added to Eu(III). The concentration of ^{241}Am was 75 Bq/ml (2.45 pM). The experiment for this system was done in the same manner as in the Eu(III)–OH–PDA system. One millilitre of the equilibrated solution at a given pH was taken out and centrifuged (18,000 rpm, 20 min). The concentrations of Eu(III) and ^{241}Am(III) in the supernatant were measured.

2.3. Measurement of absorption and fluorescence spectra

To find the most favorable excitation line for PDA, the absorption (Cary 3, Varian) and excitation (FS-900CD, Edinburgh) spectra of Eu(III)–PDA solution at pH 5.1 were measured. The maximum absorption band at 277 nm, corresponding to the π–π* electronic transition of PDA, was observed in the excitation spectra for the Eu(III)–PDA solution, while the intensities due to the direct f–f transitions of Eu^{3+} were too low to be clearly observed. The Eu(III) excitation spectra of Eu(III)–PDA solutions were measured at several pH values and PDA concentrations.

2.4. Measurement of Eu(III), PDA, and OH^- concentrations

The concentrations of dissolved Eu(III) ion in the Eu–OH–PDA system were determined by ICP-AES (ULTIMA2C, Jobin Yvon). The concentrations of dissolved Eu(III) and ^{241}Am(III) ions for the Eu(III)[^{241}Am(III)]–OH–PDA system were determined by ICP-MS (Element, Finnigan Mat) and liquid scintillation analysis (2560TR/XL, PACKARD) with a scintillation cocktail of Ultima Gold XR (Perkin-Elmer), respectively. The concentration of PDA in the aqueous phase was determined using UV–vis absorption spectrophotometry (Cary 3, Varian) from the absorbance at 272 nm at pH 8 (Tris buffer) using 10 mM EDTA as a masking agent of Eu(III). The amount of OH^- in the precipitates was calculated from the difference between the dissolved OH^- concentration and the amount of NaOH added after equilibration of Eu(III)–PDA solution at pH 7.0. The concentration of dissolved OH^- was calculated from the measured pH and the activity coefficient corrected by the Debye–Hueckel approximation. The concentration of Eu(III) and PDA removed by precipitation was determined by subtracting the concentration measured in the aqueous phase after filtration from the initial concentration, respectively.

3. Results and discussion

3.1. Potentiometric titration curves

Fig. 1 shows the pH curves as a function of the amount of OH^- added. In the absence of PDA, Eu(III) precipitation starts at about pH 8. The plateau observed in the range $0.5 < [OH^-]_{add}/[Eu]_{tot} < 2.5$ indicates the precipitation of $Eu(OH)_3(s)$. In the presence of 0.1 mM PDA, however, the precipitation begins at about pH 7.7. The slightly lower pH value for the precipitation indicates that ternary hydroxo complex of EuOHL(s) could be formed as a precipitate. The plateau is not observed in the pH curve for the sample with 0.2 mM PDA. At higher ligand concentration, $EuL_2{}^-$ may be predominant and hydrolysis and precipitation may hardly occur. Thus, we speculate that the ternary complex of EuOHL(s) can be formed most favorably at the condition of $[L]_{tot}/[Eu]_{tot} = 1$.

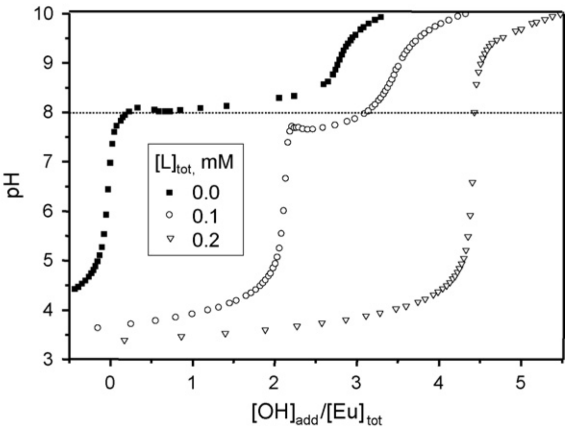

Fig. 1. Potentiometric titration of Eu(III)–L solutions of various L concentrations. $[Eu]_{tot} = 0.1$ mM, volume = 200 ml, potential change $(\Delta E/\Delta t) = 0.3$ mV/100 s and equilibrium time = 100–300 s.

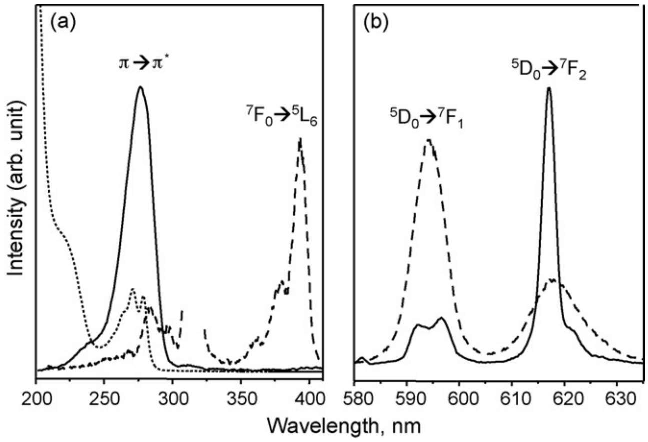

Fig. 2. Absorption and luminescence spectra of Eu(III) solutions. (a) UV–vis absorption of Eu–L, $[Eu]_{tot} = [L]_{tot} = 0.1$ mM, pH 7.3 (dotted line). Luminescence excitation of Eu–L, $[Eu]_{tot} = 0.1$ mM, $[L]_{tot} = 0.2$ mM, pH 5.1, $\lambda_{em} = 617$ nm (solid line). Luminescence excitation of Eu^{3+}, $[Eu]_{tot} = 10$ mM, $[HClO_4]_{tot} = 20$ mM, $\lambda_{em} = 592$ nm (dashed line). (b) Luminescence emission of Eu^{3+}, $[Eu]_{tot} = 10$ mM, $[HClO_4]_{tot} = 20$ mM, $\lambda_{ex} = 393$ nm (dashed line). Luminescence emission of Eu–L, $[Eu]_{tot} = 0.1$ mM, $[L]_{tot} = 0.2$ mM, pH 5.1, $\lambda_{ex} = 277$ nm (solid line).

3.2. Absorption and fluorescence spectra

To confirm the formation of the ternary hydroxo complex Eu(III)–OH–PDA, absorption and luminescence spectra were obtained for the solutions of pH below and above 8 as shown in Fig. 2. The dotted line in Fig. 2(a) presents the absorption spectrum of Eu(III)–PDA solution at pH 7.3. The typical absorption peaks were observed at 270.7 and 278.5 nm corresponding to the π–π* electronic transition of PDA and they were maintained in the pH range of 3.5–10.0 except that the background was increased by precipitation above pH 7.3. Since Eu^{3+} ion does not absorb light at these wavelengths, this observation indicates that $EuL_n{}^{(3-2n)+}$ $(n \geq 1)$ complexes are formed.

The solid line in Fig. 2(b) illustrates the excitation spectrum for Eu(III)–PDA solution at pH 5.1 with a ratio of $[L]_{tot}/[Eu]_{tot} = 2$, with an emission at 617 nm corresponding to the representative fluorescence transition $({}^5D_0 \rightarrow {}^7F_2)$ of Eu(III). A peak at 277 nm was observed, while the excitation (at 393 nm) due to the direct f–f transitions of Eu^{3+} was not clearly observed. This indicates that the intramolecular energy transfer occurred from the ligand to Eu(III) through the Eu(III)–PDA bond. It is well known that the intramolecular energy transfer from the lowest triplet state energy level of the organic ligand to the resonance energy level of the Ln(III) ion enhances the luminescence of the lanthanide when the absorption of the organic ligand has a large extinction coefficient [9]. To compare the Eu(III)–PDA solutions, the excitation spectrum of the Eu^{3+} ion solution ($[Eu]_{tot} = 10$ mM, $[H^+] = 20$ mM) was measured and the emission at 592 nm corresponding to the ${}^5D_0 \rightarrow {}^7F_1$ transition of the Eu^{3+} ion is shown by the dashed line in Fig. 2(b). In this excitation spectrum, the typical peak at 393 nm, corresponding to the ${}^7F_0 \rightarrow {}^5L_6$ transition of the Eu^{3+} ion, was observed, but there was no noticeable peak at 277 nm.

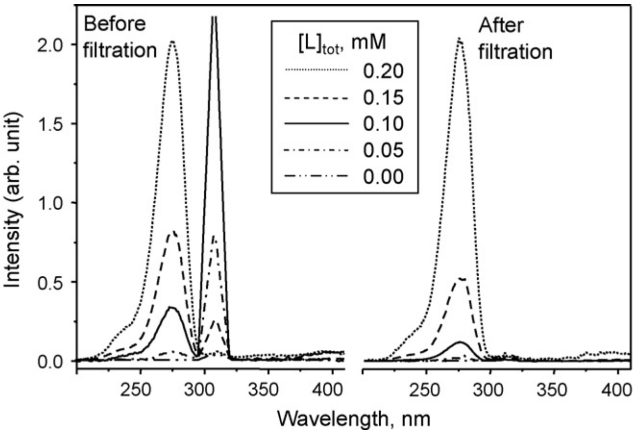

Fig. 3. Luminescence excitation spectra of Eu(III)–L solutions of various L concentrations measured before and after filtration. pH 8.1 ± 0.1, $\lambda_{em} = 617$ nm and $\lambda_{ex} = 277$ nm.

Comparison of the fluorescence intensities at 592 and 617 nm for both Eu(III) alone and Eu(III)–PDA systems provides reliable information to verify if $EuL_n{}^{(3-2n)+}$ $(n \geq 1)$ complexes are formed or not [10]. The dashed and solid lines in Fig. 2(b) show the fluorescence spectra for the Eu^{3+} ion and Eu(III)–PDA systems, respectively. In general, the intensity at 592 nm $({}^5D_0 \rightarrow {}^7F_1$ transition) is higher than that at 617 nm $({}^5D_0 \rightarrow {}^7F_2$ transition) for Eu^{3+} ion alone (dashed line). However, the reversed intensities for the Eu(III)–PDA system (solid line) suggests inner-sphere complexation in the form of $EuL_n{}^{(3-2n)+}$ $(n \geq 1)$ for the Eu(III)–PDA system.

Fig. 3 shows the fluorescence excitation spectra for the Eu(III)–PDA solutions at pH 8.1 with the emission at 617 nm. As shown in Fig. 1, the precipitate exists in the solution at this pH. Before filtration, the intensities at 277 nm increase substantially with increasing ligand concentrations from 0.05 to 0.2 mM, whereas, after filtration, the increasing behavior of the intensities become less pronounced, except for $[L]_{tot} = 0.2$ mM. The major chemical species contributing to the intensity at 277 nm are expected to be EuL^+, $EuL_2{}^-$, and EuOHL(s). At $[L]_{tot} = 0.2$ mM, $EuL_2{}^-$ is considered to be a predominant species, leading to a negligible change in the intensity at 277 nm before and after filtration. On the other hand, the removal of EuOHL(s) by filtration causes the intensity at 277 nm to lower with respect to the ligand concentration.

The excitation peak at 308.5 nm is the second harmonic of the fundamental emission wavelength of 617 nm. This peak comes from light scattering of the precipitate, thus they are observed in the spectra before filtration. It is noteworthy that the highest scattering peak is observed at the condition of $[L]_{tot} = [Eu]_{tot}$. This scattering effect provides additional evidence for ternary complex formation in the precipitate.

3.3. Measurement of species concentrations

The concentration of Eu(III) in the precipitate is calculated from the measured concentration of Eu(III) in the aqueous phase versus the initial concentration and is plotted against the pH as shown in Fig. 4. At a fixed pH, the Eu(III) concentration in

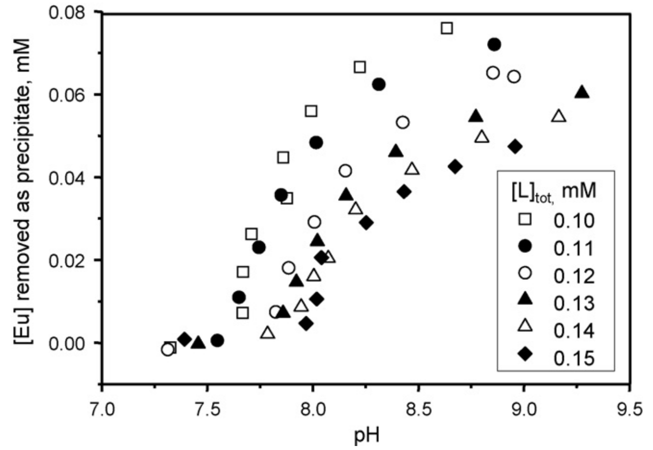

Fig. 4. The concentration of Eu(III) removed from aqueous phase by precipitation against pH at various L concentrations.

the precipitate decreases with increasing ligand concentration from 0.1 to 0.15 mM. Moreover, precipitation begins at a higher pH with increasing ligand concentration. These observations can be explained by the fact that, with increasing the ligand concentration, more of the soluble ML_2^- species is formed, thereby leading to decrease a formation of the precipitate. It is expected that the precipitate is mainly composed of EuOHL(s) and $Eu(OH)_3$(s). If the Eu_2L_3(s) is dominant in the precipitate, the Eu(III) concentrations in the precipitate should increase with increasing ligand concentrations. Thus, we can exclude the existence of Eu_2L_3(s) in the precipitate.

Using the data in Fig. 4, the concentrations of Eu(III) and PDA in the precipitate are plotted as a function of $[OH^-]_{add}/[Eu]_{tot}$ in Fig. 5. Both concentrations are almost linearly dependent on the added OH^- concentrations. The slopes of the Eu(III) and PDA are about 0.5 and 0.33, respectively. These different values indicate the existence of two different species, EuOHL(s) and $Eu(OH)_3$(s), in the precipitate.

Using the data in Fig. 5, the relative concentrations of $[OH]_p/[Eu]_p$ and $[L]_p/[Eu]_p$ in the precipitate are plotted as a function of the pH in Fig. 6. In the absence of ligand, the ratio of $[OH]_p/[Eu]_p$ is about 3, as shown by the solid square symbols in Fig. 6(a). This means that the precipitate is mainly composed of $Eu(OH)_3$(s). However, in the presence of ligand, the values of $[OH]_p/[Eu]_p$ are reduced to 1.5–2.2, which implies increasing amounts of the ternary complex of EuOHL(s) in the precipitate, along with decreasing amounts of $Eu(OH)_3$(s). Also, the values of $[L]_p/[Eu]_p$ in Fig. 6(b) are in the range of 0.55–0.75 at pH values higher than 8.

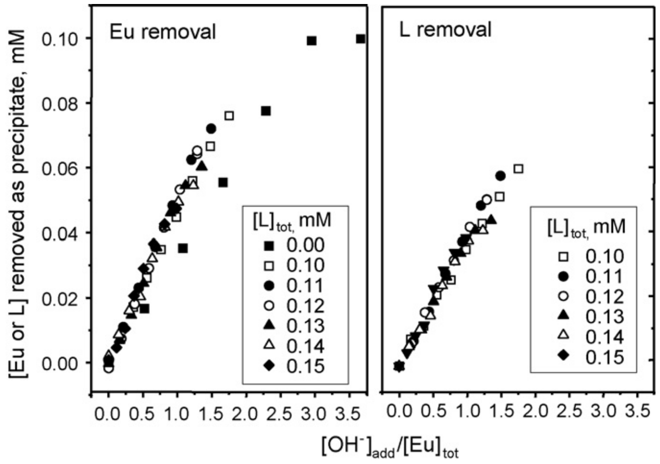

Fig. 5. Removal of Eu(III) and L by precipitation against $[OH^-]_{add}/[Eu]_{tot}$ at various L concentrations.

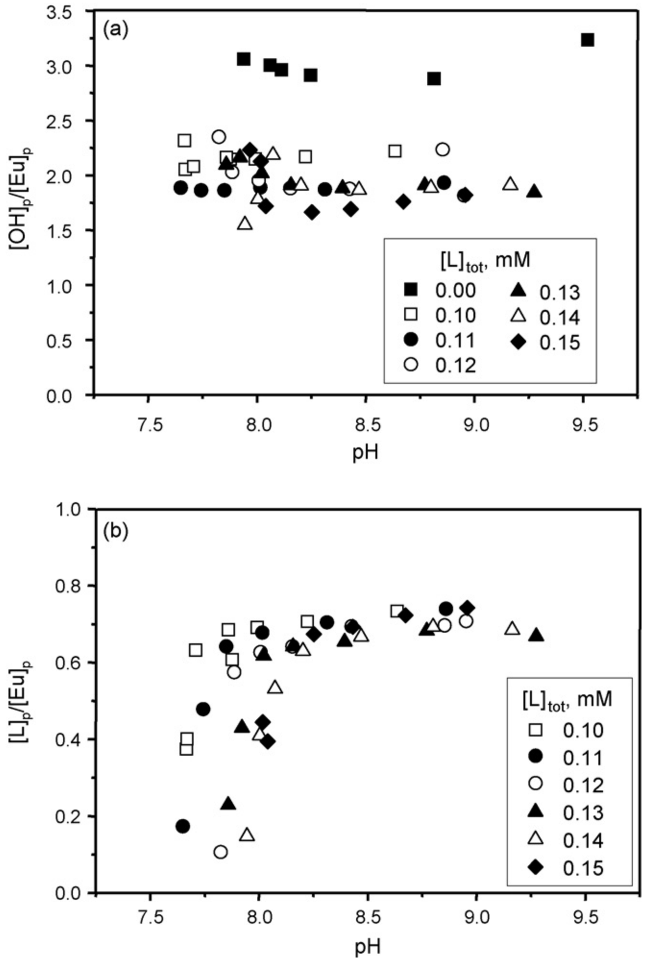

Fig. 6. Relative amounts of OH^- (a) and L (b) to Eu in precipitates against pH at various L concentrations.

Based on the above results, $[OH]_p/[Eu]_p$ and $[L]_p/[Eu]_p$ for the mixture of $Eu(OH)_3$(s) and EuOHL(s) in the precipitate can be expressed in the following equations:

$$\frac{[OH]_p}{[Eu]_p} = \frac{[EuOHL](s) + 3[Eu(OH)_3](s)}{[EuOHL](s) + [Eu(OH)_3](s)} \tag{1}$$

$$\frac{[L]_p}{[Eu]_p} = \frac{[EuOHL](s)}{[EuOHL](s) + [Eu(OH)_3](s)} \tag{2}$$

where $[OH]_p/[Eu]_p$ and $[L]_p/[Eu]_p$ are in the range of 1.5–2.2 and 0.55–0.75, respectively. The values of $[Eu(OH)_3](s)/[EuOHL](s)$ in Eqs. (1) and (2) are in the range of 0.33–1.50 and 0.33–0.82, respectively. It means that the portions of ternary complex in the precipitate are in the range of

Table 1
Thermodynamic data ($I = 0$ M, $T = 298.15$ K) used in this study for the calculation of aqueous concentration of Eu(III) species in the presence of pyridine-2,6-dicarboxylate (L)

Reaction	log K^0 [Ref.]
$LH^- \leftrightarrows H^+ + L^{2-}$	−4.51 ± 0.05 [12]
$LH_2 \leftrightarrows 2H^+ + L^{2-}$	−6.59 ± 0.10 [12]

Reaction	log K^0	
	M = Eu [Ref.]	M = Am [Ref.]
$M^{3+} + L^{2-} \leftrightarrows ML^+$	8.79[a] [13]	
$M^{3+} + 2L^{2-} \leftrightarrows ML_2{}^-$	15.86[a] [13]	
$M^{3+} + 3L^{2-} \leftrightarrows ML_3{}^{3-}$	21.32[a] [13]	
$M^{3+} + H_2O \leftrightarrows MOH^{2+} + H^+$	−7.64 ± 0.04 [11]	−7.2 ± 0.5 [14]
$M^{3+} + 2H_2O \leftrightarrows M(OH)_2{}^+ + 2H^+$	−15.10 ± 0.20 [11]	−15.1 ± 0.7 [14]
$M^{3+} + 3H_2O \leftrightarrows M(OH)_3 + 3H^+$	−23.70 ± 0.10 [11]	−26.2 ± 0.5 [14]
$M^{3+} + 4H_2O \leftrightarrows M(OH)_4{}^- + 4H^+$	−36.20 ± 0.50 [11]	
$M^{3+} + 3H_2O \leftrightarrows M(OH)_3(am) + 3H^+$	−17.60 ± 0.80 [11]	−17.0 ± 0.6 [14]

Those of Am(III) are presented together for comparison.
[a] $I = 0.5$ M.

about 40–75% and 55–75%, respectively, under the conditions of $[Eu]_{tot} = 0.1$ mM, $[L]_{tot} = 0.1$–0.15 mM, $7.7 < pH < 9.2$, and ionic strength = 0.1 M $NaClO_4$.

3.4. Solubility products

The solubility products (K_{sp}) of the EuOHL(s) and the $Eu(OH)_3(s)$ can be calculated using the following equations:

$$\mathrm{EuOHL(s)} \leftrightarrows \mathrm{Eu}^{3+} + \mathrm{L}^{2-} + \mathrm{OH}^-,$$
$$K_{sp} = [\mathrm{Eu}^{3+}][\mathrm{L}^{2-}][\mathrm{OH}^-] \quad (3)$$

$$\mathrm{Eu(OH)_3(s)} \leftrightarrows \mathrm{Eu}^{3+} + 3\mathrm{OH}^-,$$
$$K_{sp} = [\mathrm{Eu}^{3+}][\mathrm{OH}^-]^3 \quad (4)$$

To estimate the value of K_{sp}, we should know the concentrations of free Eu^{3+} and ligand (L^{2-}) which can be obtained from the following equations:

$$\begin{aligned}[\mathrm{Eu(III)}]_{meas} = {} & [\mathrm{Eu}^{3+}] + [\mathrm{EuOH}^{2+}] + [\mathrm{Eu(OH)_2}^{+}] \\ & + [\mathrm{Eu(OH)_4}^{-}] + [\mathrm{EuL}^{+}] \\ & + [\mathrm{EuL_2}^{-}] + [\mathrm{EuL_3}^{3-}] \end{aligned} \quad (5)$$

$$\begin{aligned}[\mathrm{L}]_{meas} = {} & [\mathrm{L}^{2-}] + [\mathrm{LH}^{-}] + [\mathrm{EuL}^{+}] + 2[\mathrm{EuL_2}^{-}] \\ & + 3[\mathrm{EuL_3}^{3-}] \end{aligned} \quad (6)$$

where $[Eu(III)]_{meas}$ and $[L]_{meas}$ are the concentrations of Eu(III) and PDA, respectively, measured in the aqueous phase after filtration. Reported values of log K^0 for each species used for the calculation are summarized in Table 1. The values of the solubility products (pK_{sp}^0) of EuOHL(s) and $Eu(OH)_3(s)$ are activity coefficient corrected at an ionic strength of 0.0 M and are listed in Table 2. The solubility products are almost constant, 19.2 ± 0.2 for EuOHL(s) and 24.5 ± 0.1 for $Eu(OH)_3(s)$, at the ligand concentration ranging from 0.1 to 0.15 mM. The solubility product of 24.5 ± 0.1 for $Eu(OH)_3(s)$ obtained in this work agrees well with the result obtained from literature values using the following reaction [11]:

$$\mathrm{Eu(OH)_3(am)} \leftrightarrows \mathrm{Eu}^{3+} + 3\mathrm{OH}^-, \quad pK_{sp}^0 = 24.4 \pm 0.8 \quad (7)$$

3.5. Data for trace ^{241}Am(III) with Eu(III)–OH–PDA

Similarities in the chemical behavior between the lanthanides(III) and actinides(III) ions are well known. The thermodynamic data for Am(III) in Table 1 show very similar values to those of Eu(III). Thus, the experimental results for Am(III) can be understood in the same manner as those of Eu(III) and the results are shown in Fig. 7. The relative removal ratios are about 1 in the pH range of 7.5–10.5 at various PDA concentrations. This result suggests that Am(III) may also form the ternary hydroxo complex, AmOHL(s). To obtain this evidence further experiments using pure Am(III) are being carried out.

Table 2
Solubility product of EuOHL(s) and $Eu(OH)_3(s)$ at various $[L]_{tot}$ and corrected at 0.0 M ionic strength and 25 °C

$[L]_{tot}$ (mM)	pK_{sp}^0 [a]	
	EuOHL(s)	$Eu(OH)_3(s)$
0.10	18.8 ± 0.6	24.6 ± 0.1
0.11	19.2 ± 0.5	24.7 ± 0.2
0.12	19.2 ± 0.7	24.6 ± 0.5
0.13	19.2 ± 0.6	24.4 ± 0.3
0.14	19.3 ± 0.4	24.4 ± 0.3
0.15	19.3 ± 0.3	24.5 ± 0.3
Mean	19.2 ± 0.2	24.5 ± 0.1

[a] Corrected by activity coefficient calculated from the ionic strength.

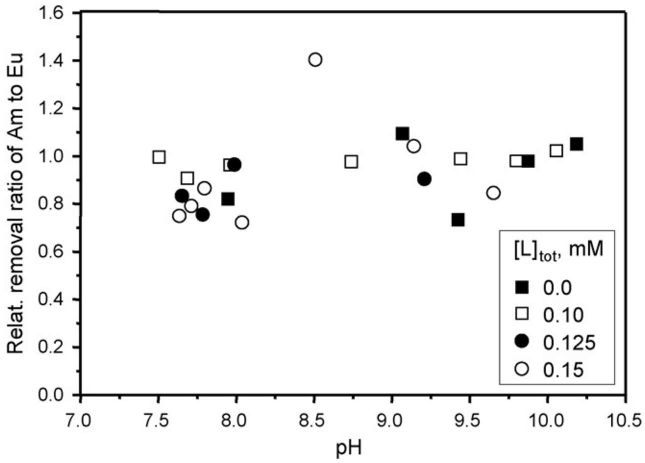

Fig. 7. Relative removal ratio of Am to Eu against pH at various L concentrations.

4. Conclusions

We report herein on the characteristics of ternary hydroxo complex formation for the Eu(III)–OH–PDA system. The formation of ternary complexes causing the precipitation of the Eu(III) has been confirmed precisely in the following manner: (1) potentiometric titration showed that the pH of the precipitation starts at a lower pH for Eu(III)–PDA than for the Eu(III) alone, (2) enhancement of the Eu(III) fluorescence by ligand excitation owing to the energy transfer from the ligand to Eu(III), (3) quantitative analysis of the concentrations of the species in the precipitate. We believe that the approach described in this work can provide useful information in investigating the chemical reactions of natural organic matter with actinides in natural groundwater.

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