

## Effects of Ligands on a Ternary Hydroxo Complex Formation with Eu(III) in a Aqueous Solution: Comparison of a Pyridine-2,6-dicarboxylate with a Phthalate

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### 1. Introduction

The interaction of a radionuclide with ligands in a groundwater influences its migration through a hydrogeological system due to a change in the characteristics of a dissolution and a sorption. Actinide ions are classified as a hard acid and strongly interact with ligands having an oxygen donor atom of a hard base such as a hydroxide, carbonate and carboxylate. These ligands reveal a large ionic bonding character. A number of experimental results on a binary complex formation of actinides have been reported.

However, actinides may easily form a ternary complex by interacting simultaneously with two different ligands, since an ionic bonding does not restrict the spatial orientation of a ligand. In previous studies, a ternary hydroxo complex formation was investigated by using pyridine-2,6-dicarboxylate (PDA)[1] or phthalate[2] as an organic ligand and Eu(III) as an analogue of an actinide(III) ion. Although these organic ligands equally contain two carboxylate groups that interact with an Eu(III) ion, their stabilities reveal big differences. PDA is a tridentate ligand forming two 5-membered chelates, while phthalate is a bidentate ligand forming a 7-membered chelate. The latter reveals a lower stability than the former due to an angle strain. This is one of the reasons for the lower stability of the Eu(III)-phthalate than that of the Eu(III)-PDA. The difference in the stabilities of binary complexes,  $\text{EuL}^+$  (L=organic ligand), influences the stabilities of the ternary hydroxo complexes,  $\text{Eu(OH)L}$ . The coordination of a phenylic or pyridine ligand can greatly enhance the fluorescence of an Eu(III) ion due to the high absorbance of a ligand by a  $\pi \rightarrow \pi^*$  transition and the transfer of this energy to an Eu(III) ion. These fluorescence characteristics in a binary complex system could be changed in a ternary complex.

In this study, the effect of a ligand on the stability of a ternary hydroxo complex is reported by comparing the stabilities of Eu-PDA with Eu-phthalate systems. The effect of a hydroxide coordination on a ligand-sensitized fluorescence of an Eu(III) ion in a ternary hydroxo complex formation is also discussed

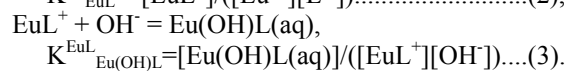
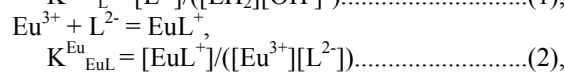
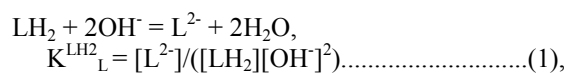
### 2. Experimental

In a comparison of both ligands effects on a ternary hydroxo complex formation, the reported stability constants are used. In the measurement of the hydroxide effect on the energy transfer from a ligand to an Eu(III)

ion, various Eu(III)-ligand solutions were prepared at a fixed Eu(III) concentration. The pH was changed at a fixed ligand concentration or ligand concentration was changed at a fixed pH. All the solutions were prepared using deionized water from a Milli-Q system, and handled under  $\text{N}_2$  or Ar gas environments. The pH of the solution was adjusted by adding a  $\text{CO}_2$ -free NaOH solution. When the pH of a solution became stable, the solution was allowed to equilibrate for 30 minutes before a fluorescence measurement. In the case where a precipitate was formed, a solution in an optical cell was stirred with a compact magnetic stirrer for a dispersion of it. Eu(III) ion was excited by an incident light corresponding to the direct f-f transitions of an  $\text{Eu}^{3+}$  ion or the  $\pi\text{-}\pi^*$  electronic transition of a ligand. The instrumental effect on the intensity variation was corrected by measuring the intensity of the direct f-f transitions of an  $\text{Eu}^{3+}$  ion (10 mM, pH 2) at the same instrumental conditions.

### 3. Results and discussion

*3.1. Ligand effect on a Eu(OH)L formation* The following three reactions in an acidic solution of an  $\text{Eu}^{3+}\text{-LH}_2$  mixture (L=PDA or phthalate) can be considered to understand the formation process of a ternary hydroxo complex with the increase of pH:



The deprotonation of carboxylate groups in the reaction (1) should be completed below the pH where the hydrolysis of  $\text{Eu}^{3+}$  ion  $\{\text{Eu}^{3+} + n \text{OH}^- = \text{Eu(OH)}_n^{(3-n)+}\}$  is not heavy. The reaction (2) is a binary complex formation. If the formation constant of  $\text{EuL}^+$  is low, it competes with the hydrolysis of  $\text{Eu}^{3+}$  ion. The reaction (3) is a ternary hydroxo complex formation. If the formation constant of  $\text{EuOHL(aq)}$  is not high, it competes with the ligand exchange by hydroxide ( $\text{EuL}^+ + \text{OH}^- = \text{EuOH}^{2+} + \text{L}^{2-}$ ). And, the second coordination of ligand ( $\text{EuL}^+ + \text{L}^{2-} = \text{EuL}_2^-$ ) is possible, if the formation constant of  $\text{EuOHL(aq)}$  is not much higher than that of  $\text{EuL}_2^-$ .

The effect of the formation constant of  $\text{EuL}^+$  on the formation of a ternary hydroxo complex was investigated by measuring the potentiometric titration

curves for the L=PDA[1] and phthalate[2] systems. The plateau indicating the formation of  $\text{Eu}(\text{OH})\text{L}(\text{s})$  is observed at  $[\text{L}]_{\text{tot}}/[\text{Eu}]_{\text{tot}} \geq 5$  for L=phthalate, while it is observed at  $[\text{L}]_{\text{tot}}/[\text{Eu}]_{\text{tot}} < 2$  for L=PDA. These results coincide with the fact that the Eu(III)-PDA complexes are much more stable than Eu(III)-phthalate complexes.

When a ternary hydroxo complex precipitate is generated in the reaction (3), the solubility product,  $K_{\text{sp}}'$ , can be considered as follows:

$$\begin{aligned} \text{EuL}^+ + \text{OH}^- &= \text{Eu}(\text{OH})\text{L}(\text{s}), \\ K_{\text{sp}}' &= [\text{EuL}^+][\text{OH}^-] \\ &= ([\text{Eu}^{3+}][\text{L}^{2-}][\text{OH}^-]) \{ [\text{EuL}^+] / ([\text{Eu}^{3+}][\text{L}^{2-}]) \} \\ &= K_{\text{sp}} K_{\text{EuL}^+} \dots \dots \dots (4). \end{aligned}$$

The logarithmic values of  $K_{\text{sp}}'$  are -10.41, -11.9 and -11.5 for the L=PDA, phthalate and  $2\text{OH}^-$ , respectively. Very small difference among the  $K_{\text{sp}}'$  values suggests that the reaction of  $\text{EuL}^+$  with  $\text{OH}^-$  is not greatly influenced by the kind of  $\text{L}^{2-}$ .

**3.2. Ligand effect on the spectroscopic properties of Eu(III).** The exchange of  $\text{H}^+$  with  $\text{Eu}^{3+}$  at phthalic acid did not appreciably affect the absorption corresponding to the  $\pi \rightarrow \pi^*$  transition of a phenyl ring. In the absorption spectrum of the PDA system, the same phenomenon was observed except for the small structuring of absorption band corresponding to the  $\pi \rightarrow \pi^*$  transition. This indicates that the interaction between  $-\text{COO}^-$  and  $\text{Eu}^{3+}$  ion is mostly ionic and slightly higher covalent in the Eu(III)-PDA than in the Eu(III)-phthalate. Eu(III) ion revealed a characteristic fluorescence spectrum with peaks corresponding to the transitions of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j=0-4$ ). The transition to the level of  $J=2$  is an induced electric dipole, and hypersensitive to a coordination environment. The excitation spectrum was obtained by monitoring the strong  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  transition at 615 nm.

The broad excitation bands centered at the wavelength corresponding to the  $\pi \rightarrow \pi^*$  transition within the PDA or phthalate ligand. This supports that the emission from the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of Eu(III) ion is greatly sensitized by the ligand to Eu(III) ion energy transfer through an Eu(III)-L bond. The measured luminescence intensities of both Eu(III)-L systems with various ligand concentrations at a fixed pH values of 6.5 were compared and shown at Fig. 1. The intensity of Eu-PDA was 11 times larger than that of the Eu-phthalate in case of  $\text{EuL}^+$  species. This is explained by the difference in energy level matching between the lowest excited triplet state of a ligand and the resonance state of an Eu(III) ion.

The measured luminescence intensities of both Eu(III)-L systems with various pH's at a fixed ligand concentration were compared and shown at Fig. 2. The intensities corresponding to the transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  of both ligand systems increase considerably in the pH region where a ternary hydroxo complex formation is observed. The intensity ratio of

${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition also showed considerable increase in the same pH region. This supports that a covalent degree in Eu-L bond and the ligand to Eu(III) ion energy transfer are increased by a ternary hydroxo complex formation.

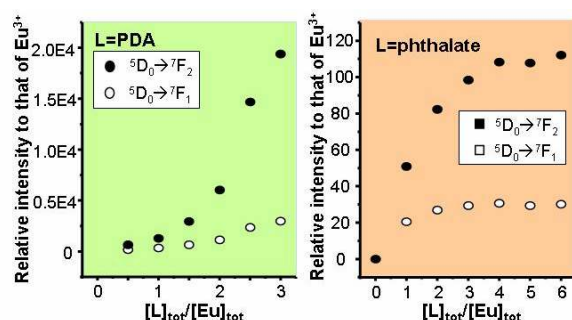


Fig. 1. Ligand-sensitized emission intensity of Eu(III) at various ligand concentrations of constant pH.

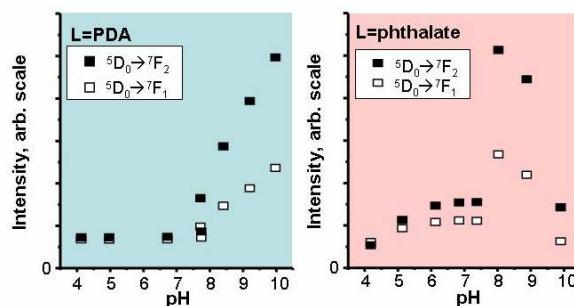


Fig. 2. Ligand-sensitized emission intensity of Eu(III) at various pHs of constant ligand concentration.

### Acknowledgements

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### References

- [1] Kyoung K. Park, et. al. J. Alloys Compds., 444-445 (2007) 677.
- [2] Kyoung K. Park, et. al. "Ternary Complex Formation of Eu(III) with Phthalate in Aquatic Solutions," Transactions of the Korean Nuclear Society Meeting (Autumn, 2006).