

## Effects of the Energy Level on an Intramolecular Energy Transfer from Ligand to Eu(III) and Tb(III) in an Aqueous Solution

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### 1. Introduction

Actinide ions of a hard acid form stable aqueous complexes with anions of a hard base such as a hydroxide, carbonate and carboxylate which are ubiquitous in natural water. Since a dissolution and sorption of actinide ions depend on their chemical species distribution in groundwater conditions which largely influences their migration through a hydrogeological system, a microscopic understanding of their interaction with a ligand functional group is required for a precise analysis of their safety in a radioactive waste disposal site.

A lanthanide ion, especially Eu(III) ion, is used as a chemical analogue of Am(III) or Cm(III) ions for the study of chemical behavior in a groundwater. Luminescence spectroscopy is one of the important techniques for a coordination chemistry study of the Eu(III) ion of a low concentration[1]. Since each lanthanide(III) ion has well-defined energy levels, they reveal different lanthanide(III)-specific energy transfer processes in a variety of chemical environments. Eu(III) ion has a characteristic fluorescence spectrum with peaks corresponding to the transitions of  ${}^5D_0 \rightarrow {}^7F_J$  ( $J=0-4$ ). The transition to a level of  $J=2$  is an induced electric dipole, and hypersensitive to a coordination environment. If the coordinated ligand deteriorates the symmetry of the central Eu(III) ion site, the  ${}^5D_0 \rightarrow {}^7F_2$  transition dominates other transitions. The luminescence of the lanthanide(III) ion is sensitized by an intramolecular energy transfer from a ligand, whose quantum yield depends on the relative energy levels of the excited lanthanide(III) ions to that of the lowest triplet state energy level of a ligand as well as the coordination structure between them. The comparison of a luminescence sensitization by various ligands provides information about the chemical interaction between a radionuclide and a ligand functional group at a very low concentration.

In this study, the luminescences of Eu(III) and Tb(III) sensitized by pyridine-2,6-dicarboxylate (PDA) and phthalate at 1:1 species were measured and the result is explained by the differences in a coordination structure and the relative energy levels.

### 2. Experimental

Ligand (PDA or phthalate) concentration was fixed at 0.1 mM in a 20 mM ( $\text{NaClO}_4$ ) ionic strength. The pH value of 6 was chosen to neglect a hydrolysis or a

ternary hydroxo complex formation of the lanthanide(III) ion. Eu(III) or Tb(III) concentration, where more than 80% of a ligand exists as a complexed species and more than 95% of Eu(III) or Tb(III) exists as a 1:1 species, was decided based on the species distribution calculation by using reported thermodynamic data in a chosen pH and ligand concentration. All the solutions were prepared using deionized water from a Milli-Q system, and handled under a  $\text{N}_2$  or Ar gas environment. The pH of the solutions was adjusted by adding a  $\text{CO}_2$ -free NaOH solution. Eu(III) or Tb(III) ion was excited by an incident light corresponding to 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  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  (10 mM, pH 2) at the same instrumental condition. The measured intensity was converted to the intensity per a complexed ligand by using the calculated species distribution.

### 3. Results and discussion

Luminescence spectra of Eu(III) solutions containing PDA or phthalate are shown in Fig. 1. The emission intensity of the hypersensitive  ${}^5D_0 \rightarrow {}^7F_2$  transition is larger compared to the  ${}^5D_0 \rightarrow {}^7F_1$  transition for both ligand systems. The relative intensity of the  ${}^5D_0 \rightarrow {}^7F_2$  to  ${}^5D_0 \rightarrow {}^7F_1$  transition is much larger for Eu(III)-PDA than for Eu(III)-phthalate, indicating a stronger Eu(III)-ligand interaction in the former than the latter system. The emission peak corresponding to the  ${}^5D_0 \rightarrow {}^7F_2$  transition of the Eu(III)-phthalate system is broader compared to that of Eu(III)-PDA, which is compared by using FWHM values of 7.6 and 4.2 nm for the Eu(III)-phthalate and Eu(III)-PDA, respectively. This indicates that the coordination structure of Eu(III)-carboxylate in the phthalate system has a higher freedom, and lower order and rigidity than that in the PDA system. This means that an Eu(III) ion is more tightly bound to carboxylates in PDA than that in phthalate, coinciding with the fact that the Eu(III) complexes of PDA are more stable than those of phthalate. This is explained by the difference in the chelate structure between the two ligands systems. In the case of the phthalate ligand, the two oxygen atoms of adjacent carboxylate groups bind to an  $\text{Eu}^{3+}$  ion to form a 7-membered chelate, which is unfavorable for the formation of a stable coplanar chelate ring of two carboxylate groups with a benzene ring due to an angle strain and an interelectronic repulsion between two oxygen atoms. This results in a

90° dihedral angle of a carboxylate plane to the plane of a benzene ring and another carboxylate group. However, in the case of PDA, two oxygen atoms of two carboxylate groups and a nitrogen atom of a pyridine ring are able to coordinate to a  $\text{Eu}^{3+}$  ion in a plane to form very stable two 5-membered chelates.

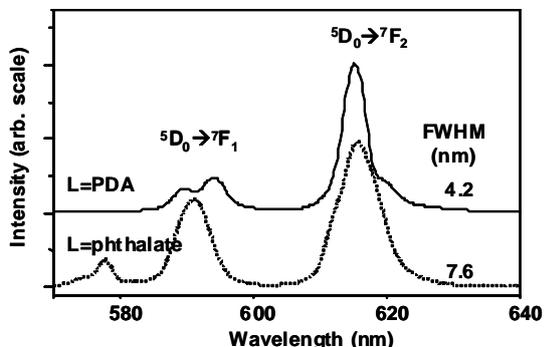


Fig. 1. Luminescence spectra of the Eu-L solutions (L=PDA and phthalate).

For the comparison of a ligand effect on the intramolecular energy transfer, the luminescence intensities of both 1:1 Eu(III)-ligand species were compared. The ratio of the luminescence intensity of the Eu-PDA to that of the Eu-phthalate is larger than their ratio of the extinction coefficient, indicating that the difference in absorbance alone does not explain the luminescence intensity difference. The ligand sensitized luminescence, though it is influenced by the distance of the Eu(III)-ligand and the shielding by a ligand against a quencher, is heavily influenced by the intramolecular energy transfer rate as well as the absorbance. The intramolecular energy transfer rate is expected to be high when the energy level of the lowest triplet state of a ligand is higher than those of a lanthanide (III) ion excited state.

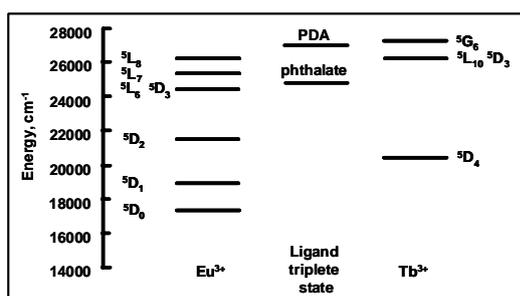


Fig. 2. The lowest triplet states of the ligands and the resonance levels of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ .

The lowest triplet state energy levels of PDA ( $27050 \text{ cm}^{-1}$ ) and phthalate ( $24770 \text{ cm}^{-1}$ ) and the excited state energy levels of Eu(III) and Tb(III) are compared in Fig. 2. Since the energy level distribution of the excited states is different between Eu(III) and Tb(III), the dependency of the energy transfer rate from the lowest triplet state energy levels of the ligands should be different between them. It has been proven by the plotting of a quantum yield for the fluorescence of

Eu(III) and Tb(III) against the triplet state energy levels of various ligands, and an empirical correlation between them has been deduced [2]. In the case of the Eu(III) ion, the quantum yield for PDA (0.1 as a reported value) is larger than that for phthalate (0.03 as an estimated value from the empirical correlation), supplementing the deficiency in the explanation of the luminescence intensity difference based on the absorbance difference alone. However, in the case of the Tb(III) ion, the values of the quantum yield for PDA and phthalate are 0.2 and 0.6, respectively, which is a reversed order in magnitude in a comparison with the case of the Eu(III) ion. The measurement of the intramolecular energy transfer in the Tb(III)-PDA and -phthalate systems is now underway and the result will be presented as experimental proof.

#### 4. Conclusion

We compared the effects of PDA and phthalate ligands on the fluorospectroscopic features of Eu(III) and Tb(III) ions. In the case of the Eu(III) ion, the observation of the peak broadening of the hypersensitive  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition and the relative intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition coincides with a larger stability of the two 5-membered chelate rings of Eu(III)-PDA compared to a 7-membered chelate ring of Eu(III)-phthalate. The higher luminescence intensity of Eu(III)-PDA than that of Eu(III)-phthalate is explained by the absorbance difference of the ligands and the reported empirical correlation between the luminescence quantum yield and the energy level of the lowest triplet state of a ligand. If Eu(III) is replaced by Tb(III), the intensity in the phthalate ligand is expected to be higher than that in the PDA ligand, whose experimental proof will be presented.

#### Acknowledgements

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#### References

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