# Fluorospectroscopic Study on a Ternary Surface Complex of Eu(III) with an Organic Ligand onto an Oxide Surface

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## 1. Introduction

The interaction of ligand with radionuclides in a groundwater affects their migration in a hydrogeological system by influencing the dissolution and sorption characteristics. Thus, an understanding of this nanochemistry in a groundwater condition[1] is necessary in the calculation of a radiological safety for the disposal of radioactive waste. Although many papers investigating actinides sorption onto various oxide surfaces in the presence of an organic ligand have been reported, the role of an organic ligand on the nanochemical behaviors of actinide on a mineral surface is not fully understood yet.

For the quantitative explanation of a metal ion sorption onto metal oxides, a surface complexation model has been reported[2]. When a ligand takes part in a sorption reaction, one of two surface complex types can be formed as follows,

$$\equiv\text{S-OH} + \text{ML} \rightleftharpoons \equiv\text{S-O-M-L} + \text{H}^+,$$

$$\equiv\text{S-OH} + \text{ML} \rightleftharpoons \equiv\text{S-L-M} + \text{OH}^-.$$

The symbol in the first equation, ≡S-O-M-L, represents a type A ternary surface complex, where L is usually an inorganic ligand or sometimes an organic ligand. The symbol in the second equation, ≡S-L-M, means a type B ternary surface complex, where ≡S and L is a Lewis acid site and a polydentate ligand, respectively.

Humate forms a ternary complex in an aqueous solution and a ternary surface complex on an oxide surface with Am(III) or Eu(III)[3-5]. A precise understanding of this ternary surface complex formation is difficult due to the chemical complexity of humate. Ternary surface complex formation of humate with Eu(III) on a montmorillonite surface was proposed based on a sorption study using a chemically simple poly-acrylate or poly-methacrylate as an analogue to humate[6]. Although salicylate is a chemically simple molecule and considered as a good analogue to humate, a poor dissociation of phenolic hydroxide constrains the experiment in the alkaline pH range where a hydrolysis dominates over the surface complex formation of actinides. Other aromatic ligands forming a stable complex in an acidic range are required for the study of a ligand effect on an actinide sorption.

In this study, we show that a metal ion reacting with hydroxide is sorbed well onto an oxide surface. Since pyridine-2,6-dicarboxylate (PDA) and phthalate form electrically neutral ternary hydroxo complexes with Eu(III), it is expected that the complexes including these ligands, {Eu(III)-L}$^+$, will react well with a surface hydroxide instead of an aqueous hydroxide ion to form a ternary surface complex as expressed in the first reaction. The effect of picolinate is compared to both ligands; the similar coordination mode to PDA and the comparable stability of the Eu(III) complex to phthalate. To convince the ligand effect, we have performed a fluorospectrocopic measurement for Eu(III) ion species formed on a $Al_2O_3$(rhombohedral) or $SiO_2$(amorphous) surface in the presence of these three different organic ligands.

## 2. Experimental

The experiments were done in the pH range of 5 to 10 at a 0.1 M ($NaClO_4$) ionic strength and 25 $^oC$. The concentrations of Eu(III) and oxide were 0.1 mM and 20 g/L, respectively. The concentration of PDA, phthalate and picolinate were 0.1, 0.3 and 0.4 mM, respectively. The solution was allowed to equilibrate for more than 30 minutes when the pH change of the solution was negligible after an addition of NaOH for a pH adjustment. An appropriate amount of the solution was taken off and filtrated, and the concentrations of Eu(III) and ligand at an aqueous phase were determined by ICP-AES(ULTIMA2C, Jobin Yvon) and an UV-Visible absorption spectrophotometer(Cary 3, Varian), respectively. An appropriate amount of the solution was transferred to a triangular cell, and the fluorescence spectra of Eu(III) on a sedimented oxide layer was measured(FS900CD, Edinburgh).

## 3. Results and discussion

*3.1. Ligand effect on a Eu(III) sorption.* The effect of a ligand on the sorption of Eu(III) at various pHs was dependent on the kind of ligand and oxide. In the case of PDA, the ligand reduced the sorption onto $SiO_2$ by a soluble complex formation, while it showed no observable effect for $Al_2O_3$. The PDA was not sorbed onto $SiO_2$ while it was sorbed onto $Al_2O_3$. This could be explained by a ternary surface complex formation or by a precipitation of a ternary hydroxo complex.

In the case of phthalate, the ligand had no observable effect on a Eu(III) sorption onto $SiO_2$ while it slightly enhanced the sorption onto $Al_2O_3$. The phthalate was not sorbed onto $SiO_2$ while it was sorbed onto $Al_2O_3$ with a maximum sorption around pH 7.8. The enhancement could not be explained by the precipitation of a ternary hydroxo complex since the pH for the sorption(pH edge=7.0) was lower than that for the precipitation(pH>7.8). Phthalate has two carboxylate groups to form a chelate with a sorbed Eu(III) ion (type A ternary surface complex) or a bridge between a Eu(III) ion and an acidic surface site (type B ternary surface complex). The reduction of a ligand sorption above pH 7.8 could be explained by the competition of phthalate with a hydroxide during a surface species formation.

In the case of picolinate, the ligand had no observable effect on a Eu(III) sorption onto both $SiO_2$ and $Al_2O_3$. Picolinate was sorbed onto $Al_2O_3$ regardless of the Eu(III) ion presence, while it was sorbed onto $SiO_2$ only in the presence of the Eu(III) ion as shown in Fig. 1. It showed a maximum sorption around pH 7.8. Picolinate can not form a precipitate with the Eu(III) ion in the experimental condition and can not afford a bridge between a Eu(III) ion and an acidic surface site like as phthalate. This indicates that the Eu(III) ion and the picolinate ligand form a ternary surface complex of type A which competes with a hydrolysis at a pH value above 7.8.

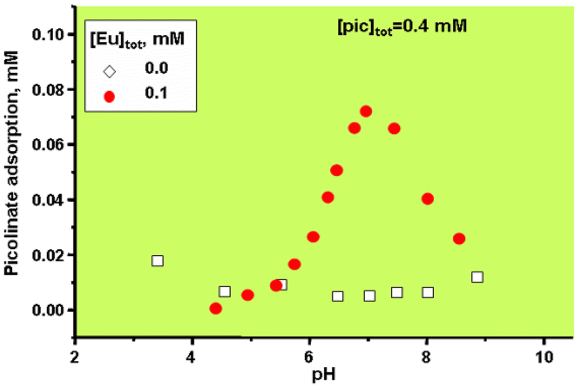

Fig. 1. The sorption of picolinate onto oxide surface in the absence and presence of Eu(III) as a function of pH.

*3.2. Spectroscopic properties of Eu(III) species on an oxide surface*. The fluorescence corresponding to the emission of the Eu(III) ion ($^5D_0 \rightarrow {}^7F_j$, j=0 to 4) in a ligand solution or on an oxide surface was monitored by the excitation of a $\pi$-$\pi$* electronic transition of ligands. For the cases of the PDA-$Al_2O_3$, phthalate-$Al_2O_3$ and picolinate-$SiO_2$ systems, a largely enhanced fluorescence by a intramolecular energy transfer from a ligand to a Eu(III) ion was observed, which supports the chemical bonding between them. The possible species of Eu(III) ion for the energy transfer on the oxide surface are the precipitated ternary hydroxo complex {Eu(OH)L(s), L=PDA or phth) and/or the sorbed ternary surface complex ($\equiv$S-O-M-L or $\equiv$S-L-M). The chemical environments of both the Eu(III) ions in the ternary hydroxo complexes formed on the oxide surface and formed in the aqueous phase are the same. However, it is different from that of the Eu(III) ion in a ternary surface complex, which could be reflected in the fluorescence spectra of Eu(III), especially at the wavelength corresponding to the hypersensitive transition of $^5D_0 \rightarrow {}^7F_2$.

In the case of the PDA-$Al_2O_3$ and phthalate-$Al_2O_3$ systems, since a large background in the fluorescence was caused by the $Al_2O_3$ particle, it was hard to discriminate between a precipitation and a surface complex formation(PDA) or type A and type B of the surface complexes(phthalate) by the fluorescence measurement. However, in the case of the picolinate-$SiO_2$ system, the pH dependency of the spectral features of the Eu(III) emission corresponding to a hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition showed a difference of the Eu(III) environment between the species in the solution and on the $SiO_2$ surface as shown in Fig. 2. The splitting of the peak for the species on the surface indicates a reduced symmetry by a simultaneous coordination with the surface hydroxide and picolinate. The relative intensity ($^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$) of the species on the surface is larger than that in the solution suggesting that the covalency in the coordination of Eu(III) is higher for the species on the surface than those in the solution. These prove the sorption of the Eu(III) ion onto the $SiO_2$ surface by a ternary surface complex formation in the presence of picolinate.

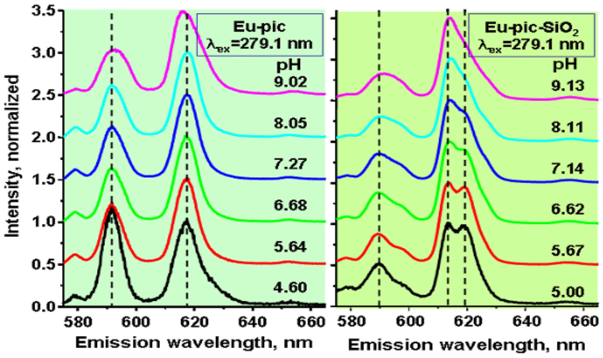

Fig. 2. Fluorescence emission spectra of Eu(III) in solution and on $SiO_2$ surface for picolinate ligand.

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## References

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