Ternary Complex Formation of Eu(III) with Phthalate in Aquatic Solutions

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1. Introduction

Complex formation of radionuclides in a groundwater affects their migration in hydrogeological systems by influencing the dissolution and sorption of them. A number of studies on actinides binary complex formation have been reported. Recently, a ternary complex such as the hydroxocarbonate-actinide complex has attracted considerable attention in the researches on a solubility[1, 2] and a sorption[3, 4]. There is also a possibility to form a ternary complex containing hydroxide or carbonate together with natural organic matter such as humic and fulvic acids since they are ubiquitous in natural aquatic systems. For this reason, the prediction of a radionuclides' migration obtained from a modeling without considering a ternary complex formation may have a large uncertainty when compared to a natural phenomenon. In a previous study, a ternary hydroxo complex formation was investigated by using pyridine-2,6-dicarboxylate(PDA) as an organic ligand and Eu(III) as a metal ion[5]. Especially, in the case where a ternary complex formation leads to a precipitation of the Eu(III) ion, the confirmation was done in the following manner: 1) potentiometric titration shows that the pH of the precipitation starts at a lower pH for the Eu(III)-ligand than for the Eu(III) ion alone, 2) appearance of an Eu(III) emission by a ligand excitation due to an energy transfer from a ligand to the Eu(III) ion, 3) analysis of the concentration of the Eu(III) and the ligand in the precipitate. In this study, a ternary hydroxo complex formation of Eu(III) with phthalate was investigated and the result was compared with that of a PDA.

2. Experimental

The experiments were done in the pH range of 7 to 10 at a 0.1 M (NaClO$_4$) ionic strength and 25 ^{o}C. The concentrations of Eu(III) and phthalate were 0.1 and 0 to 0.15 mM, respectively. To adjust the pH of the solution, a carbonate free NaOH solution was added to a Eu(III)-L (L=phthalate) solution by using a titrator under an Ar gas flow. The solution was allowed to equilibrate for more than 30 minutes when the pH change of solution was negligible after an addition of NaOH. An appropriate amount of the solution was taken off and filtrated by using a filter with a pore size of 0.1 μm, and the concentrations of Eu(III) and phthalate at an aqueous phase were determined by ICP-AES(ULTIMA2C, Jobin Yvon) and an UV-Visible

absorption spectrophotometry(Cary 3, Varian), respectively. The phthalate was determined from a measurement of the absorbance at 273 nm under the conditions of pH 8(Tris buffer) and 10 mM EDTA as a masking agent of the Eu(III). The concentration of Eu(III) and phthalate removed by a precipitation was calculated by subtracting the concentration determined at an aqueous phase from the initial concentration. To confirm the formation of the Eu(III)-L bond in precipitated species, the fluorescence emission of Eu(III) was monitored at 616 nm corresponding to the f-f transition of Eu(III) by using the excitation wavelength(280 nm) of the phthalate π-π* electronic transition.

3. Results and discussion

3.1. Potentiometric titration. The pH curves obtained from the potentiometric titration of the Eu(III)-L solutions([L]$_{tot}$/[Eu]$_{tot}$ = 0, 1, 2, 5) are shown as a function of the amount of added NaOH in Fig. 1. In the absence of phthalate, the Eu(III) precipitation started at about pH 8 and NaOH was continuously consumed until [OH]$_{add}$/[Eu]$_{tot}$ reached 3, indicating Eu(OH)$_3$(s) formed. In the presence of phthalate, however, the Eu(III) precipitation started at a slightly lower pH than 8, suggesting that another Eu(III) precipitate is formed. This was observed in the presence of a ligand, even at [L]$_{tot}$/[Eu]$_{tot}$ = 5. These observations seem to provide a possibility that a ternary hydroxo compex(Eu-OH-L) is formed as a Eu(III)-precipitate.
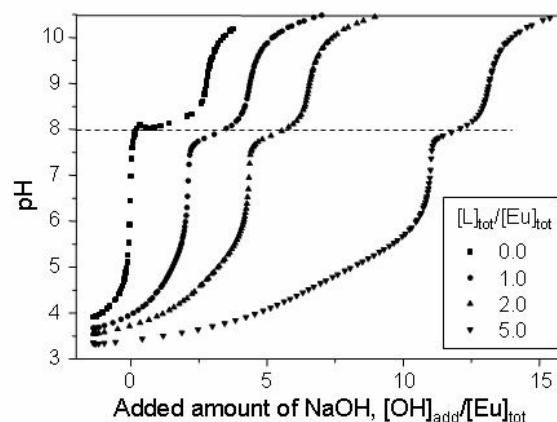

Fig. 1. The pH curves from the potentiometric titration of the Eu(III)-phthalate solutions as a function of the added amount of NaOH.

3.2. Confirmation of a ternary complex{Eu(III)-OH-L} by an Eu(III) excitation spectra. Since Eu(III) ions are not excited by the excitation at 280 nm which is an absorption wavelength corresponding to the π-π* electronic transition of phthalate, an appearance of an Eu(III) emission by a 280 nm-excitation indicates an intramolecular energy transfer from a ligand to Eu(III). The fluorescence intensity was monitored at a 616 nm-emission of Eu(III)($^5D_0 \rightarrow {}^7F_2$) by using a 280 nm-excitation. Fluorescence excitation spectra for Eu(III)-L solutions with various phthalate concentrations were measured at pH 7(no precipitation observed) and pH 8.5(precipitation observed), respectively and are shown in Fig. 2, together with the spectra for the solutions of pH 8.5 with the precipitates removed. The appearance of a maximum peak at 280 nm indicates that the species with a Eu(III)-L bond are formed. The removal of the precipitates caused the intensity to decrease, showing that the precipitate contained species with a Eu(III)-L bond and probably {EuOHL}^{0}(s).
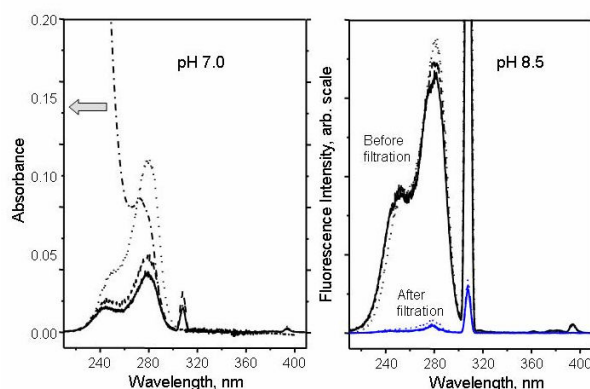

Fig. 2. Fluorescence excitation spectra of the Eu(III)-phthalate solutions with various phthalate concentrations. $[L]_{tot}/[Eu]_{tot}$=1.00(solid), 1.25(dash), 3.00(dot) and 1.00 for absorbance(dash-dot). λ_{em} = 616 nm.

3.3. Analysis of the Eu(III) precipitates. The concentrations of Eu(III) and phthalate in the precipitate at various initial phthalate concentrations are plotted against the pH in Fig. 3. The concentration of phthalate was lower than that of Eu(III) over all the pH range investigated, showing that the Eu(III) precipitates consist of not a unique EuOHL(s) but a mixture of EuOHL(s) and Eu(OH)$_3$(s).

3.4. Solubility product of Eu(III)-OH-L. The solubility products(K_{sp}) of EuOHL(s) and Eu(OH)$_3$(s) were calculated from the following equations,

$$Eu^{3+}+L^{2-}+OH^- \leftrightarrows EuOHL(s), \quad K_{sp}=[Eu^{3+}][L^{2-}][OH^-] \quad (1)$$
$$Eu^{3+}+3OH^- \leftrightarrows Eu(OH)_3(s), \quad K_{sp}=[Eu^{3+}][OH^-]^3 \quad (2).$$

The concentrations of free Eu^{3+} ion and phthalate(L^{2-}) were calculated by considering all the soluble Eu(III) and ligand species and using the reported formation constants[6, 7]. The values of pK_{sp}^0 for EuOHL(s) obtained from various phthalate concentrations was
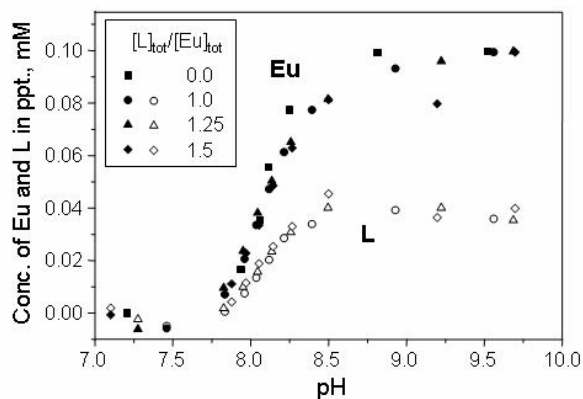

Fig. 3. The concentrations of Eu(III) and L in the precipitate at various ligand concentrations as a function of the pH.

15.9±0.6. In a previous study[5], in the case of PDA, the values of pK_{sp}^0 for EuOHL(s) was 19.2±0.2. Compared to phthalate, PDA forms a more stable ternary hydroxo complex since PDA has a nitrogen atom with a non-bonding electron pair and coordinates Eu(III) as a tridentate. Both PDA and phthalate have two negatively charged –COO$^-$ groups when they are completely dissociated, their ternary hydroxo complexes of {EuOHL}^{0} are electrically neutral and easily precipitated. This result would provide useful information to investigate the chemical reaction of natural organic matter with actinides in groundwater.

References

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