

Energy Transfer between U(VI) and Eu(III) Ions Adsorbed on a Silica Surface

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1. Introduction

Understanding of chemical behavior of actinide in a groundwater flow is important for assessing the possibility of their migration with water flows in a radioactive waste disposal site. Uranium is ubiquitous in the environment and a major actinide in a nuclear fuel cycle. Americium and curium having isotopes of long half life are minor actinides in a spent fuel. If a minor actinide coexists with uranium in a groundwater flow, some interactions between them could be expected such as minor actinide adsorption onto uranium precipitates and competition with each other for an adsorption to a mineral surface site. Eu(III) ion is frequently used as a chemical analogue of Am(III) and Cm(III) ions in a migration chemistry. The luminescent spectra of U(VI) and Eu(III) ions show a dependency on the coordination symmetry around them, and the changes in intensity or bandwidth of spectra can yield valuable informations on their local environment. The luminescent lifetime also strongly depends on the coordination environment, and its measurement is valuable in probe studies on micro-heterogeneous systems. The excited U(VI) ion can be quenched through Stern–Volmer process, hydrolysis of excited species, exciplex formation, electron transfer or energy transfer [1]. In case of U(VI)-Eu(III) system, the interaction between two ions can be studied by measuring the effect of Eu(III) ion on the quenching of U(VI) ion luminescence. There are only a few investigations on the interaction between an excited U(VI) ion and a lanthanide(III) ion. In perchlorate solution, the energy transfer to Eu(III) ion occurred only in solutions of $\text{pH} > 3.87$ [2]. In this study, the quenching of U(VI) luminescence by Eu(III) on a silica surface was measured. The results will be discussed on the basis of a chemical interaction between them.

2. Experimental

UO_2^{2+} and Eu^{3+} in $\text{HClO}_4\text{-NaClO}_4$ (0.1 M) solution was adsorbed onto a silica surface (amorphous, specific surface area=375 m^2/g , 8.3 g/L) by increasing pH with CO_2 free NaOH at room temperature in a nitrogen atmosphere. The concentration of Eu(III) was increased from 1 to 100 $\mu\text{mol/g}$ at a constant U(VI) concentration of 10 $\mu\text{mol/g}$. After equilibration for 24 h, the phase was separated by centrifugation (15,000 rpm, 30 min, Centrikon T-2060, Kontron) and the pH of supernatant was measured to be 7.01 ± 0.10 . At this adsorption condition, U(VI) and Eu(III) ions were quantitatively adsorbed. The aqueous silica phase was transferred to a optical quartz cell and the emission spectra and lifetime

were measured using TRLFS (constructed in laboratory and described in the previous work [3]). The excitation wavelength was 355 nm, and the emission wavelength for lifetime measurement were 505 and 695 nm for U(VI) and Eu(III) ions, respectively.

3. Results and discussion

3.1. Luminescent spectroscopy. Fig. 1 shows representative luminescent spectra of U(VI) on a silica surface adsorbed together with various amount of Eu(III). Eu(III) ion adsorbed alone on a silica surface emitted luminescence of negligible intensity at the excitation wavelength. However, Eu(III) adsorbed together with U(VI) showed its luminescent spectra with enhanced intensity together with that of U(VI). Though the adsorbed amount of U(VI) was constant, the luminescent intensity of U(VI) decreased while that of Eu(III) increased as the adsorbed Eu(III) amount increased. This intensity change is the result of energy transfer from excited U(VI) to Eu(III). The same energy transfer in perchlorate solution is explained by the intramolecular interaction mechanism in a heteropolynuclear complex [2]. The energy transfer on a silica surface could be understood as the chemical interaction between U(VI) and Eu(III) on the analogy of the energy transfer mechanism in solution.

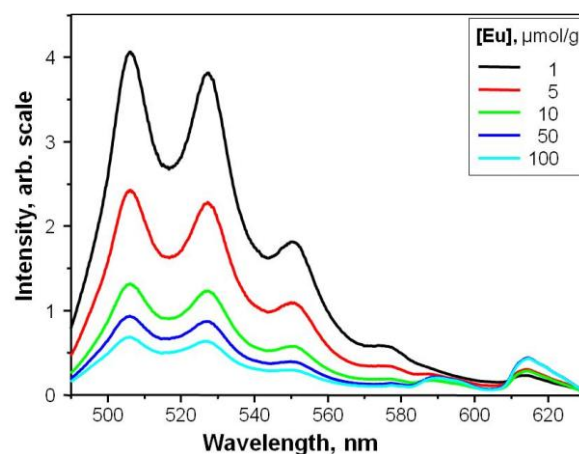


Fig. 1. The emission spectra of U(VI)-Eu(III) on SiO_2 surface at various europium concentration. $[\text{Eu(III)}]_{\text{tot}}=1$ to 100 $\mu\text{mol/g}$, $[\text{U(VI)}]_{\text{tot}}=10$ $\mu\text{mol/g}$, $\text{pH}=7.01 \pm 0.10$.

Since the adsorbed amount of U(VI) was constant, the U(VI) emission intensity at 505 nm were normalized and the spectra measured at various Eu(III) amount were compared. There was no change in spectrum shape except in Eu(III) emission intensity, which is shown at Fig. 2. The increase of intensity

against Eu(III) amount showed a reflection point at about 10 $\mu\text{mol/g}$ which is equal to that of U(VI), suggesting a change in chemical interaction between U(VI) and Eu(III) by the increase of Eu(III) amount. The change of interaction was also supported by the result of Stern-Volmer equation application to the U(VI) emission intensity at 505 nm $\{I_0/I = 1 + K[\text{Eu(III)}]\}$. Here, I_0 and I are U(VI) emission intensities in the absence and presence of Eu(III), respectively, and K is a constant corresponding to the product of a quenching rate constant and lifetime of excited state of U(VI). The intensity ratio I_0/I against Eu(III) concentration $[\text{Eu(III)}]$ showed two linear relationships of steeper and slower slopes before and after the 10 $\mu\text{mol/g}$ concentration value, respectively. The linearity indicates that the energy is transferred at the state of chemical bonding between U(VI) and Eu(III). And, the slope change suggests that the bonding is affected by the concentration ratio of Eu(III) to U(VI).

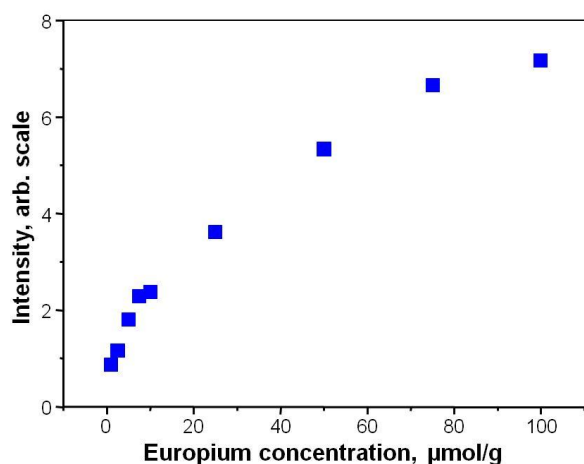


Fig. 2. The emission intensities of Eu(III) corresponding to the transitions of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (613 nm) at various Eu(III) concentrations. $[\text{U(VI)}]_{\text{tot}} = 10 \mu\text{mol/g}$.

3.2. Luminescent lifetime. Luminescent lifetime of a metal ion yields good information on the coordination environment. U(VI) adsorbed alone on a silica surface showed a luminescent lifetime of about 325 μs , which decreased to 120 μs when coadsorbed Eu(III) concentration was smaller than U(VI) concentration. This indicates that the excited U(VI) was quenched due to an energy transfer to Eu(III). The measured luminescent lifetime of Eu(III) also depended on its concentration; about 320 μs when its amount is much less than that of U(VI) while about 215 μs when more than that of U(VI). In case of U(VI) luminescence, since both water molecules coordinated in an inner- and outer-sphere affect the nonradiative decay of excited U(VI), the deduction of coordination environment change from the measured lifetime is not easy. In case of Eu(III), however, only water molecule in an inner-sphere affects that of excited Eu(III) and the measured lifetime may yield a clue to the calculation of hydration number and to the understanding of change in inner-

sphere coordination environment. The hydration number was calculated by using the measured decay constant [4]. It decreased from 2-3 to 4-5 with increasing Eu(III) concentration. It suggests that the interaction between U(VI) and Eu(III) was weakened and the coordination of water to Eu(III) increased with increasing Eu(III) concentration.

4. Summary

The chemical interaction between U(VI) and Eu(III) ions on a silica surface was proved by the observation of an energy transfer from excited U(VI) to Eu(III), which results in a quenching of U(VI) luminescence and an enhancement of Eu(III) luminescence. The result of Stern-Volmer equation application suggests that the energy is transferred at the state of chemical bonding between U(VI) and Eu(III) which is affected by the concentration ratio of Eu(III) to U(VI). The quenching effect of Eu(III) decreased the luminescent lifetime of U(VI). The luminescent lifetime of Eu(III) was also decreased by an increased Eu(III) concentration, supporting that the chemical interaction type of U(VI)-Eu(III) on a silica surface depends on the Eu(III) concentration.

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