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Speciation of Europium(III) Sorbed on a Montmorillonite Surface in the Presence of Polycarboxylic Acid by Laser-Induced Fluorescence Spectroscopy

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Laser-induced fluorescence spectroscopy was applied for the characterization of Eu(III) species sorbed on organic–inorganic hybrids such as montmorillonite coated with poly(acrylic acid) or poly(methacrylic acid) in aqueous solution (suspension). The emission lifetime and the emission spectra of Eu(III) sorbed on the organic–inorganic hybrid indicated that Eu(III) can be sorbed as an Eu(III)–polycarboxylate complex on montmorillonite. The stabilities of the Eu(III)–polycarboxylate complex and inorganic Eu(III) species sorbed on montmorillonite control the species of Eu(III), i.e., organic or inorganic, sorbed on the organic–inorganic hybrid. It was suggested that Eu(III) can be sorbed as a humate complex when an Eu(III) ion is contacted with an organic–inorganic hybrid, such as a humic acid–clay mineral hybrid, in a natural aquifer.

Introduction

The environmental behavior of actinide elements has aroused much concern in terms of radioactive waste disposal (1). Among the actinide elements, trivalent actinides of ²⁴¹Am and ²⁴⁴Cm are major long-lived radionuclides in waste (1). To assess their behavior, speciation of actinide(III) in a natural aquifer is of paramount importance (2). In this study, we will focus on the identification of the sorbed species of Eu(III), which is an analogue of actinide(III), on the montmorillonite surface, since the chemical state of actinide(III) or Eu(III) sorbed on natural particulate matter has not been fully clarified yet. For particulate matter, clay minerals play important roles in the migration of Eu(III) (3). However, in the environment, the surface of such inorganic particles is often coated with humic substances, due to the very strong affinity between humic acid and clay mineral (4, 5). Therefore,

it is of great interest to clarify the Eu(III) species sorbed on montmorillonite in the presence of humic substances or polyorganic acid. It is, of course, possible that the Eu(III) species remains the same as the inorganic species sorbed on “neat” clay minerals (i.e., clay minerals not coated with polyorganic acid), regardless of the addition of polyorganic acids. On the other hand, it is also probable that Eu(III) ions are sorbed as organic complexes with polyorganic acid, since such organic substances can form stable complexes with Eu(III) or actinides(III) in the environment (3, 6–8). The third possibility is that the ternary complexes of polyorganic acid–Eu(III)–montmorillonite may form; both polyorganic acid and montmorillonite may influence the chemical environment of Eu(III) in the ternary complex. In this study, we will deal with the Eu(III) species sorbed on montmorillonite in the presence of polyorganic acid, which may provide important information on the reaction of metal ions with the organic–inorganic hybrid widely found in natural systems.

Metal ions sorbed on the organic–inorganic hybrid have not been characterized structurally at the molecular level, due to the lack of appropriate analytical methods. In this sense, laser-induced fluorescence spectroscopy (LIF) is a useful technique to deduce information on the chemical environment of Eu(III) as seen from its application to Eu(III) species in water and solid phases and at the solid–water interface (9–15). In being applied to the sorbed species, LIF has a merit in that it can be employed in the presence of an aqueous phase. This means that before the analyses, one does not need to employ dry samples which may cause some changes in the chemical environment of Eu(III). In our recent works, LIF was applied to Eu(III)–PAA and Eu(III)–PMAA hybrids in aqueous solution and Eu(III) sorbed on “neat” montmorillonite (12, 14), which are the two binary systems also examined in the present study. In this work, LIF was applied to Eu(III) species in the ternary system: Eu(III) species sorbed on montmorillonite in the presence of polycarboxylic acids such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA). Following studies employing PAA and PMAA as analogues of humic acid (15–17), PAA and PMAA were used in this study as model substances of humic acid. These two polycarboxylate ligands, which have different affinities with Eu(III) (12), were chosen to examine the influence of the stabilities of Eu(III)–polycarboxylate complexes on the Eu(III) species at the montmorillonite surface in the ternary system. Based on the results using PAA and PMAA and on the stability constants of Eu(III) complexes with PAA, PMAA, and humic acid, the role of humic acid in the sorption of Eu(III) ions on the organic–inorganic hybrid in a natural aquifer is discussed.

Experimental Section

PAA, the mean molecular weight (mean MW) of which is 250 000, was purchased from Aldrich Chemical Co., Inc. PMAA (mean MW: 100 000) was purchased from Polyscience Inc. Montmorillonite was purchased from Nacalai Tesque, Inc. The surface area of montmorillonite was $5.5 \times 10^2 \text{ m}^2/\text{g}$, as determined by the BET method (N_2), and the cation exchange capacity (CEC) was determined by the modified Schofield method (pH 8, NH_4Cl 2.0 mM) as $3.0 \times 10^{-1} \text{ meq/g}$ (18). Cation exchange capacities of PAA and PMAA were determined by pH titration to be 10.8 and 10.5 meq/g, respectively (12).

Suspended solutions of various pH, containing montmorillonite, Eu(III), and polycarboxylic acid (PAA or PMAA),

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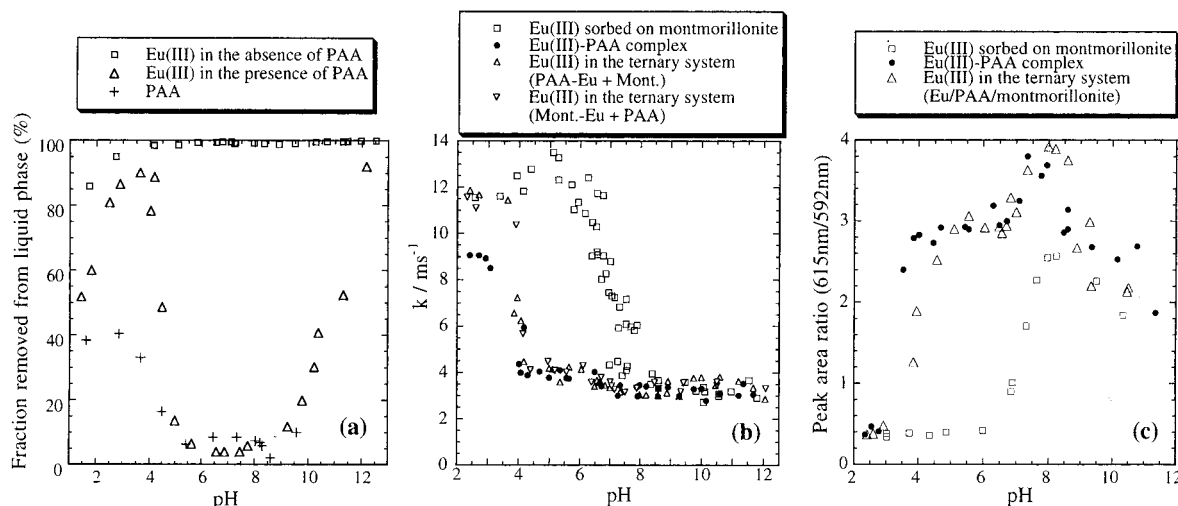


FIGURE 1. (a) Distribution of PAA and Eu(III), (b) k values, and (c) $R_{615/592}$ values for Eu(III) sorbed on montmorillonite, Eu(III)-PAA complex, and Eu(III) in the ternary system (Eu(III)/PAA/montmorillonite system) at various pH. $[PAA]_{\text{total}} = 8.0 \text{ meq/dm}^3$; $C_s = 0.020 \text{ M}$; $[Eu] = 0.20 \text{ mM}$; montmorillonite concentration: 4.0 g/dm^3 . In (a), the percentages of the fractions in the absence and presence of PAA are shown for Eu(III). For PAA, the percentage of PAA fraction in the presence of Eu(III) is shown.

were prepared. The solid/liquid ratio of montmorillonite was fixed at 4.0 g/dm^3 . Concentration of Eu(III) was 0.20 mM , while that of the supporting electrolyte (C_s) was adjusted to 0.020 or 1.0 M by NaClO_4 . Two solutions with various concentrations of PAA ($[PAA]_{\text{total}}: 8.0$ or 1.0 meq/dm^3) were examined, while $[PMAA]_{\text{total}}$ was fixed at 8.0 meq/dm^3 . After being shaken for 2 days, the suspended montmorillonite particles were exposed to laser light at 395 nm emitted from a dye laser (PBBO, Lambda Physik SCANmate2) pumped by a XeCl excimer laser (Lambda Physik, COMPEX201). The fluorescence emitted from Eu(III) at a constant wavelength was measured by a photomultiplier tube (Hamamatsu R3896) with a time-resolved digital oscilloscope (Hewlett-Packard 54510A). In this study, the decay curve of fluorescence at 615 nm ($^5D_0 \rightarrow ^7F_2$) was mainly observed. The emission spectra vs wavelength were also recorded using a multiple photodiode array (DIDA-512, Princeton Instruments, Inc.). In the measurement, the scattering of light was avoided by appropriately timed gate delays (e.g., $10 \mu\text{s}$). The fluorescence decay curves and the emission spectrum were also recorded for Eu(III) in the residual Eu(III) polycarboxylate solution. The decay curves were fitted by an exponential curve to give the decay constant k (ms^{-1}). Relative standard deviation of k was less than 5%.

For the Eu(III)/PAA/montmorillonite system, two series of samples were prepared depending on the order of injection of Eu(III), PAA, and montmorillonite. In the A-series, PAA and Eu(III) were mixed first, and montmorillonite was added later; in the B-series, Eu(III) was mixed with montmorillonite suspension first, and PAA was then added. For the Eu(III)/PMAA/montmorillonite system, only the A-series was prepared.

The partitioning of polycarboxylic acid and Eu(III) between liquid and solid phases was determined by batch experiments. In the experiments, a membrane filter ($0.45 \mu\text{m}$) was used to separate the two phases. The partitioning of polycarboxylic acid was examined by a total organic carbon analyzer, while that of Eu(III) was determined using a Eu(III)-152 radioactive tracer and its radioactivity counted. Total Eu(III) concentration was maintained the same as that of samples for laser experiments by adding stable Eu(III) isotopes. All experiments in this study were conducted at 298 K .

Results and Discussion

Eu(III)/PAA/Montmorillonite System. (A) Partitioning of Eu(III). The partitioning of PAA and Eu(III) between the liquid

phase and the montmorillonite surface was examined at various pH, and the results are shown in Figure 1a. PAA was partly sorbed on montmorillonite at any pH examined, though the percentage of sorbed PAA was less than 10% between pH 5 and 9. The addition of Eu(III) (0.20 mM) did not have any influence on the partitioning of PAA (and PMAA). More than 80% of Eu(III) was removed from the liquid phase above pH 2 in the absence of PAA. In the presence of PAA (ternary system), the amount of Eu(III) dissolved in the liquid phase increased due to the formation of the dissolved Eu(III)-PAA complex. Moreover, it should be noted that the percentages of Eu(III) and PAA removed from the liquid phase were similar between pH 5 and 10. This suggests that Eu(III) exists as an Eu(III)-PAA complex both in the liquid phase and at the montmorillonite surface. Similar results were obtained when humic acid was employed as a polyorganic acid (19, 20). The sorption of these polycarboxylates (PAA and humic acid) on the solid surface takes place through van der Waals forces, hydrogen bonding, and entropic effects (4, 21).

When most Eu(III) is removed from the liquid phase in the presence of PAA, the suspension can be exposed to the laser beam for the purpose of obtaining information on the sorbed Eu(III) species. However, if the amount of Eu(III) removed from the liquid phase is low in the ternary system where PAA can retain a considerable amount of Eu(III) in the liquid phase, one may detect a signal from the dissolved fraction of Eu(III) species in LIF experiments. To exclude the dissolved Eu(III) species in the ternary system in the measurement, the slurry separated from the liquid phase was mixed with a few ml of water having identical pH and C_s to the liquid phase which was previously contacted with the particles. The tube was shaken vigorously and centrifuged again for LIF measurement. During the process, the distribution of Eu(III) between the solid and liquid phases was also monitored. As a result, more than 95% of Eu(III) was sorbed on the solid phase in the slurry separated from the suspension at any pH examined. By this procedure, it was possible to obtain signals from Eu(III) species sorbed on montmorillonite selectively in the ternary system.

(B) LIF Analysis. In this study, the decay constant (k), the emission spectrum, and the ratio of the intensities of emissions at 592 and 615 nm , namely $R_{615/592}$, are employed to characterize Eu(III) species. In Figure 1b, the k values for

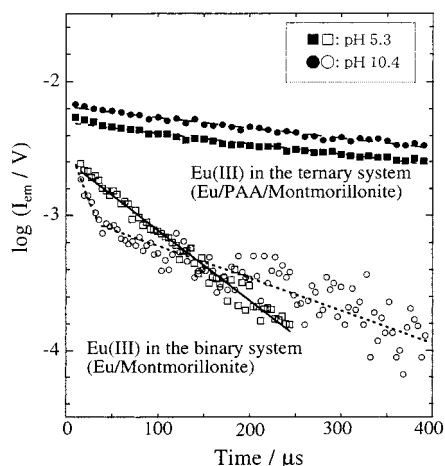


FIGURE 2. Decay curves of Eu(III) fluorescence in the binary (Eu(III)/montmorillonite system) and ternary (Eu(III)/PAA/montmorillonite system) systems at pH 5.3 and 10.4. $[PAA]_{total} = 8.0 \text{ meq/dm}^3$; $C_s = 0.020 \text{ M}$; $[Eu] = 0.20 \text{ mM}$; montmorillonite concentration: 4.0 g/dm^3 .

Eu(III) in the two binary systems (Eu(III)/montmorillonite system and Eu(III)/PAA system) are shown at various pH. The k values are directly related to the number of water molecules in the first coordination sphere of Eu(III), since OH vibration is a powerful quencher for excited Eu(III) (9, 10). In the binary system of Eu(III)/montmorillonite, the k values were approximately $12\text{--}13 \text{ ms}^{-1}$ at pH below 6. Above pH 6, the values decreased with pH. Above pH 8, the k values were $3\text{--}4 \text{ ms}^{-1}$, showing that more than six water molecules are removed from the first coordination sphere of Eu(III) in this pH region (14). Above pH 8, another component having a larger k value is found in the decay curves, in addition to the component shown in Figure 1b (14). Examples of the decay curves are shown in Figure 2. At pH 10.4, for example, two components were clearly observed for the Eu(III) species sorbed on montmorillonite (○), in contrast to the decay curve at pH 5.3 (□). The component having larger k values can be assigned to Eu(III) precipitates ($\text{Eu}(\text{OH})_3$ or $\text{Eu}(\text{OH})\text{CO}_3$) due to the energy transfer among neighboring Eu(III) ions (14). In another binary system of Eu(III)/PAA, the k values decreased around pH 3 due to the formation of a Eu(III)–PAA complex (Figure 1b). As pH increases, the k values gradually decreased with pH, showing that a larger number of carboxylate ligands in PAA were bound to Eu(III) (12, 15, 22).

In the ternary system (Eu(III)/PAA/montmorillonite), the k values shown were around 12 below pH 2 (Figure 1b), which was identical to the results of Eu(III) in the binary system of Eu(III)/montmorillonite. This shows that Eu(III) ions sorbed on the inorganic–organic hybrid mainly interact with the montmorillonite surface in this pH region, even in the presence of PAA on the surface. Between pH 4 and 8, the k values were identical to those of the Eu(III)–PAA complex, showing that Eu(III) is sorbed as a Eu(III)–PAA complex on montmorillonite. It is worthwhile to note that there is a mode of sorption of metal ions on the organic–inorganic hybrid as a metal–polycarboxylate complex, as directly revealed by LIF. The results remain the same even if the order of Eu(III) and PAA injection was changed (Figure 1b); the triangles (Δ) show the results when the aqueous solution containing Eu(III) and PAA was mixed with montmorillonite (A-series), while the upside-down triangles (▽) show the results when PAA solution was injected after the sorption of Eu(III) on montmorillonite (B-series). These results show that the formation of the Eu(III)–PAA complex on montmorillonite surface is not a kinetic phenomenon depending on the order of injection but is due to the higher stability of the Eu(III)–

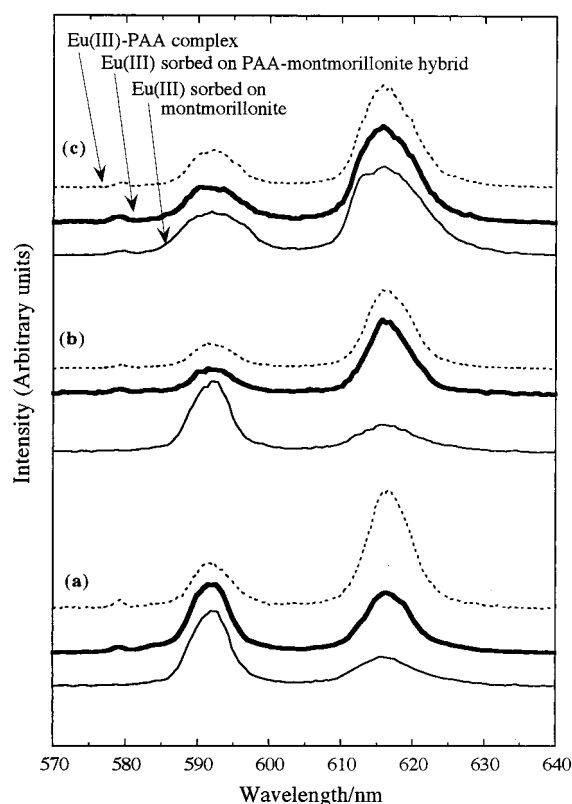


FIGURE 3. Emission spectra of Eu(III) sorbed on montmorillonite, Eu(III)–PAA complex, and Eu(III) in the ternary system (Eu(III)/PAA/montmorillonite system). The experimental conditions are similar to those noted in the caption of Figure 1, while pH is (a) 3.8, (b) 5.1, and (c) 9.6.

PAA complex than that of the inorganic surface complex of Eu(III) with montmorillonite.

The result that Eu(III) is sorbed as a PAA complex on montmorillonite coated with PAA is confirmed by the emission spectra (Figure 3). Because of the apparent difference in the absorption coefficient and the emission of Eu(III) species, which depends on the sample conditions in each measurement, it is not possible to evaluate the absolute intensity normalized to the amount of Eu(III) sorbed on the particles. Therefore, the spectra were plotted as arbitrary units by multiplying appropriate values by raw data to facilitate comparison. In general, two major peaks are observed around 592 ($^5D_0 \rightarrow ^7F_1$) and 615 nm ($^5D_0 \rightarrow ^7F_2$). In addition, an emission at 578 nm ($^5D_0 \rightarrow ^7F_0$) is sometimes observed.

At pH 5.1 (spectrum (b) in Figure 3), the spectrum in the ternary system is almost identical to that of the Eu(III)–PAA complex, while the spectrum is different from that of Eu(III) sorbed on montmorillonite. This indicates that Eu(III) is sorbed as a PAA complex on montmorillonite in the ternary system. However, the similarity between spectra of the ternary and Eu(III)/PAA systems cannot be found at pH 3.8 (spectrum (a) in Figure 3). To clarify the pH dependence of the spectra, the ratio of emission intensities at 615 nm to 592 nm ($R_{615/592}$) was utilized to compare the Eu(III) species at various pH (14, 23). The $R_{615/592}$ values in the ternary system were identical to those in the Eu(III)/PAA system between pH 5 and 8, as shown in Figure 1c, which confirms the results obtained from the k values.

Above pH 8, we cannot distinguish whether Eu(III) is sorbed as organic or inorganic species from measurement of k , since k values in the Eu(III)/montmorillonite and Eu(III)/PAA systems are similar in this pH region. The $R_{615/592}$ values of Eu(III) in the ternary system seem to be similar to

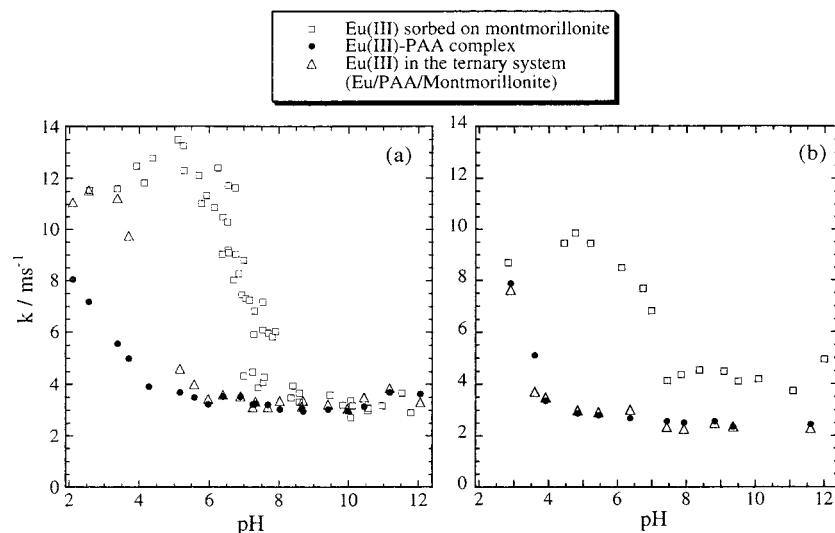


FIGURE 4. The k values for Eu(III) sorbed on montmorillonite, Eu(III)–PAA complex, and Eu(III) in the ternary system (Eu(III)/PAA/montmorillonite system) at various pH. (a) $[PAA]_{\text{total}} = 1.0 \text{ meq/dm}^3$; $C_s = 0.020 \text{ M}$; $[Eu] = 0.20 \text{ mM}$; montmorillonite concentration: 4.0 g/dm^3 . (b) $[PAA]_{\text{total}} = 8.0 \text{ meq/dm}^3$; $C_s = 1.0 \text{ M}$; $[Eu] = 0.20 \text{ mM}$; montmorillonite concentration: 4.0 g/dm^3 .

those of the Eu(III)/PAA system, though the $R_{615/592}$ values above pH 8 are rather scattered. As shown in the spectra at pH 9.6 (spectrum (c) in Figure 3), the emission spectrum of Eu(III) in the ternary system is similar to that of the Eu(III)–PAA complex, while that of Eu(III) sorbed on montmorillonite, broadened to some degree, is somewhat different from the spectrum of the ternary system. In the decay curve of the Eu(III) emission at pH > 8, the appearance of another component having a larger k value due to the formation of Eu(III) precipitates found in the Eu(III)/montmorillonite system was not found in the decay curve of the ternary system (Figure 2). In our previous study, it was shown that the amount of precipitated Eu(III) is larger than that of Eu(III) sorbed on montmorillonite in the absence of PAA (i.e., the Eu(III)/montmorillonite system) (14). Based on these results, it is suggested that complexation with PAA inhibits the formation of Eu(III) precipitates in the system and that Eu(III) is sorbed as a PAA complex on montmorillonite coated with PAA above pH 8.

Between pH 2 and 4, k values in the Eu(III)/PAA/montmorillonite system were intermediate between those in the Eu(III)/PAA system and the Eu(III)/montmorillonite system. This shows that the Eu(III) species detected in this condition is a mixture of inorganic Eu(III) species sorbed on montmorillonite and the Eu(III)–PAA complex. The difference in k values between the inorganic and the organic species is not large enough to reveal the contributions of these two species in the decay curve. Therefore, a single-exponential decay curve was employed to analyze the decay curve; the k values are intermediate for the sorbed Eu(III) species between pH 2 and 4. From the emission spectrum at pH 3.8 (spectrum (a) in Figure 3), we can observe that the spectrum of the ternary system is a mixture of the spectra of the two Eu(III) species: the PAA complex and the species sorbed on montmorillonite. This also confirms that two Eu(III) species, organic and inorganic, are formed in the pH region of 2–4.

In this section, it was shown in our experiments that Eu(III) can be sorbed as a polycarboxylate complex on montmorillonite above pH 4, while the ternary complex suggested in the Introduction could not be detected in the ternary system. The present results imply that Eu(III), or other lanthanide(III) and actinide(III), can be sorbed as polycarboxylate complexes, such as a humate complex, on the organic–inorganic hybrid in a natural aquifer.

(C) Effect of PAA Concentration and C_s . Similar experiments were conducted where $[PAA]_{\text{total}}$ or C_s (supporting electrolyte concentration) was changed (Figure 4). When $[PAA]_{\text{total}}$ was reduced to 1.0 meq/dm^3 (Figure 4a), the pH region where Eu(III) was sorbed as a PAA complex on montmorillonite was above pH 6. The lower pH limit of the pH region, where the k values in Eu(III)/PAA and ternary systems were similar (i.e., Eu(III) exists as the Eu(III)–PAA complex on the surface), increased from pH 4 to pH 6 for the case of $[PAA]_{\text{total}} = 1.0 \text{ meq/dm}^3$ in comparison with that of $[PAA]_{\text{total}} = 8.0 \text{ meq/dm}^3$ shown in Figure 1b. This may be because the contribution of Eu(III)–PAA complex to Eu(III) species is decreased by the decrease in the number of available carboxylate ligands.

The increase in C_s generally reduces the stabilities of the metal–polycarboxylate complex and the sorbed species of metal ions on montmorillonite (24, 25). When C_s was 1.0 M , the k values of the sorbed Eu(III) species in the ternary system were identical to those of the Eu(III)–PAA complex throughout the pH range investigated, as shown in Figure 4b. Although the stability constant of the Eu(III)–PAA complex decreases with an increase in C_s (12), the present results indicate that the increase in C_s has a larger influence on the sorption of metal ions by montmorillonite; the supporting cation added inhibits more strongly the sorption of Eu(III) by montmorillonite.

Eu(III)/PMAA/Montmorillonite System. The results when PMAA was employed as the polycarboxylic acid are shown in Figure 5. The partitioning of PMAA and Eu(III) in the ternary system (Figure 5a) seems to be similar to those in the Eu(III)/PAA/montmorillonite system (Figure 1a). The k values of the Eu(III)/PMAA/montmorillonite system are shown in Figure 5b. The results are rather different from those of the Eu(III)/PAA/montmorillonite system (Figure 1b). The k values of the Eu(III)/PMAA/montmorillonite system were not identical to those of the Eu(III)–PMAA complex even between pH 4 and 7, while the k values of the Eu(III)/PAA/montmorillonite system in that pH region agreed with those of the Eu(III)/PAA system (Figure 1b). The $R_{615/592}$ values (Figure 5c) show that all of the Eu(III) ions were not sorbed on the particles as Eu(III)–PMAA complex, since $R_{615/592}$ values in the ternary system were discrepant from those of the Eu(III)/PMAA system. The k and $R_{615/592}$ values of the Eu(III)/PMAA/montmorillonite system were between the values of the Eu(III)/montmorillonite system and the Eu(III)/PMAA

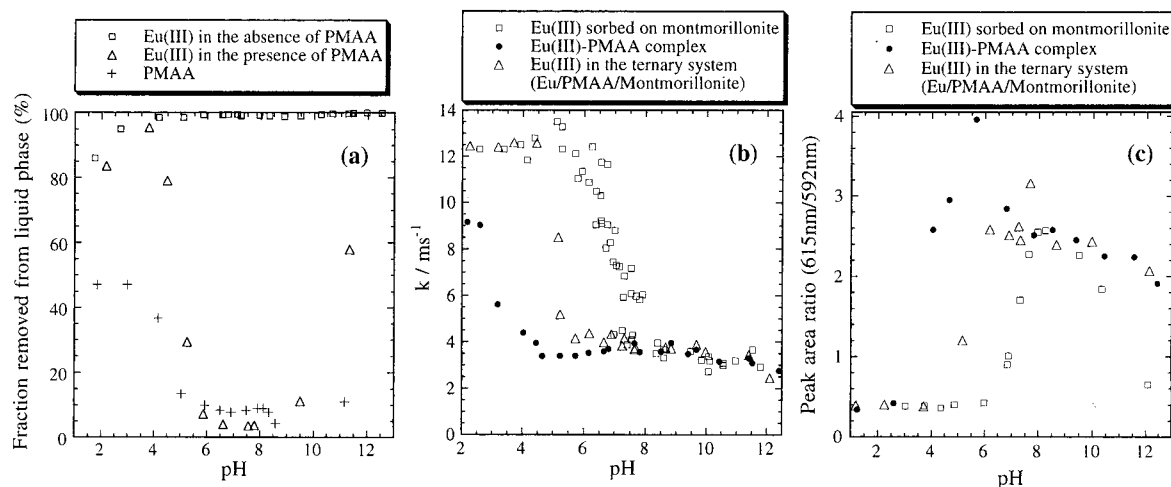


FIGURE 5. (a) Distribution of PMAA and Eu(III), (b) k values, and (c) $R_{615/592}$ values for Eu(III) sorbed on montmorillonite, Eu(III)-PMAA complex, and Eu(III) in the ternary system (Eu(III)/PMAA/montmorillonite system) at various pH. [PMAA]_{total} = 8.0 meq/dm³; C_s = 0.020 M; [Eu] = 0.20 mM; montmorillonite concentration: 4.0 g/dm³.

system between pH 4 and 7. Above pH 7, k and $R_{615/592}$ values of the ternary system were identical to those of the Eu(III)-PMAA system, revealing that Eu(III) is sorbed as a Eu(III)-PMAA complex on montmorillonite. In general, the stability of the metal-polycarboxylate complex increases with pH, which leads to the increase in the number of Eu(III)-PMAA complexes among Eu(III) species apparently sorbed on montmorillonite.

Evaluation of Eu(III) Species from Their Stabilities. The considerable contribution of inorganic Eu(III) species sorbed on montmorillonite in the Eu(III)/PMAA/montmorillonite system, compared to that in the Eu(III)/PAA/montmorillonite system, may be due to the lower stability of the Eu(III) complex with PMAA than with PAA. Logarithms of the stability constant, $\log\{\beta/(\text{eq}^{-1} \text{dm}^3)\}$, of Eu(III) with PAA or PMAA were determined previously (12). The definition of β is as follows

$$\beta = [\text{RCOO-Eu(III)}]/([\text{Eu(III)}][\text{RCOO}^-])$$

where $[\text{RCOO}^-]$ is expressed as the equivalent concentration (eq/dm^3) of carboxylate groups in PAA or PMAA, as determined by pH titration. In previous studies, $\log\{\beta/(\text{eq}^{-1} \text{dm}^3)\}$ was determined at $C_s = 0.020$ M to be 5.8 ± 0.1 for the Eu(III)-PMAA complex and 6.9 ± 0.1 for the Eu(III)-PAA complex at pH 4.8 (12, 26). This indicates that the stability of the Eu(III) complex with PAA is higher than that with PMAA. The difference in the stability is considered to be crucial in determining whether Eu(III) can be sorbed as a polycarboxylate complex on montmorillonite. From the partition experiments, 0.57% of Eu(III) was dissolved in the Eu(III)/montmorillonite system at pH 4.8 when the solid/liquid ratio (R_{s-1}) was 4.0 g/dm³ and C_s was 0.020 M. Since neither carbonate nor hydroxide complex of Eu(III) is formed in the liquid phase at this pH, the distribution coefficient, K_d (dm^3/g), can be obtained as

$$K_d (\text{dm}^3/\text{g}) = [\text{Eu}]_{\text{mon}}/[\text{Eu}]_{\text{aq}}/R_{s-1} = (100-0.57)/0.57/4.0 = 44$$

where $[\text{Eu}]_{\text{mon}}$ and $[\text{Eu}]_{\text{aq}}$ show the concentrations of Eu(III) sorbed on montmorillonite and free Eu(III) ion dissolved in the liquid phase, respectively. Employing $\log\{\beta/(\text{eq}^{-1} \text{dm}^3)\}$ and K_d , the relative stabilities of the Eu(III)-PAA or the Eu(III)-PMAA complex and the inorganic Eu(III) species sorbed on montmorillonite can be compared, though $\log\{\beta/(\text{eq}^{-1} \text{dm}^3)\}$ is determined for Eu(III) species in the aqueous phase. For the ternary system examined in LIF experiments

at pH 4.8, the following ratios are obtained

$$[\text{Eu}]_{\text{mon}}/[\text{Eu}]_{\text{aq}} = 1.8 \times 10^2$$

$$[\text{Eu-PAA}]/[\text{Eu}]_{\text{aq}} = \beta(\text{Eu-PAA}) \times [\text{PAA}]_{\text{total}} \times \alpha(\text{PAA}) = 1.7 \times 10^4$$

$$[\text{Eu-PMAA}]/[\text{Eu}]_{\text{aq}} = \beta(\text{Eu-PMAA}) \times [\text{PMAA}]_{\text{total}} \times \alpha(\text{PMAA}) = 6.1 \times 10^2$$

where $\alpha(\text{PAA})$ and $\alpha(\text{PMAA})$ are the degrees of ionization of PAA and PMAA, respectively; $[\text{PAA}]_{\text{total}}$ and $[\text{PMAA}]_{\text{total}}$ are $8.0 \times 10^{-3} \text{ eq/dm}^3$; and $\alpha(\text{PAA})$ and $\alpha(\text{PMAA})$ are 0.12 and 0.27, respectively, as determined by pH titration at pH 4.8 (12). These results show that the stabilities of the Eu(III)-PMAA complex and the inorganic Eu(III) species sorbed on montmorillonite are comparable, while the Eu(III)-PAA complex is much more stable. This implies that the difference in the stability of each species determines the major fraction of Eu(III) sorbed on montmorillonite, as already suggested from LIF results. It should be noted that the stability constant determined for the species in the aqueous phase is possibly applicable to estimate the sorbed species at the solid-water interface.

Based on the above results, the contribution of humate complex as sorbed species can be also estimated. At pH 4.8 and $C_s = 0.020$ M, $\alpha(\text{humic acid})$ and $\log\{\beta/(\text{eq}^{-1} \text{dm}^3)\}$ of Eu(III)-humate are 0.56 and 9.5, respectively (8). If the total concentration of humic acid $[\text{HA}]_{\text{total}}$ is fixed at $8.0 \times 10^{-3} \text{ eq/dm}^3$, the ratio of $[\text{Eu-humate}]/[\text{Eu}]_{\text{aq}}$ is

$$[\text{Eu-humate}]/[\text{Eu}]_{\text{aq}} = \beta(\text{Eu-humate}) \times [\text{HA}]_{\text{total}} \times \alpha(\text{humic acid}) = 1.4 \times 10^7$$

which is far above the ratios for $[\text{Eu}]_{\text{mon}}/[\text{Eu}]_{\text{aq}}$, $[\text{Eu-PAA}]/[\text{Eu}]_{\text{aq}}$, and $[\text{Eu-PMAA}]/[\text{Eu}]_{\text{aq}}$ under the same conditions as those determined above. This shows that the humate complex may be important as sorbed species on the humic acid-montmorillonite hybrid, which had been estimated from previous partition studies (19, 20). If we set the conditions as $[\text{HA}] = 5.0 \times 10^{-5} \text{ eq/dm}^3$ (or 10 mg/dm³ as dissolved organic carbon) and $R_{s-1} = 10 \text{ g/dm}^3$ (concentration of suspended particulate matter), which can be found in river water (2), $[\text{Eu-humate}]/[\text{Eu}]_{\text{aq}}$ ($= 8.8 \times 10^4$) is still larger than $[\text{Eu}]_{\text{mon}}/[\text{Eu}]_{\text{aq}}$ ($= 4.5 \times 10^2$). These results suggest that Eu(III) can be sorbed on particulate matter as a humate complex in a natural aquifer, since humic acid forms a stable

complex with metal ions and a stable organic–inorganic hybrid with particulate matter such as clay minerals and iron oxides (4, 5, 27).

In summary, this study shows that Eu(III) can be sorbed as a polycarboxylate complex on montmorillonite, different from inorganic species directly sorbed on the montmorillonite surface, by laser-induced fluorescence spectroscopy. By comparing the stability constants of Eu(III) complexes with those of synthetic polycarboxylic acid (PAA and PMAA) and humic acid, it is estimated that Eu(III) can exist as a humate complex when sorbed on an organic–inorganic hybrid in a natural aquifer. These results show that humic acid has a considerable effect on the fixation of Eu(III), or of other lanthanide(III) and actinide(III), on solid and colloidal surfaces in a natural aquifer.

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