

Adsorption of europium(III) and americium(III) on kaolinite and montmorillonite in the presence of humic acid

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Distribution of trace amount of Eu(III), or Am(III), in the aqueous/solid system containing humic acid and kaolinite, or montmorillonite, was studied by batch experiments. Humic acid was also adsorbed on the clay minerals and its adsorption isotherm can be regarded as a Langmuir type. It is shown that Eu(III), or Am(III), exists as humate complex either in the aqueous or on solid phase in the system including kaolinite, or montmorillonite. These results suggest that the organic-inorganic complex like clay minerals coated with humic substances is important as metal reservoir in the environment.

Introduction*

The behavior of actinide elements in the environment has been the subject of numerous studies in recent years, since it is important from the viewpoint of nuclear waste management.¹ It has been recognized that trivalent actinides such as Am(III) may form stable complexes with humic substances in natural waters^{2,3} in the same way as trivalent lanthanides.⁴ Humic substances are naturally occurring as polyorganic acids which have strong affinity with polyvalent cations.^{5,6} Although it has been reported about humate formation with actinides(III) and lanthanides(III) in aqueous phase based on thermodynamic data,^{4,7,8} we have to consider the species adsorbed on solid or colloidal surfaces so as to examine the influence of the adsorption on the chemical equilibrium in the aqueous phase. Thus, the effect of humate formation on the adsorption of various metal ions on solid or colloidal surfaces has been discussed in recent works.^{9,10} In the present study, we have investigated Am(III) or Eu(III) adsorption on clay minerals (kaolinite and montmorillonite) in the absence and presence of humic acid. Preliminary work was reported previously,¹¹ and comparison of lanthanide(III) with other elements was described elsewhere.¹² The present work concentrates on the influences of pH and Na salt upon the adsorption behavior of Eu(III) and Am(III) on the clay minerals. The adsorption of humic acid on kaolinite or montmorillonite was also studied.

Experimental

Humic acid was extracted from paddy soil of Tochigi Prefecture, Japan, and purified as described previously.⁵ It was characterized by UV spectroscopy, IR spectroscopy, thermal analysis, and C-13 NMR as reported previously.^{11,13} Proton exchange capacity was

6.1 meq/g and stability constants of humate complexes with Am(III) and Eu(III) were reported earlier.^{4,8,11} Kaolinite and montmorillonite were purchased from Wako Pure Chemical Ind. Ltd. and Nacalai Tesque, Inc., respectively, and characterized by powder X-ray diffraction and IR spectroscopy. The analysis showed that the kaolinite sample contained halloysite as a minor component which is also classified as kaolin mineral.¹⁴

Kaolinite, or montmorillonite, was weighed and suspended in ion-exchange distilled water. Humic acid was dissolved in a NaOH solution. The suspension of the clay mineral and the humic acid solution were mixed in plastic test tubes, then ¹⁵²Eu or ²⁴¹Am tracer was injected. A small amount of a NaOH, or HClO₄, solution was added to adjust pH. The aqueous/solid ratio was 5.0 ml to 10 mg in batch experiments, except for kinetic study where the ratio was 4.0 ml to 20 mg. After shaking, the aqueous phase was separated by filtration with 0.45- μ m membrane filter to remove the clay mineral particles. Radioactivity of the aqueous phase was determined by a NaI(Tl) scintillation counter. The dissolved fraction of Eu(III), or Am(III) $\{R_{M-dis} (\%)$, where M is Eu(III), or Am(III) $\}$ and that of humic acid $\{R_{HA-dis} (\%)$ $\}$ for the particular solid/water ratio was obtained as follows:

$$R_{M-dis} = 100 A_d/A_i \quad (1)$$

$$R_{HA-dis} = 100 B_d/B_i \quad (2)$$

where A_i is the initial radioactivity of the 1 ml aliquot of aqueous phase (cpm); A_d is the radioactivity of the 1 ml aliquot of aqueous phase after filtration (cpm); B_i is the initial absorbance at 420 nm of the aqueous phase; B_d is the absorbance at 420 nm of the aqueous phase after filtration. Supporting electrolyte concentration (C_s) was adjusted by NaClO₄. These R values can be expressed by distribution coefficient K_d (ml/g) as $R = 100/(WK_d/V + 1)$ where V is the volume of the aqueous phase (ml); W is the mass of the clay mineral (mg).

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For the purpose of investigating the adsorption isotherm of humic acid on the clay mineral, following experiments were conducted: 5 ml of humic acid solution was mixed with 10 mg of kaolinite or montmorillonite. The concentration of humic acid solution was adjusted to below a certain level where the humic acid did not precipitate. After shaking for 2 weeks, the amount of humic acid adsorbed was obtained from a decrease of humic acid in the solution after filtration (0.45- μm) determined spectrophotometrically. When almost all the humic acid in the solution was adsorbed, a successive adsorption experiment was conducted: after careful centrifugation and removal of a large part of the aqueous phase, another portion of the humic acid solution was added to the remaining sample of clay mineral partly coated with humic acid. The samples were shaken again and subjected to the same procedure as above. Such a successive procedure was repeated until we could obtain the amount of humate adsorption equilibrated with a humic acid solution at high concentration.

Results and discussion

In order to understand the distribution behavior of Eu(III) between solid and aqueous phases, speciation of Eu(III) in the solution is indispensable. Based on stability constants of inorganic complex of Eu(III) in literature (for carbonates: $\log\beta_1=8.3$, $\log\beta_2=14.2$; for hydroxides: $\log\beta_1=6.2$, $\log\beta_2=11.8$, $\log\beta_3=16.8$),^{10,15} Eu(III) species in the solution equilibrated with air ($P_{\text{CO}_2}=0.03\%$) were calculated. Free Eu(III) ion is predominant below pH 6, whereas carbonate complexes are predominant above pH 6. In the system containing humic acid under our experimental condition ($[\text{HA}]=30\text{ mg/dm}^3$), humate species are taken into account on the basis of our previous data of Eu(III)-humate stability constants.^{4,8,13} It is assumed that the increase of stability constants of humate complex vs. pH in the literature is extrapolated up to pH 9, and that the stability constant is constant above pH 9 where the carboxylates in humic acid are deprotonated completely. As a result, humate complexes are estimated to be predominant as Eu(III) species in the solution between pH 3 and 10.

The adsorption of Eu(III) on kaolinite, or montmorillonite, at $C_s=0.020$ and 0.10M in the absence of humic acid (binary system) was examined. In kaolinite system, less than 10% of Eu(III) was dissolved in the aqueous phase above pH 4.5 and 6 for $C_s=0.020$ and 0.10M , respectively. Montmorillonite adsorbed Eu(III) with higher affinity than kaolinite, since ca. 90% of Eu(III) was adsorbed on montmorillonite even at pH 3 ($C_s=0.020\text{M}$).

Kinetics of adsorption of Eu(III) in the presence of humic acid

When humic acid was present (ternary system), adsorption of humic acid on kaolinite was observed. Therefore, it is difficult to decide whether Eu(III) is adsorbed on kaolinite directly or adsorbed as a humate complex. In order to resolve Eu(III) species on the clay mineral and to examine the equilibrium, adsorption kinetics of Eu(III) and humic acid was investigated. Two series of experiments were conducted:

Series A: Europium-152 tracer was adsorbed on kaolinite by shaking overnight, and then, a small amount of humic acid solution was added so as to yield 20 mg/dm^3 humic acid solution.

Series B: Europium-152 tracer was added immediately after the mixing of humic acid solution with kaolinite suspension.

In Fig. 1 are shown time dependences of Eu(III) and humic acid distributions in both series. The time was referred to the point when the humic acid solution was added. In the absence of humic acid, Eu(III) was adsorbed on kaolinite completely as described in the previous section. As observed in Series A, Eu(III) was dissolved into the aqueous phase after the addition of humic acid, indicating the formation of humate complex. Simultaneously, the humic acid began to be adsorbed on kaolinite slowly, leading to the decrease of $1/K_{d-\text{Eu(III)}}$ in Series A. As for Series B, the adsorption of Eu(III) proceeded more slowly than in the absence of humic acid, since Eu(III) was adsorbed as humate complex. After 160 hours, three kinds of plots in Fig. 1 tended to converge. These results may suggest that Eu(III) in the ternary system exists predominantly as a humate complex either in the aqueous phase or on kaolinite. Since the concentration of Eu(III) was negligibly low as compared with that of humate ligand (ca. 10^{-4} eq/dm^3), the adsorption behavior of the humate complex can be regarded as identical with that of humic acid. Since the distribution of Eu(III) reached equilibrium, or pseudoequilibrium within ca. 10 days, being controlled by the slow adsorption of humic acid on kaolinite, the samples in the following experiments were shaken for 2 weeks.

Eu(III) distribution in the ternary system (Eu(III), humic acid, and clay minerals) at various C_s and pH

In Figs 2a and 2b, $R_{\text{HA-dis}}$ in the presence of kaolinite at $C_s=0.020$ and 0.10M are compared with that in the absence of kaolinite. Since humic acid precipitates at lower pH,⁵ humic acid was removed from the aqueous phase below pH 2 even in the absence of kaolinite.

The presence of kaolinite reduced humic acid concentration in the aqueous phase over wide pH range by adsorption. The adsorption of humic acid on kaolinite was observed to be more effectively at $C_s = 0.10\text{M}$ than at $C_s = 0.020\text{M}$. The increase in pH, or the decrease in C_s , induces more negative charges on a humic acid molecule, preventing the polymolecule from being adsorbed on kaolinite with negative charges above pH 4.¹⁶

In Figs 2a and 2b are also demonstrated plots of $R_{\text{Eu(III)-dis}}$ in the ternary system (Eu(III), kaolinite, and humic acid) at $C_s = 0.020$ and 0.10M . Comparison of the distribution of Eu(III) with that of humic acid indicated that $R_{\text{Eu(III)-dis}}$ is essentially identical with $R_{\text{HA-dis}}$ between pH 3 and 9.5 at $C_s = 0.020$ and 0.10M . Similar results were obtained for Am(III) at $C_s = 0.020\text{M}$ (Fig. 2c), showing that we can estimate the behavior of Am(III) on the basis of the results concerning Eu(III). These results indicate that Eu(III) or Am(III) is distributed as humate complex either in the aqueous phase, or on kaolinite in the pH and C_s region of $3 < \text{pH} < 9.5$ and $0.020\text{M} < C_s < 0.10\text{M}$ at the aqueous/solid ratio of 5 ml to 10 mg. Consequently, the presence of humic acid enhanced adsorption of Eu(III), or Am(III), below pH 3.5 and 4.5 for $C_s = 0.020$ and 0.10M , respectively, as revealed by comparing with the results in the absence of humic acid. On the other hand, the presence of humic acid enhanced the dissolution of Eu(III) or Am(III) above pH 3.5 and 4.5 for $C_s = 0.020$ and 0.10M , respectively, due to the dissolution of the humate complexes. Therefore, the aqueous/solid distributions of Eu(III) and Am(III) should be determined by the distribution of humic acid in these conditions. Below pH 2.5, $R_{\text{Eu(III)-dis}}$ or $R_{\text{Am(III)-dis}}$ was higher than $R_{\text{HA-dis}}$, since the protonation of humic acid may interfere with the formation of humate complex. Above pH 9.5, $R_{\text{Eu(III)-dis}}$ or $R_{\text{Am(III)-dis}}$ was not identical with $R_{\text{HA-dis}}$, since the humate complex is not regarded as dominant species of Eu(III), or Am(III), in the aqueous/solid system, suggesting the formation of inorganic species, which is consistent with the speciation calculation.

In employing montmorillonite as adsorbents, similar results are obtained (Fig. 2d). Between pH 3 and 9, $R_{\text{Eu(III)-dis}}$ was identical with $R_{\text{HA-dis}}$, showing that the humate complexes are regarded as dominant species for Eu(III) also in this ternary system. In consequence, a larger amount of Eu(III) was removed from the aqueous phase than in the kaolinite system, since the amount of humic acid (or humate complex) adsorbed on montmorillonite was greater than that on kaolinite. The adsorption behavior of humic acid on montmorillonite was different from that on kaolinite: $R_{\text{HA-dis}}$ decreased with increasing pH at pH above 9 in the montmorillonite system. This phenomenon cannot be interpreted simply in terms of the change of negative charges on humic acid molecule and montmorillonite surface, since the

adsorption should occur to a lesser extent at higher pH region where the repulsive force between the polymolecule and the mineral surface should be enhanced due to the increase of negative charges on them. Schulthess reported similar results on the humic acid adsorption on montmorillonite and ascribed it to the interaction with gibbsite surface: gibbsite layer is exposed by the dissolution of siloxane layer at higher pH and preferentially adsorbs humic acid.⁹

In summary, the distribution of humic acid is a decisive factor controlling the aqueous/solid distribution of Eu(III) and Am(III). The strong correlation between $R_{\text{M-dis}}$ and $R_{\text{HA-dis}}$ was observed in particular for lanthanide(III) in our similar adsorption study involving various metal ions such as alkaline metal ions, alkaline earth metal ions, and transition metal ions.¹²

Adsorption of humic acid on kaolinite and montmorillonite

For understanding the distribution of Eu(III) or Am(III) in the ternary system, the adsorption of humic acid on kaolinite and montmorillonite should be studied extensively. Adsorption isotherm was then examined at various pH and C_s conditions; an example is shown in Fig. 3a. Since these isotherms can be regarded as the Langmuir type,^{17,18} the amount of the maximum adsorption (Γ_{max}) of humic acid on kaolinite or montmorillonite can be obtained. If the concentration of humic acid is not so large to cause its precipitation,

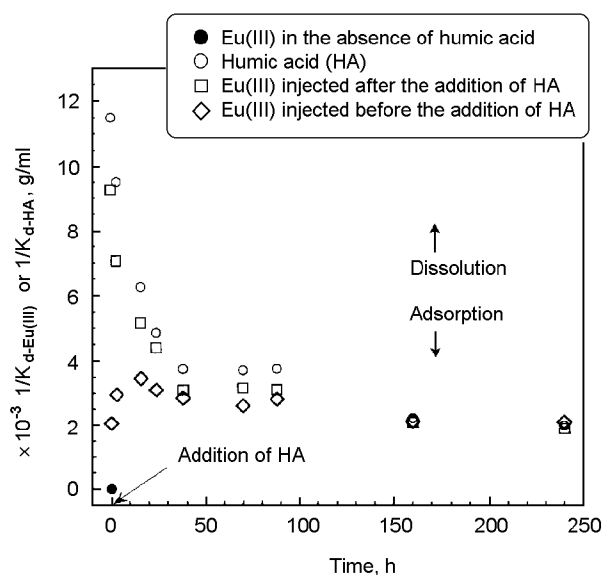


Fig. 1. Time dependences of the reciprocals of distribution coefficients of Eu(III) and humic acid ($K_{d-\text{Eu(III)}}$ or $K_{d-\text{HA}}$ ml/g) at pH 6.1 and $C_s = 0.020\text{M}$. Aqueous phase: humic acid solution (initial concentration: 20 mg/dm^3 ; volume: 4.0 ml). Solid phase: kaolinite 20 mg (coated with humic acid after its addition)

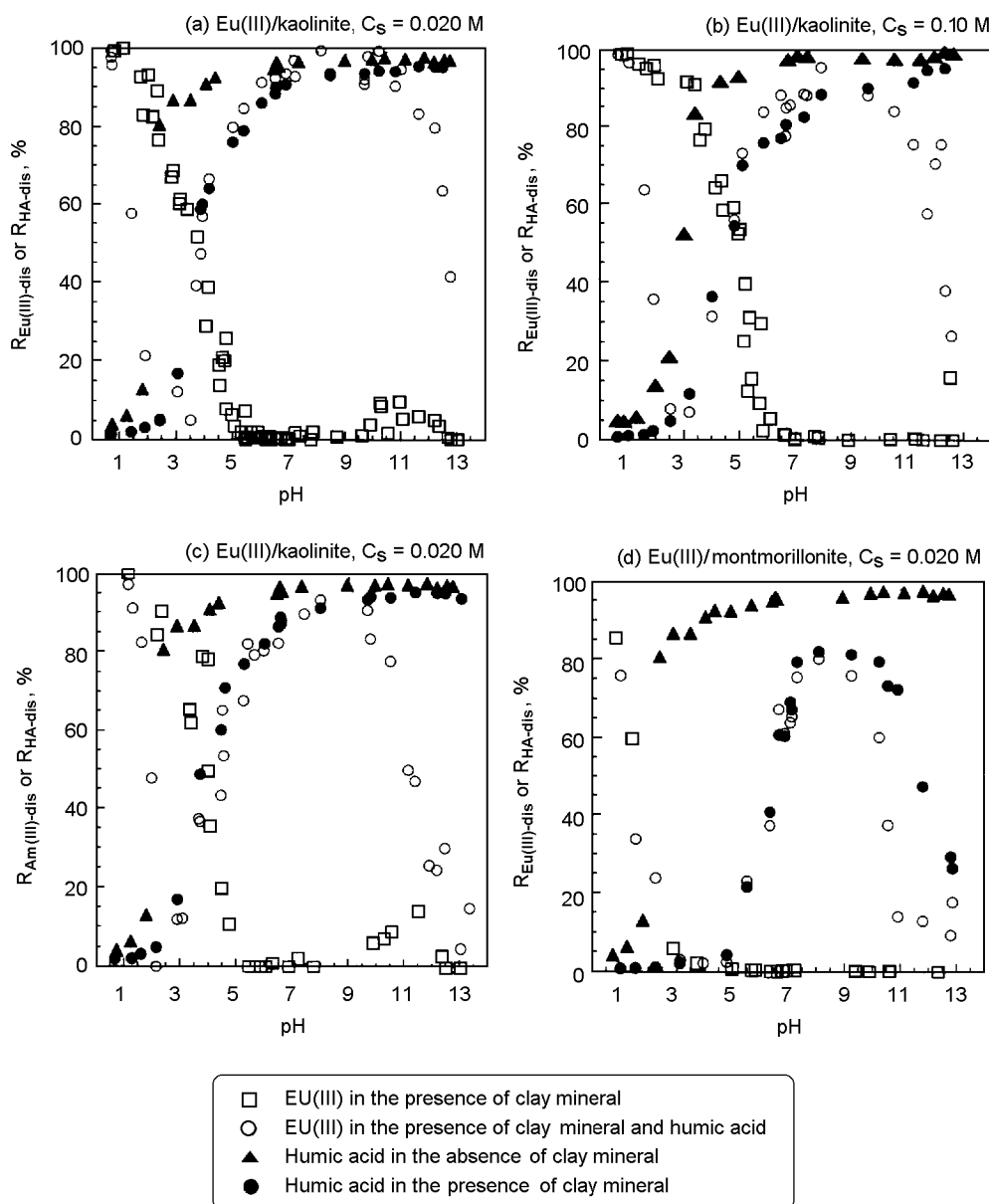


Fig. 2. The dissolved fraction of Eu(III) or Am(III) ($R_{\text{Eu(III)-dis}}$ or $R_{\text{Am(III)-dis}}$) in contact with clay mineral (kaolinite or montmorillonite) in the presence and absence of humic acid. The dissolved fraction of HA ($R_{\text{HA-dis}}$) in the presence and absence of the clay mineral is also shown. C_s : 0.020M or 1.0M. The aqueous/solid ratio: 5 ml to 10 mg. Initial concentration of humic acid: 30 mg/dm³

Γ_{max} is calculated from the slope of Eq. (3) by the least squares iteration between C_{HA}/Γ and C_{HA} :

$$C_{\text{HA}}/\Gamma = 1/(K\Gamma_{\text{max}}) + C_{\text{HA}}/\Gamma_{\text{max}}, \quad (3)$$

where C_{HA} is the concentration of humic acid in the aqueous phase (mg/dm³); Γ is the amount of adsorption (mg/g); K is a constant. In Fig. 3b, pH dependence of Γ_{max} at $C_s=0.020$ and 0.10M are shown. The Γ_{max} decreased with pH and increased with C_s . The increase in pH induces negative charges on the polymolecule.

The repulsion between ligands in the humic acid molecule deprotonated by the increase in pH makes the humic acid molecule to take linear configuration. Such changes in charge density and configuration depending on pH may reduce humate adsorption at higher pH.¹⁶ On the other hand, the increase in C_s may weaken the repulsion and induce a spherical configuration of the humic acid. The shielding effect by the salt enhances the adsorption of the humic acid on kaolinite, or montmorillonite. It was also observed that Γ_{max} on montmorillonite is greater than that on kaolinite.

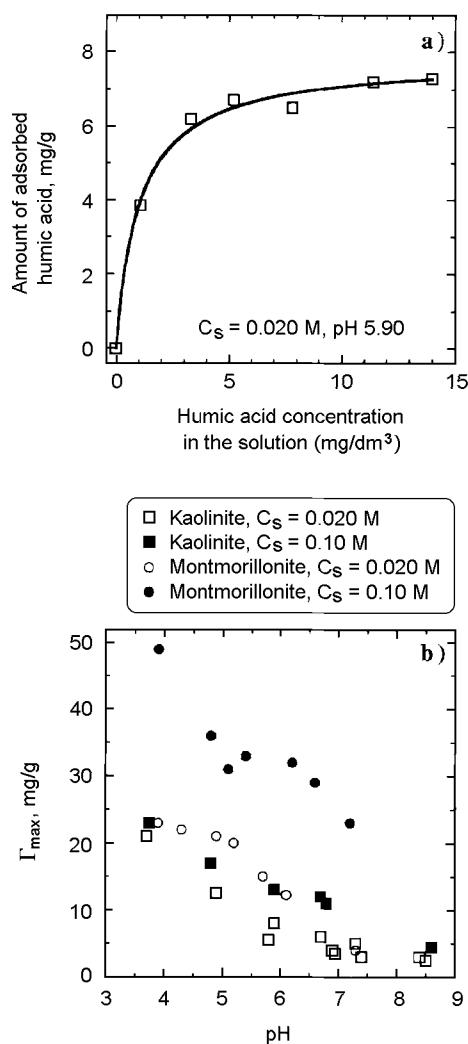


Fig. 3. Adsorption isotherm of humic acid on kaolinite (a); pH and Na salt concentration dependences of Γ_{\max} of humic acid on kaolinite or on montmorillonite obtained by assuming the Langmuir Equation (b)

Humic acid-clay mineral complex was so stable that humic acid was not extracted even after one-week shaking of the complex with humic acid-free water whose pH and C_s were identical with those of the aqueous phase once in contact with humic acid-clay mineral complex samples. This shows that the adsorption of humic acid reaches a maximum when its concentration in the equilibrated solution is quite dilute.

Regarding the mechanism of the adsorption, various forces such as Van der Waals forces, hydrogen bonding, etc. may cooperate to generate such stable complex.^{15,18,19} The pH and C_s dependences observed in the present study imply the contribution of heterogeneous coagulation between humic acid and clay mineral particles interpreted by electric double layer model.¹⁹

Estimation of Eu(III) and Am(III) behavior in the ternary system

In this section, we will try to estimate the aqueous/solid distribution of Eu(III) or Am(III) in freshwater based on the results above. The results indicate that distributions of humic acid and Eu(III), or Am(III), between aqueous and solid phases are closely correlated over a wide pH and C_s ranges of $3 < \text{pH} < 9$ and $0.020 \text{ M} < C_s < 0.10 \text{ M}$. The correlation was also confirmed for various aqueous/solid ratios (dm^3/g) as 0.2, 0.5, and 1.0, and for various $\log\{K_{d\text{-HA}}/(\text{ml/g})\}$ values between 0 and 3. Thus, it follows that Eu(III), or Am(III), exists as humate complex in the system and the behavior of humic acid governs that of Eu(III) or Am(III). In environment, the amount of adsorption of humic acid on kaolinite, or montmorillonite, can be regarded to reach a maximum, since it can be thought that dissolved organics are constantly supplied with flowing water. Hence, if we postulate that distributions of humic acid and Eu(III) or Am(III) are identical, and that humic acid is adsorbed on kaolinite or montmorillonite completely, $R_{\text{Eu(III)-dis}}$ or $R_{\text{Am(III)-dis}}$ at the equilibrium can be estimated for specific pH, C_s , and C_{HA} . We also assume that the amount of the maximum adsorption of humic acid (Γ_{\max}) remains constant for different solid/aqueous ratios. Based on these assumptions, $R_{\text{M-dis}}$ ($\text{M} = \text{Eu(III)}$ or Am(III)) in the ternary system can be estimated as follows:

$$\begin{aligned} R_{\text{M-dis}} &= \frac{[\text{M}_{\text{total}}]_{\text{sol}}}{([\text{M}_{\text{total}}]_{\text{ads}} + [\text{M}_{\text{total}}]_{\text{sol}})} \\ &= \frac{[\text{M}_{\text{humate}}]_{\text{sol}}}{([\text{M}_{\text{humate}}]_{\text{ads}} + [\text{M}_{\text{humate}}]_{\text{sol}})} \\ &= C_{\text{HA}} (\text{mg}/\text{dm}^3) / \{r (\text{g}/\text{dm}^3) \Gamma_{\max} (\text{mg}/\text{g}) + \\ &\quad + C_{\text{HA}} (\text{mg}/\text{dm}^3)\}, \end{aligned} \quad (4)$$

where r is solid/aqueous ratio and M, Eu(III) or Am(III). Subscripts sol and ads denote the species in aqueous and solid phases, respectively. Although r and C_{HA} show variability in freshwater (e.g., dissolved organic carbon: 2–100 mg/dm^3 ; suspended particulate matter: 0.08–38 g/dm^3 in river waters),²⁰ an example of estimated values of $R_{\text{Eu(III)-dis}}$ and $R_{\text{Am(III)-dis}}$ in freshwater is shown in Fig. 4, assuming $r = 5 \text{ g}/\text{dm}^3$ and $C_{\text{HA}} = 2 \text{ mg}/\text{dm}^3$. As pH increases, a larger amount of Eu(III), or Am(III), is dissolved into the aqueous phase unlike in the absence of humic acid. The increase in C_s enhances the adsorption of humic acid on kaolinite, or montmorillonite, leading to the increase of metal ions' adsorption on kaolinite or montmorillonite as the humate complexes. At pH 7 and $C_s = 0.020 \text{ M}$ (simulating freshwater), 5–15% of Eu(III), or Am(III), may be dissolved into the aqueous phase in the condition assumed in Fig. 4. The difference in the dissolved percentages between kaolinite and montmorillonite

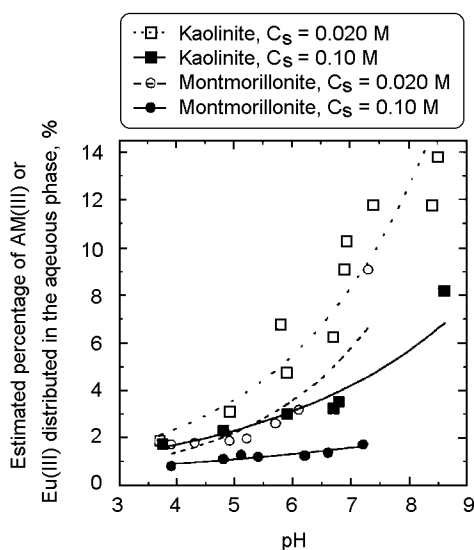


Fig. 4. Estimated values of dissolved species of Eu(III) or Am(III) in the aqueous/solid system which consists of humic acid and kaolinite or montmorillonite at various pH and C_s . Solid phase: 5 g of kaolinite or montmorillonite which is coated with humic acid; aqueous phase: 1 dm³ of humic acid solution (2 mg/dm³)

systems is due to the difference in the amount of the humic acid adsorbed on them. These results also show that pseudocolloidal humic acid (e.g., clay minerals coated with humic substances) is substantially important as a reservoir of lanthanide(III) and actinide(III) in the environment. It can be said that, in the environment where such colloids may generate to a greater extent, a larger amount of lanthanide(III) and actinide(III) may be adsorbed on the colloidal or solid surface.

Conclusions

In this paper, the aqueous/solid distribution of Eu(III), or Am(III), at trace level in the system containing humic acid and kaolinite, or montmorillonite, has been investigated under various conditions of pH and Na salt concentrations. It was shown that Eu(III), or Am(III), is predominantly bound to humic acid in the ternary system. Since the humate complex is strongly adsorbed on kaolinite or montmorillonite, the

aqueous/solid distributions of these metal ions are greatly affected by that of humic acid. Thus, the environmental behavior of trivalent actinide, or lanthanide, can be influenced by complexation with humic acid, even in taking account of the influence of colloidal, or solid phase, like clay minerals. The adsorption reaction with colloidal or solid phase like clay minerals is more or less altered by the coating of organics like humic substances. The organic-inorganic complex like clay minerals coated with humic substances is important as a reservoir of lanthanide(III) and actinide(III) in the environment.

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