

The Effect of Na⁺, Mg²⁺, and Ca²⁺ Ions on the Formation of Eu(III)-Humate Complex

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Formation of Eu(III)-humate at various concentrations of Na⁺, Mg²⁺, and Ca²⁺ in a wide pH range (4 < pH < 8) was studied by the solvent extraction method using ¹⁵²Eu tracer. Concentrations of Na⁺, Mg²⁺, and Ca²⁺ ranged from 0.020 to 1.0 M, 10⁻⁶ to 10⁻³ M, and 10⁻⁶ to 10⁻³ M, respectively. The dependence of the stability on pH and concentrations of Na⁺, Mg²⁺, or Ca²⁺ was interpreted by considering the polyelectrolyte nature of humic acid. Concentration ratios of Eu(III)-humate complex to free Eu(III) ion in fresh water and seawater was estimated based on the relations between the stability of Eu(III)-humate complex and concentrations of Na⁺, Mg²⁺, or Ca²⁺. Speciation calculations of Eu(III) species dissolved in fresh water and seawater were conducted based on the relations. As a result, it was suggested that humate complex could be more important species of Eu(III) dissolved in fresh water compared with inorganic complexes such as carbonate and hydroxide. In seawater, however, the carbonate complex can be more important species, since Mg²⁺ and Ca²⁺ in seawater at a 10⁻² M level greatly inhibit the formation of the humate complex of Eu(III).

1. Introduction

Humic substances like humic acid, fulvic acid, and humine interact with metal ions in the environment.^{1,2} Humic substances are a general term for the heterogeneous polymeric organoacids widely found in soils, sediments, fresh water, and seawater.^{3,4} The carboxyl and phenolic groups are the main functional groups of the polyacid. Humic substances form stable complexes with metal ions by these functional groups in the environment. Since humic and fulvic acids are soluble, they influence the migration of cations in the environment.

The migration of actinide elements in the environment is of particular interest to the topic of radioactive waste problems.⁵ There are a lot of studies dealing with the speciation of actinide elements (III–VII) to predict their environmental behavior, where the discussion was based on each oxidation state.^{2,6,7} For the trivalent actinide, it has been suggested that humate complex is the predominant species in natural waters.^{2,6–9} In this work, we study the interaction between humic acid and Eu(III) employed as an analogue of actinides(III). Since stability constants of Eu(III) and Am(III) are similar for their various complexes,^{8–10} it is expected that we can extend the results on Eu(III) in this study to Am(III), or other actinides(III). In fact, our previous study showed that the stability constants of humate complexes are similar between Eu(III) and Am(III) for the humic acid also employed in this study.⁸

The stability of the humate complex apparently varies with pH, ionic strength (*I*_s), and concentrations of polyvalent cations.^{10–14} However, the stability constants of humate with lanthanides(III) and actinides(III) under environmental conditions such as a pH above 6, *I*_s up to 0.7 M, and presence of millimolar Ca²⁺ or Mg²⁺ have not yet been fully determined. Therefore, the effects of pH and Na⁺, Mg²⁺, and Ca²⁺ ions on the stability of Eu(III)-humate were studied in this work. In particular, the complexation of Eu(III)-humate in the presence

of millimolar Ca²⁺ or Mg²⁺ has not been thoroughly studied so far, where divalent cations at millimolar level may considerably influence the stability of humate with trace Eu(III) (< 10⁻⁹ M). These parameters have wide ranges in natural aquifer; pH 8, *I*_s = 0.7 M, [Mg²⁺] = 0.06 M, and [Ca²⁺] = 0.01 M in seawater, while pH 6–8, *I*_s < 0.01 M, [Mg²⁺] = 0.1 mM, and [Ca²⁺] = 0.2 mM in fresh water.¹⁵ Although we have already reported a part of the results for pH and *I*_s dependences (4 < pH < 6, 0.020 M < [Na⁺] < 0.70 M),⁸ the main purpose of the present study is to elucidate the effects of Na⁺, Mg²⁺, and Ca²⁺ ions on the stability constants of Eu(III)-humate. Empirical relations between stabilities of humate complexes and the concentration of Ca²⁺ ions obtained in this study, were employed for estimating dissolved species of Eu(III) under various environmental conditions.

In determining stability constants, many methods have been used such as radioisotope tracer technique,^{10,16} spectroscopy,¹⁷ ion-selective electrode,¹⁸ etc. Among them, we employed radioisotope tracer technique. For trivalent ions, it is necessary to employ a phase separation method such as solvent extraction, ion exchange, or dialysis to distinguish free metal ions from the metal ions bound to humate. However, in the environment, concentrations of dissolved actinide and lanthanide ions are considered to be at trace level (at least below 10⁻⁹ M for lanthanides). The stability constant of the humate complex is a conditional value which is greatly affected by the degree of metal loading (= concentration ratio of metal ion to humic acid) due to the polyelectrolyte character of humic acid. Radioisotope tracer technique is sensitive enough to detect metal ions below 10⁻⁹ M. Therefore, we can reduce the concentration ratio of complexed metal ion to ligand of humate by the radioisotope tracer technique lower than by any other methods. Therefore, we employed the solvent extraction method using a radioisotope tracer, to determine the stability constants of Eu(III) with humate. Solvent extraction is an excellent method to determine the concentration of free metal ions in the aqueous phase, compared with the ion exchange method, since humic acid itself can be adsorbed by the ion exchange resin. To discuss

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the effect of Ca^{2+} ion, the stability constant of Ca-humate was also determined using a ^{45}Ca tracer in the presence of various concentrations of Ca^{2+} ions to clarify the influence of divalent cations on the stability of Eu(III)-humate.

2. Experimental Details

The humic acid employed in this study was extracted from paddy soil (Andosol) in Tochigi prefecture, Japan, and was purified following conventional methods.^{3,4} The characteristics of the humic acid were determined using UV/VIS spectroscopy, IR spectroscopy, thermal analysis, elemental analysis, pH titration, and C-13 NMR.^{19,20} All other chemicals used in this study were of reagent grade or better.

pH titration. For pH titration of humic acid, back-titration was employed, because the humic acid we extracted did not dissolve easily in water. Frozen-dried humic acid was dissolved to a 0.100 M NaOH solution, where the concentration of humic acid was about 200 mg/dm³. The solution was titrated by 0.0100 M HClO₄ solution under N₂ atmosphere at room temperature with an automatic titration system (autoburette: Metrohm E552-20B; pH meter: Metrohm 654) controlled by a personal computer (NEC PC-9801). The pH drift was monitored after each addition of a small amount of the acid. The reading was recorded when the pH drift was less than 0.001 pH per 5 min. Ionic strength (I_s) was adjusted to 0.020, 0.50, 0.10, 0.20, 0.50, 0.70, and 1.0 M by NaClO₄.

Solvent extraction to determine stability constants. The aqueous phase was humic acid solution containing a buffer reagent to adjust pH with NaClO₄, MgClO₄, or CaCl₂ to adjust I_s , $[\text{Mg}(\text{II})]_t$, or $[\text{Ca}(\text{II})]_t$ (= total concentrations of Mg or Ca species). When Mg or Ca salt was added, I_s was adjusted by NaClO₄ to 0.020 M. The concentration of humic acid ranged from 0 to about 1×10^{-3} eq/dm³ (≈ 150 mg/dm³). Four buffer reagents were used to maintain pH: 3-chloropropionic acid (2.5 mM) for pH around 4; acetic acid (1.0 mM) for pH around 5; hydroxylammonium chloride (0.010 M) for pH around 6; and Tris buffer (0.010 M) for pH from 7 to 8. Each tracer (^{152}Eu and ^{45}Ca) was prepared as perchloric acid solution (1.0 mM). The extraction reagent was di-(2-ethylhexyl)-phosphoric acid (DEHP), which was purified prior to use.²¹ The organic phase (DEHP/toluene solution) was pre-equilibrated by the buffer solution in order not to alter the pH of the aqueous phase.

The organic phase and the aqueous phase with a small amount of tracer solution were mixed and shaken at room temperature in glass vials for three days, which was long enough to reach an equilibrium in the aqueous-organic distribution of the radioisotopes. The carrier concentration of Eu(III) in the solution was 1×10^{-9} M. After centrifugation, the two phases were separated and distribution ratios were obtained by measuring radioactivities with a well-type NaI(Tl) counter for ^{152}Eu (III) and with a liquid scintillation counter for ^{45}Ca . The concentration of humic acid was monitored by absorbance at 400 nm.

Experiments in the presence of Ca^{2+} ion were conducted as follows. The stability constant of Ca-humate was determined using ^{45}Ca as described above, where the carrier concentration of Ca from the ^{45}Ca solution was 2×10^{-9} M in the solvent extraction system. A part of each phase was taken for the detection of β -rays of ^{45}Ca by a liquid scintillation counter. Quenching of the luminescence of scintillator (PICO-FLUOR 40, Packard Instrument Company, Inc.) by humic acid in the aqueous phase was corrected depending on the concentration of humic acid. Afterwards, ^{152}Eu tracer was injected into the residual water-toluene solution. The injection of a small amount of ^{152}Eu tracer solution did not affect the humate equilibrium with Ca^{2+} ions, since Eu(III) concentration and the acidity of the Eu tracer solution were low enough to keep the equilibrium between Ca^{2+} ions and humic acid. The pH values showed little variation before and after the injection of the Eu

tracer, which suggests that the equilibrium was maintained. The distribution ratio of Eu(III) was determined by detecting γ -rays of ^{152}Eu by NaI(Tl) detector, while β -ray of ^{45}Ca was not detected by the NaI(Tl) detector. This procedure enables us to determine the stability of Ca-humate and Eu(III)-humate under identical conditions.

In this study, solvent extraction above pH 6 was also carried out. Generally speaking, Eu(III) can be readily adsorbed on the wall of glass vials above pH 6, which results in a loss of radioactivity in the solvent extraction system.^{2,22} To avoid such adsorption, silanols of the glass surface (Si-OH) were substituted to methoxides by $(\text{CH}_3)_2\text{SiCl}_2$ and methanol.

3. Principles and Data Treatment

Principles to obtain stability constants. The method to determine the stability constants by solvent extraction follows the description in Reference 10. In the solvent extraction system, D_0 , D_1 , and D_2 were considered:

$$1/D_0 = [\text{M}^{z+}]_a / [\text{M}((\text{DEHP})_2)_z]_o \quad (1)$$

$$1/D_1 = ([\text{M}^{z+}]_a + [\text{MB}]_a) / [\text{M}((\text{DEHP})_2)_z]_o \quad (2)$$

$$1/D_2 = ([\text{M}^{z+}]_a + [\text{MA}]_a + [\text{MB}]_a) / [\text{M}((\text{DEHP})_2)_z]_o \quad (3)$$

$$= 1/D_1 + [\text{MA}]_a / [\text{M}((\text{DEHP})_2)_z]_o$$

(M: Eu(III) or Ca; z: charge of the ion; o: organic phase; a: aqueous phase, A: ligand of humic acid; B: other ligands such as OH^- , CO_3^{2-} , and buffer anions).

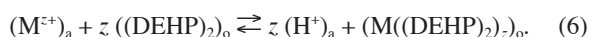
The stability constant, β_M , of humate with metal ion (M^{z+}) is expressed as

$$\beta_M = [\text{MA}]_i / ([\text{M}^{z+}][\text{A}]^i) \quad (4)$$

where i is the number of ligands bound to one metal ion. Based on eqs 1–4, we can obtain

$$D_0(1/D_2 - 1/D_1) = \Sigma \beta_M [\text{A}]^i \quad (5)$$

D_1 and various D_2 were obtained according to the concentration of free ligands in humic acid in the unit of equivalent concentration of the ligands (= $[\text{A}]$ eq/dm³). The $[\text{A}]$ is determined from the proton exchange capacity of humic acid (PEC) and the degree of ionization (α) at each pH ($[\text{A}] = \alpha \times \text{PEC}$), as determined by pH titration. When we obtain $[\text{A}]$, we assume that the trace amount of metal ions does not influence the equilibrium of proton dissociation of humic acid (however, this assumption cannot be maintained in the presence of larger $[\text{Ca}]_t$ as we will discuss below). The extraction reaction of metal ions (M^{z+}) by DEHP can be written as



When $[\text{M}]_t$ (= total concentration of M in the aqueous phase) is small enough, the concentration of free $(\text{DEHP})_2$ in the organic phase does not change by the formation of $\text{M}((\text{DEHP})_2)_z$ species in the organic phase. In this case, D_0 in eq 5 (= $[\text{M}((\text{DEHP})_2)_z]_o / [\text{M}^{z+}]_a$) can be obtained from the extraction properties of DEHP as

$$\log D_0 = a \text{pH} + b \log[(\text{DEHP})_2]_o + \log K_{\text{ex}} \quad (7)$$

where a and b are expected to be equal to z and K_{ex} an extraction constant defined as:

$$K_{\text{ex}} = [\text{H}^+]_a^z [\text{M}((\text{DEHP})_2)_z]_o / ([\text{M}^{z+}]_a [(\text{DEHP})_2]_o^z) \quad (8)$$

The K_{ex} and coefficients a and b in eq 7 were determined

experimentally by solvent extraction in the low pH region where hydrolysis and carbonate complexation are negligible.²³ Based on eqs 1 and 7, we can determine $[M^{2+}]_a$ in the aqueous phase by the solvent extraction experiments.

Data treatment. Variation of I_s (or ionic strength) essentially influences the experimental data of pH and stability constants, since it affects the activities of chemical species in the aqueous phase. We did not use proton activity but pCH (concentration of proton) to determine pH in this study. The Debye-Hückel equation enables us to calculate pCH from pH at $I_s = 0.10$ M as following:

$$\text{pCH} = \text{pH} (I_s = 0.10 \text{ M}) + 0.11. \quad (9)$$

At other I_s , differences of pH at $I_s = 0.10$ M were determined experimentally by measuring the pH of NaOH-HClO₄ solution at each I_s , where the degree of ionization of NaOH or HClO₄ in aqueous solution was regarded as unity.

For the speciation calculation, we need the stability constants of Eu(III) complexes at various I_s found in natural water conditions. In general, the stability constant of metal complex in the aqueous phase decreases with the increase in I_s . Specific Interaction Theory was often used to estimate the thermodynamic data at higher I_s .^{9, 24, 25} In this theory, the stability constant at a certain I_s can be obtained by the next equation:

$$\log \beta(I_s) = \log \beta(0) + \Delta z^2 D + \Delta \epsilon I_s, \quad (10)$$

where D is the Debye-Hückel term expressed as $D = 0.51 I_s^{1/2} / (1 + 1.5 I_s^{1/2})$, $\beta(0)$ is the stability constant at $I_s = 0$ M, and Δz^2 is equal to $\sum z^2(\text{products}) - \sum z^2(\text{reactants})$ where z is the charge of each ion. The $\Delta \epsilon$ is equal to $\epsilon(\text{products}) - \epsilon(\text{reactants})$, where ϵ is a parameter which is related to the specific interaction between each pair of cation and anion in the corresponding complex. The parameters of the Specific Interaction Theory and the stability constants of carbonate,²⁶ hydroxide,⁷ and chloride²⁶ for Eu(III), or Am(III), are listed in Table 1, where the stability constants calculated at a particular I_s which we used in the speciation calculations are also shown. For sulfate and hydrophosphate, literature data of the stability constants were used directly in the speciation calculations, due to the absence of parameters in the Specific Interaction Theory.

4. Results and Discussion

pH titration. The proton exchange capacity of the humic acid was 6.1 ± 0.4 meq/g ($n = 10$). The apparent $\text{p}K_a$ of humic acid can be determined by the next equation where α is the degree of ionization of humic acid:²⁷

$$\text{p}K_a = \text{pH} - \log\{\alpha/(1 - \alpha)\}. \quad (11)$$

The apparent $\text{p}K_a$ increased with α and decreased with I_s as shown in Figure 1. The increase against α is partly induced by different dissociation groups within humic acid molecules. In

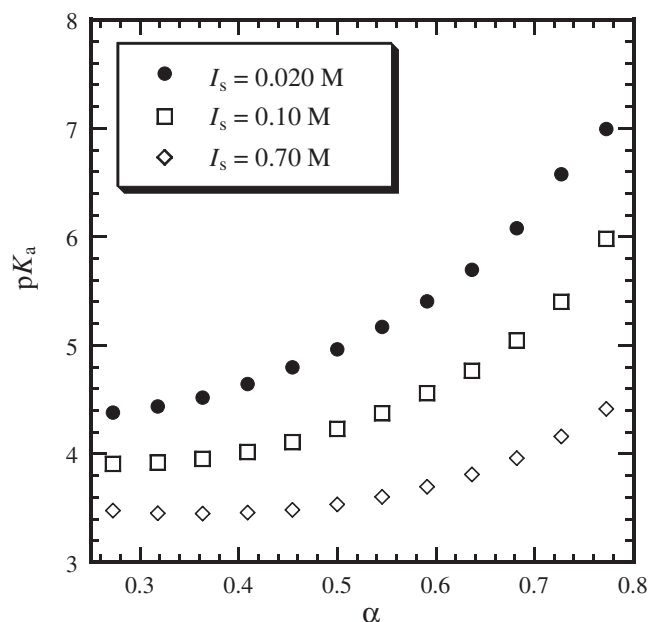


Figure 1. Variation of apparent $\text{p}K_a$ at different degrees of ionization (α) of humic acid at various I_s adjusted by NaClO₄.

addition, the increase in $\text{p}K_a$ is also due to the increase of negative charges on humic acid molecule at larger α , where protons are attracted more strongly to the macromolecule. This phenomenon was characteristic of polyelectrolyte like humic acid.^{14, 28–30} On the other hand, supporting cations ($= \text{Na}^+$) shield the attraction between humic acid and proton, which results in decrease of $\text{p}K_a$ at larger I_s .^{14, 27–29}

Extraction equilibrium of Eu(III) and Ca(II) by DEHP.

From D_0 dependence on (i) pH ($\text{pH} < 2$) at constant $[(\text{DEHP})_2]_0$ and (ii) $[(\text{DEHP})_2]_0$ at constant pH in solvent extraction experiments, eq 7 was obtained experimentally for each I_s by least squares analyses ($r > 0.99990$). We obtained $a = 2.85 \pm 0.04$ and $b = 2.88 \pm 0.04$ as averaged values for Eu(III). The K_{ex} apparently decreased with I_s as shown in Figure 2. The data were used for solvent extraction experiments at each I_s for determining the stability constants. For Ca, a and b in eq 7 were 1.87 ± 0.03 and 1.80 ± 0.04 , respectively, and $\log K_{\text{ex}}$ of Ca by DEHP was -3.80 at $I_s = 0.020$ M.

Apparent stability constants of Eu(III)- or Ca(II)-humate at various pH and I_s . Plots of $D_0(1/D_2 - 1/D_1)$ against $[A]$ at constant I_s as expressed by eq 5 have often been interpreted as quadratic curves for Eu(III) or Am(III), which gives two stability constants, β_{M1} and β_{M2} , corresponding to MA and MA₂ complexes.^{10, 12, 19} However, the meaning of β_{M1} and β_{M2} is still not clear in terms of the stoichiometry of the complexation reaction. Since humic acid is polyacids having large molecular weights, local structure around the metal ions in humate complex would not change when the concentration of humic acid ($= [A]$) increases at constant $[M]_i$, because $[M]_i$ is at trace levels. It is most likely that trace metal ion is bound to

TABLE 1: Stability Constants Used for the Speciation Calculations and Parameters in Specific Interaction Theory

Species	$\log \beta_i$	[References]	$I_s = 0.020$ M	$I_s = 0.70$ M	Δz^2	$\Delta \epsilon$
EuCO_3^+	8.1 ($I_s = 0$ M)	[25]	7.4	6	-12	0.25
$\text{Eu}(\text{CO}_3)_2^{2-}$	12.9 ($I_s = 0$ M)	[25]	12	10.1	-16	0.2
EuOH^{2+}	-7.5 ($I_s = 0.10$ M)	[7]	-7.3	-7.8	-4*	-0.05*
$\text{Eu}(\text{OH})_2^+$	-15.4 ($I_s = 0.10$ M)	[7]	-15.4	-15.8	-6*	-0.01*
EuCl^{2+}	-0.1 ($I_s = 1.0$ M)	[25]	0.37	-0.14	-6	-0.4
EuSO_4^+	1.9 ($I_s = 0.50$ M)	[40]				
EuHPO_4^+	4.2 ($I_s = 0$ M)*	[41]				

*Data for Am complex are used.

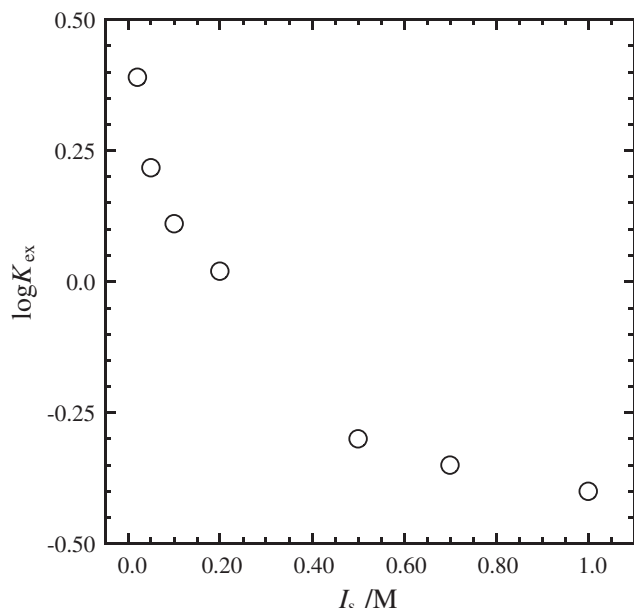


Figure 2. Extraction constants (K_{ex}) of Eu(III) by DEHP at various I_s .

specific binding sites in the macromolecule even if $[A]/[M]_t$ changes to some degree. Therefore, we think that β_{M1} and β_{M2} do not contain any structural information, but only distinguish the metal-humate species from free metal ions.³¹ According to Reference 8, the ratio $\beta_{M2}/\beta_{M1} \{= [MA_2]/([MA][A])\}$ under natural water conditions is less than 10^3 for Eu(III). Since humic acid concentration in the environment is below about 10 mg/dm^3 (ca. $[A] = 0.5 \times 10^{-4} \text{ eq/dm}^3$), the ratio $[MA_2]/[MA]$ is less than 0.05. This shows that β_{M1} , which gives $[MA]$, is the major parameter to describe the humate species of Eu(III) in the environment. We will evaluate the metal-humate interaction through β_{M1} in this paper due to these reasons, as written above, and hereinafter β_M means β_{M1} .

The dependences of the stability constants of Eu(III)-humate on pH and α at $I_s = 0.10 \text{ M}$ are shown in Figure 3, and indicate that the stability constant increased with pH, or α . This trend can also be explained by the polyelectrolyte effect, as described in the pK_a results. The increase in pH (or α) gives more negative charges to humic acid molecule, which enhances the strength of the electric field at the surface of the humic acid molecule. Because of the electrostatic force, metal ions are attracted to the humic acid molecule to a greater degree when pH increases. The fraction of metal ions attracted electrostatically to humic acid is theoretically distinguished from another fraction which is directly bound to binding sites in humic acid. In order to compare $\log \beta_{Eu(III)}$ of Eu(III)-humate with simple monomeric acid, the stability constant of Eu(III)-propionate was determined at several α by the solvent extraction method (Figure 3). There was little variation in the stability constant of the propionate at different α , suggesting that pH dependence on the stability constants of humate is peculiar to polyelectrolyte like humic acid.

In Figure 4, the pH dependence of $\log \beta_{Ca}$ is shown at $I_s = 0.020 \text{ M}$, accompanied by $\log \beta_{Eu(III)}$ at $I_s = 0.020, 0.10,$ and 0.70 M . The $\log \beta_{Ca}$ values are smaller than $\log \beta_{Eu(III)}$, and the slope of $\log \beta_M$ versus pH is greater for Eu(III)-humate than Ca-humate, because electrostatic attraction to humic acid is greater for trivalent ions than for divalent ions. The dependence of β_M on pH (or α) was interpreted based on a simple electrostatic model.^{29, 32-34} In the theory, pK_a and $\log \beta_M$ can be written as a function of α :

$$pK_a = pK_{int} - 0.434 e \phi(\alpha)/kT \quad (12)$$

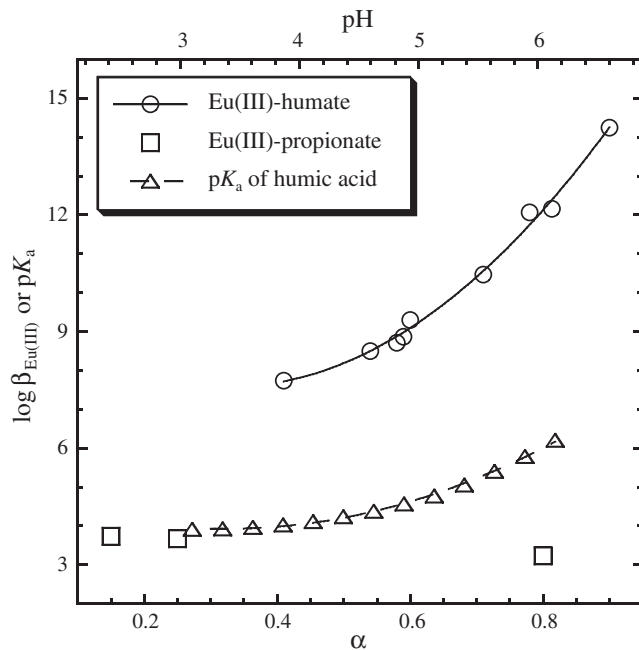


Figure 3. Apparent stability constants of Eu(III)-humate and Eu(III)-propionate at various degrees of ionization (α) at $I_s = 0.10 \text{ M}$ (NaClO_4). Variation of apparent pK_a was also shown.

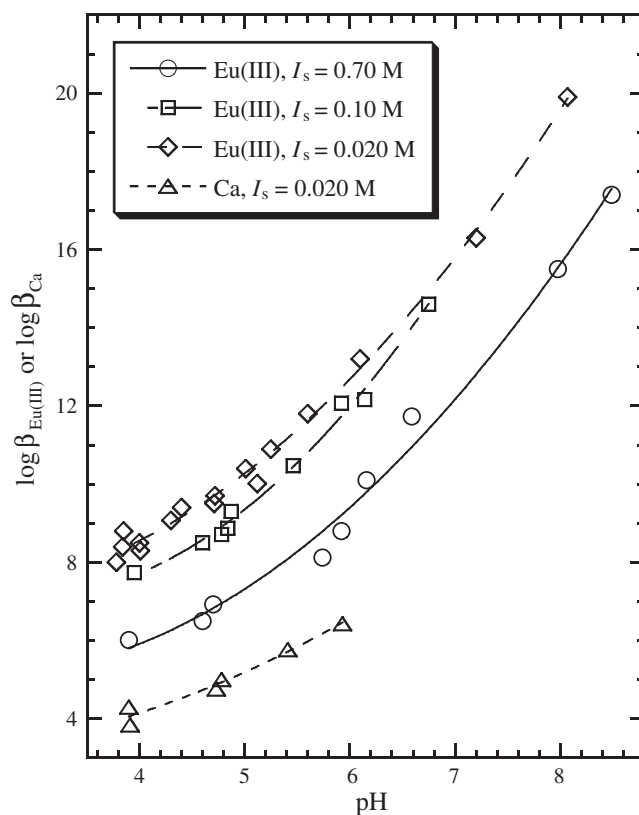


Figure 4. The pH dependence of apparent stability constants of Eu(III)-humate at $I_s = 0.020, 0.10,$ and 0.70 M and Ca-humate at $I_s = 0.020 \text{ M}$.

$$\log \beta_M = \log \beta_{M-int} - 0.434 z e \phi(\alpha)/kT \quad (13)$$

(k : Boltzman constant, e : elementary electric charge, z : charge of metal ion)

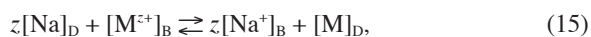
In these equations, pK_{int} and $\log \beta_{M-int}$ are the intrinsic pK_a and $\log \beta_M$, respectively, and $\phi(\alpha)$ is the strength of the electric field in the vicinity of negatively charged humic acid as a function of α . The region at the vicinity of humic acid is called the Donnan phase in the theory. In this paper, only one binding site was assumed in humic acid below pH 8 as the simplest case,

where the dissociation of the phenolate site can be negligible below pH 8. In this case, the variation of pK_{int} and $\log \beta_{\text{M-int}}$ is attributed to the electrostatic effect and that two species of metal ions are considered. One species is directly complexed to the binding site and the other is in the Donnan phase. From eqs 12 and 13,

$$\log \beta_{\text{M}} = \log \beta_{\text{M-int}} + z \int (\text{dp}K_{\text{a}}/\text{d}\alpha) \text{d}\alpha \quad (14)$$

was derived. The relation between pK_{a} and α was obtained empirically as a quadratic function by least squares analysis for the experimental data shown in Figure 1. Based on this relation, the second term in the right hand of eq 14 can be obtained by assuming the valence of the metal ion. This allows us to fit $\log \beta_{\text{M}}$ variation against α . The fitted curves converted to the relationship between $\log \beta_{\text{M}}$ and pH are depicted in Figure 4, showing that the curves derived by assuming z (2 for Ca and 3 for Eu) in eq 14 can simulate the experimental data. The $\log \beta_{\text{Eu-int}}$ and $\log \beta_{\text{Ca-int}}$ values obtained by the fittings were 7.6 and 3.6 at $I_{\text{s}} = 0.020$ M, respectively. The fact that we can simulate the results by eq 14 for Eu(III) and Ca at various I_{s} suggests that electrostatic interaction is important to humate formation.

The I_{s} dependences of $\log \beta_{\text{Eu(III)}}$ and $\log \beta_{\text{Ca}}$ at constant α was shown in Figure 5, where an example at $\alpha = 0.5$ was indicated. This result shows that the stability constants apparently decreased with I_{s} . The decrease was possibly caused by the shielding effect of supporting cations (= Na⁺), showing the presence of electrostatic interaction between metal ions and humic acid. The I_{s} dependence was also explained by the simple electrostatic model. From the charge balance in the Donnan phase, the next equation can be formed:



where D and B denote the Donnan phase and the bulk solution, respectively. The equilibrium constant k_{Na} can be written as ($\text{M} = \text{Eu(III)}$ or Ca)

$$([\text{M}]_{\text{D}}/[\text{M}^{z+}]_{\text{B}}) ([\text{Na}^+]_{\text{B}}/[\text{Na}]_{\text{D}})^z = k_{\text{Na}} \quad (16)$$

to give next equation:

$$z \log ([\text{Na}]_{\text{D}}/[\text{Na}^+]_{\text{B}}) + \log k_{\text{Na}} = \log ([\text{M}]_{\text{D}}/[\text{M}^{z+}]_{\text{B}}). \quad (17)$$

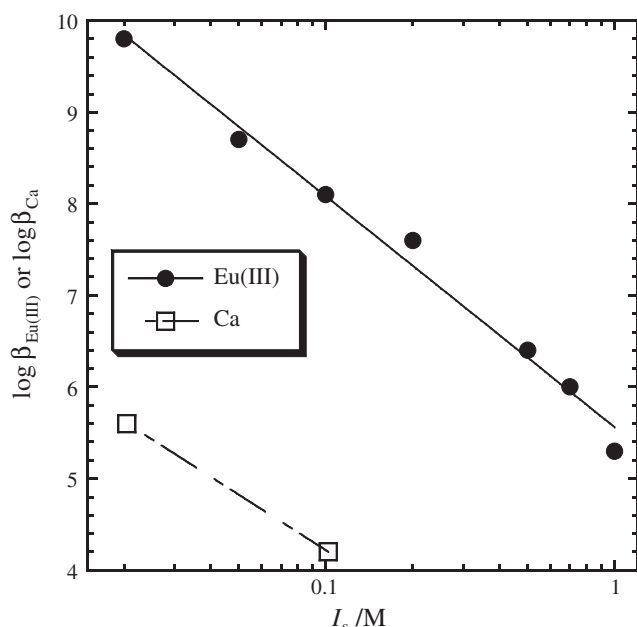


Figure 5. Apparent stability constants of Eu(III)- and Ca-humates at various I_{s} when α (degree of ionization) is 0.5.

$[\text{Na}]_{\text{D}}$ is considered to neutralize the charge of humic acid. Since $[\text{M}]_{\text{t}}$ and $[\text{A}]_{\text{t}}$ are below $n\text{M}$ and meq/dm^3 , respectively, $[\text{Na}]_{\text{D}}$ is considered to be constant, when I_{s} is above 0.020 M. These facts lead to eq 18 at constant α , if we assume that $[\text{M}]_{\text{D}}$ is approximately equal to the total concentration of complexed species of M^{z+} (in other words, $[\text{MA}]_{\text{int}}$ directly bound to binding site of humic acid is negligible compared with $[\text{M}]_{\text{D}}$ under the condition):

$$\log \beta_{\text{M}} = -z \log ([\text{Na}^+]_{\text{B}}) + \log C' \quad (C': \text{constant}). \quad (18)$$

Since $[\text{Na}^+]_{\text{B}}$ is approximately equal to I_{s} , the result in Figure 5 was fitted to eq 18, where the slopes obtained are -2.8 and -2.0 for Eu(III)- and Ca-humate, respectively. These results suggest that most part of Eu(III) apparently bound to humic acid is attracted electrostatically to the Donnan phase of humic acid.

Speciation calculations of Eu(III) considering the pH and I_{s} effects. As shown in Table 2, carbonate species would be the dominant dissolved species of Eu(III) both in fresh water and seawater without taking account of humic substances. The influence of humate formation was estimated based on the stability constants considering the pH and I_{s} effects determined above. From Figure 5, $\log \beta_{\text{Eu(III)}}$ under the conditions of pH and I_{s} in fresh water (pH = 7, $I_{\text{s}} = 0.020$ M) and seawater (pH = 8, $I_{\text{s}} = 0.70$ M) were estimated to be 15.4 and 15.5, respectively. To take account of the influence of humic acid, the concentration of humic acid, or humic substances, in natural water is needed. In fresh water, the concentration of humic substances is $2 - 10 \text{ mg}/\text{dm}^3$.³³ In seawater, the concentration is $0.06 - 2.5 \text{ mg}/\text{dm}^3$.^{34, 35} Therefore, the ranges of $-6 < \log\{[\text{A}]_{\text{total}}/(\text{eq}/\text{dm}^3)\} < -4$ and $-7 < \log\{[\text{A}]_{\text{total}}/(\text{eq}/\text{dm}^3)\} < -4$ are assumed for the concentrations of the ligand of dissolved humic substances in fresh water and seawater, respectively. The estimated values of dissolved species of Eu(III) are shown against the concentration of humic substances for fresh water and seawater in Figure 6, respectively, where the lined area shows the possible condition in natural waters. It is suggested that humate complex may be the predominant species of dissolved Eu(III) species in both fresh water and seawater, as

TABLE 2: Estimated $\log([\text{EuL}_i]/[\text{Eu}^{3+}])$ in Fresh Water and Seawater Considering Carbonate, Hydrolysis, Chloride, Sulfate, and Hydrophosphate

Fresh water ($I_{\text{s}} = 0.020$ M, pH 7)

Ligand	[L]/M	i	$\log([\text{EuL}_i]/[\text{Eu}^{3+}])$
CO ₃ ²⁻	5.1 × 10 ⁻⁷	$i = 1$	1.1
		$i = 2$	-0.7
OH ⁻	1 × 10 ⁻⁷	$i = 1$	-1.3
		$i = 2$	-3.1
Cl ⁻	1.6 × 10 ⁻⁷	$i = 1$	-6.2
SO ₄ ²⁻	1.1 × 10 ⁻⁷	$i = 1$	-5.1
HPO ₄ ²⁻	2.1 × 10 ⁻¹⁰	$i = 1$	-5.5

Seawater ($I_{\text{s}} = 0.70$ M, pH 8)

Ligand	[L]/M	i	$\log([\text{EuL}_i]/[\text{Eu}^{3+}])$
CO ₃ ²⁻	2.4 × 10 ⁻³	$i = 1$	3.5
		$i = 2$	4.9
OH ⁻	1 × 10 ⁻⁶	$i = 1$	0.2
		$i = 2$	0.2
Cl ⁻	5.4 × 10 ⁻¹	$i = 1$	-0.4
SO ₄ ²⁻	2.8 × 10 ⁻²	$i = 1$	0.4
HPO ₄ ²⁻	2.1 × 10 ⁻⁸	$i = 1$	-3.5

Concentrations of the ligands (= L) are also shown.¹⁵

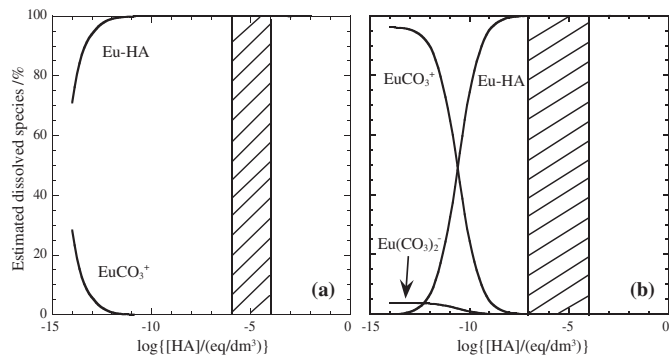


Figure 6. Percentages of dissolved species of Eu(III) in (a) fresh water (pH = 7, $I_s = 0.020$ M) and (b) seawater (pH = 8, $I_s = 0.70$ M) as a function of the concentration of humic substances [A] (eq/dm³) without considering the effect of Ca^{2+} and Mg^{2+} ions. Lined area shows the possible condition of [A] in each system.

compared with any other species. For the purpose of more precise estimation of Eu(III) behavior, however, it is necessary to consider the effect of Ca^{2+} and Mg^{2+} ions.

The influence of Ca^{2+} and Mg^{2+} ions on the stability of Eu(III)-humate. The stability of Eu(III)-humate in the presence of Mg^{2+} or Ca^{2+} ion was also determined by the solvent extraction technique. In the experiments, it is possible that extracted Mg or Ca in the organic phase may interfere with the extraction equilibrium of Eu(III) by DEHP, because the concentration of free (DEHP)₂ in the organic phase was assumed to be constant in the solvent extraction experiments expressed in eq 6. In the extraction reaction by DEHP, Ca is extracted more readily than Mg, since $\log K_{\text{ex}}$ of Mg was reported as -4.45 ,²³ whereas $\log K_{\text{ex}}$ of Ca was determined to be -3.80 in this study. Therefore, the extracted Ca in the organic phase was monitored by adding ⁴⁵Ca tracer to examine the interference caused by the extracted Ca^{2+} ion. In the worst case, about 8% of DEHP in the organic phase formed a complex with Ca at $[\text{Ca}]_i = 1.0$ mM (pH: 5.4, initial $[(\text{DEHP})_2]_0: 1.00 \times 10^{-3}$ M). DEHP bound with Ca in the organic phase was not included as the extracting reagent of Eu(III) and the fraction of free $[(\text{DEHP})_2]$ became 92% in the worst case, where the decrease in concentration of free (DEHP)₂ reduces $\log \beta_{\text{Eu(III)}}$ by only 0.1, which can be neglected in this study. Hence, below pH 5.4, Ca^{2+} ions will not affect the extraction behavior of Eu(III) by DEHP in our experimental system.

As described in the experimental section, the stability constants of Ca- and Eu(III)-humate were determined under identical experimental conditions in the presence of various $[\text{Ca}]_i$. However, it is difficult to determine [A] in the plot of $D_0(1/D_2 - 1/D_1)$ versus [A] (eq 5), when $[\text{Ca}]_i$ is not negligible compared with [A], because the presence of Ca^{2+} ions affect the equilibrium of proton dissociation of humic acid between [HA] and [A] to a great degree at larger $[\text{Ca}]_i$. This situation inhibits the determination of stability constants at larger $[\text{Ca}]_i$, because the ratio $[\text{Eu(III)A}]/[\text{Eu}^{3+}]$ or $[\text{CaA}]/[\text{Ca}^{2+}]$ obtained from $D_0(1/D_2 - 1/D_1)$ must be normalized by [A] in order to obtain β_M . The aim of the present study is the speciation of Eu(III) in the presence of $[\text{Ca}]_i$ above 10^{-4} M level as found in natural waters. For this purpose, it is enough to obtain the ratio $[\text{Eu(III)A}]/[\text{Eu}^{3+}]$ in the presence of Ca^{2+} ions. Therefore, we tentatively determined the ratios of $[\text{Eu(III)A}]/[\text{Eu}^{3+}]$ and $[\text{CaA}]/[\text{Ca}^{2+}]$ when the concentration of humic acid was 100 mg/dm³ (Figure 7). In this calculation, $[\text{Eu}^{3+}]$ and $[\text{Ca}^{2+}]$ in the aqueous phase were determined based on the relations in eqs 1 and 7. As a result, it is clear that $\log([\text{CaA}]/[\text{Ca}^{2+}])$ decreased with $[\text{Ca}]_i$ due to the saturation of binding sites and the shielding effect of the electrostatic potential at the surface of humic acid by added Ca^{2+} . Similarly, $\log([\text{Eu(III)A}]/[\text{Eu}^{3+}])$ decreased with the increase in $[\text{Ca}]_i$. In our experiments, if pH and $[\text{Ca}]_i$ are identical, α and $[\text{CaA}]$ should be identical for the two

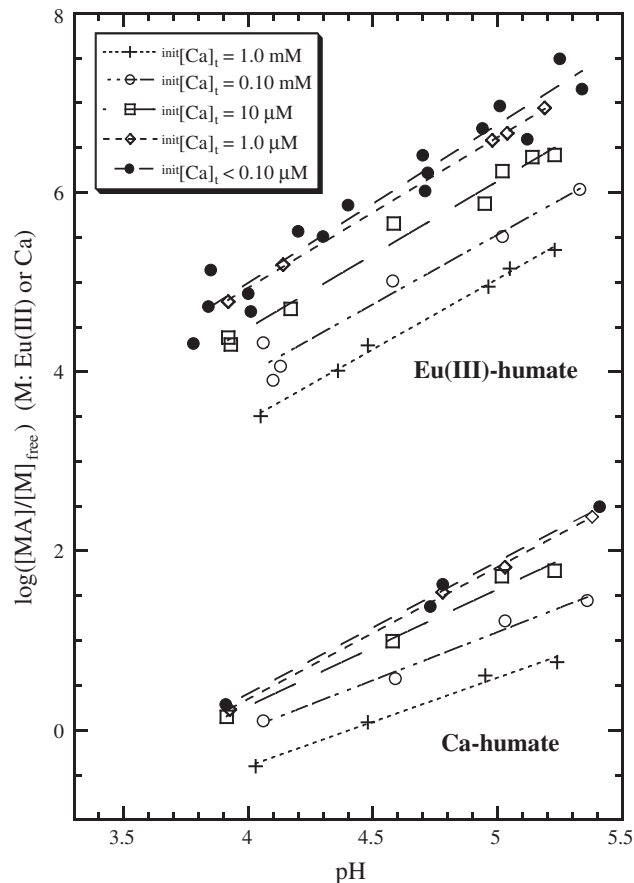


Figure 7. The concentration ratio of Eu(III)- and Ca-humates and free metal ions at various initial concentrations of Ca^{2+} ion ($= \text{ini}[\text{Ca}]_i$) in the aqueous phase when the concentration of humic acid was fixed at 100 mg/dm³.

values, $[\text{Eu(III)A}]/[\text{Eu}^{3+}]$ and $[\text{CaA}]/[\text{Ca}^{2+}]$. Thus, these two series of data ($[\text{Eu(III)A}]/[\text{Eu}^{3+}]$ and $[\text{CaA}]/[\text{Ca}^{2+}]$) can be compared directly, as shown in Table 3. It was found that there is an empirical relationship between $\log([\text{Eu(III)A}]/[\text{Eu}^{3+}])$ and $\log([\text{CaA}]/[\text{Ca}^{2+}])$ as shown in Figure 8, with which speciation calculation in the presence of Ca^{2+} and Mg^{2+} ions will be conducted. In Table 3, $[\text{CaA}]$ must be lower than the total concentration of ligands in humic acid, which was not the case at initial $[\text{Ca}]_i = 1.0$ mM and in pH 4.95 and 5.24. The reason for this is not clear at present, but could be due to the contribution of additional ligands in humic acid, such as phenolate, which were not determined in pH titration.

For Mg^{2+} ions, we have only obtained the $[\text{Eu(III)A}]/[\text{Eu}^{3+}]$ ratio at various $[\text{Mg}]_i$ (Figure 9), showing that $\log([\text{Eu(III)A}]/[\text{Eu}^{3+}])$ decreased with the increase in $[\text{Mg}]_i$. From the data, it was revealed that the effect of Mg^{2+} ion is similar to that of Ca^{2+} .

Speciation calculations of Eu(III) considering the effect of Ca^{2+} and Mg^{2+} ions. For the purpose of more precise estimation of Eu(III) species in natural waters, the effect of Ca^{2+} and Mg^{2+} ions are included in the speciation. In the calculation, it is regarded that the effect of the Mg^{2+} ion is identical to that of the Ca^{2+} ion. First, the fresh water system is considered, where we assume following conditions: pH 7 and concentrations of $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}]$ are 0.1 mM and 0.2 mM, respectively. The lowest concentration of humic acid, $\log\{[\text{A}]_{\text{total}}/(\text{eq/dm}^3)\} = -6$, within the range assumed in this study ($-6 < \log\{[\text{A}]_{\text{total}}/(\text{eq/dm}^3)\} < -4$) was employed in the calculation. In this case, $[\text{Ca}^{2+}] + [\text{Mg}^{2+}] (= 0.3$ mM) is larger than $[\text{A}]_{\text{total}}$ by more than two orders of magnitude, where we can assume that all sites in humic substances are occupied by Ca^{2+} and Mg^{2+} ions (i.e., $[\text{CaA}] + [\text{MgA}] = 10^{-6}$ M). When we assume that the effect of the Mg^{2+} ion is identical to that of the Ca^{2+} ion, $\log([\text{CaA}]/[\text{Ca}^{2+}])$ becomes -2.5 . Based on the empirical relations in Figure 8, $\log([\text{EuA}]/[\text{Eu}^{3+}])$ becomes 1.2, which

TABLE 3: Log([CaA]/[Ca²⁺]) and Log([EuA]/[Eu³⁺]) Values for Various pH and Initial [Ca]_i in the Aqueous Phase

pH	initial [Ca] _i	log([CaA]/[Ca ²⁺])	[CaA]	log([EuA]/[Eu ³⁺])
4.03	1.0 mM	-0.35	0.291 mM	3.50
4.48	1.0 mM	0.09	0.538 mM	4.30
4.95	1.0 mM	0.61	0.789 mM	4.95
5.24	1.0 mM	0.76	0.790 mM	5.36
4.06	0.10 mM	0.11	53.3 μM	4.32
4.59	0.10 mM	0.58	76.3 μM	5.01
5.03	0.10 mM	1.22	91.2 μM	5.51
5.36	0.10 mM	1.45	85.2 μM	6.03
3.91	10 μM	0.15	5.84 μM	4.34
4.58	10 μM	0.99	8.75 μM	5.65
5.02	10 μM	1.72	9.65 μM	6.24
5.23	10 μM	1.78	9.45 μM	6.42
3.93	1.0 μM	0.23	0.451 μM	4.78
4.78	1.0 μM	1.54	0.964 μM	6.25
5.03	1.0 μM	1.82	0.969 μM	6.67
5.38	1.0 μM	2.38	0.971 μM	7.26
3.91	0.10 μM	0.29	0.0660 μM	5.13
4.78	0.10 μM	1.63	0.0977 μM	6.25
4.73	0.10 μM	1.38	0.0960 μM	6.22
5.41	0.10 μM	2.49	0.0997 μM	7.15

*[CaA] + [Ca²⁺] is not equal to initial [Ca]_i when Ca complexed to DEHP in the organic phase is not negligible. Total concentration of ligands in humic acid is 0.61 meq/dm³.

is slightly larger than log([EuCO₃⁺]/[Eu³⁺]), most important inorganic species of Eu(III) in fresh water (Table 2). Considering that the concentration of humic substances assumed in this calculation is at the lowest value, it is suggested that the humate complex is predominant for Eu(III) species dissolved in fresh water even considering the effect of Mg²⁺ and Ca²⁺ ions. This estimation is consistent with the analyses of natural waters which show that rare earth elements are associated with organic materials in fresh water.^{36, 37}

In seawater, the effect of Mg²⁺ and Ca²⁺ ions should be much more intensive, since [Mg]_i and [Ca]_i in seawater are 0.053 M and 0.013 M, respectively. In this case, we employed the largest concentration of humic substances, log{[A]_{total}/(eq/dm³)} = -4, within the range considered in this study for seawater (-7 < log{[A]_{total}/(eq/dm³)} < -4). In this case, we assumed that all the binding sites in the humic substances were occupied by Ca²⁺ and Mg²⁺ ions (i.e., [CaA] + [MgA] = 10⁻⁴ M) due to the much larger concentrations of these ions in seawater compared with those of humic acid and other polyvalent cations. When we assume that the effect of the Mg²⁺ ion is identical to that of the Ca²⁺ ion, log([CaA]/[Ca²⁺]) becomes -2.8. In this case, log([EuA]/[Eu³⁺]) becomes 0.84 according to the relation shown in Figure 8. In seawater, log([EuCO₃⁺]/[Eu³⁺]) = 3.5 and log([Eu(CO₃)₂⁻]/[Eu³⁺]) = 4.9, which shows that the carbonate complex is much more important than humate for the dissolved species of Eu(III) in seawater. In the marine geochemistry of rare earth elements (REE), the REE pattern of seawater is explained by the equilibrium between the carbonate complexation in the aqueous phase and the adsorption on inorganic particulate matters.^{38, 39} By contrast to previous studies on the stability constants of Eu(III)-humate suggesting that humate is the exclusively dominant species for actinides(III) and lanthanides(III) in seawater,^{8, 10} the present results show the importance of the carbonate complex for the dissolved species of lanthanides(III) and actinides(III) in seawater when taking account of the effect of Mg²⁺ and Ca²⁺ ions, because the pres-

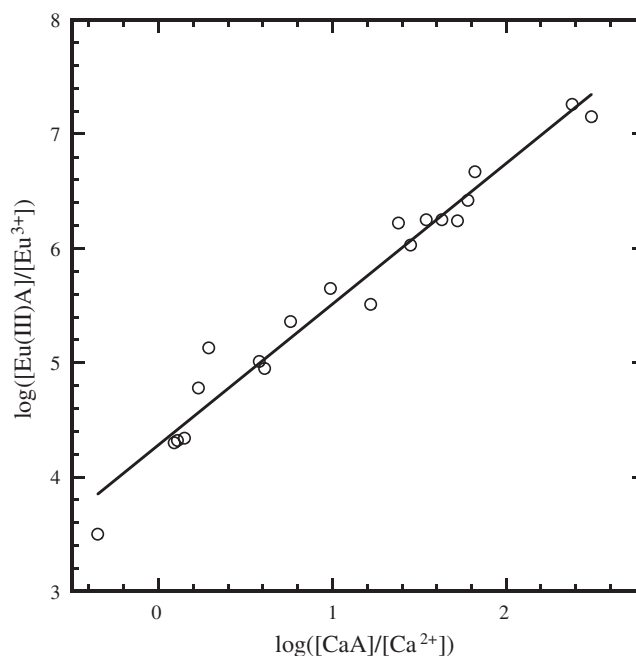


Figure 8. Relationship between log([CaA]/[Ca²⁺]) and log([Eu(III)A]/[Eu³⁺]) at various initial [Ca]_i.

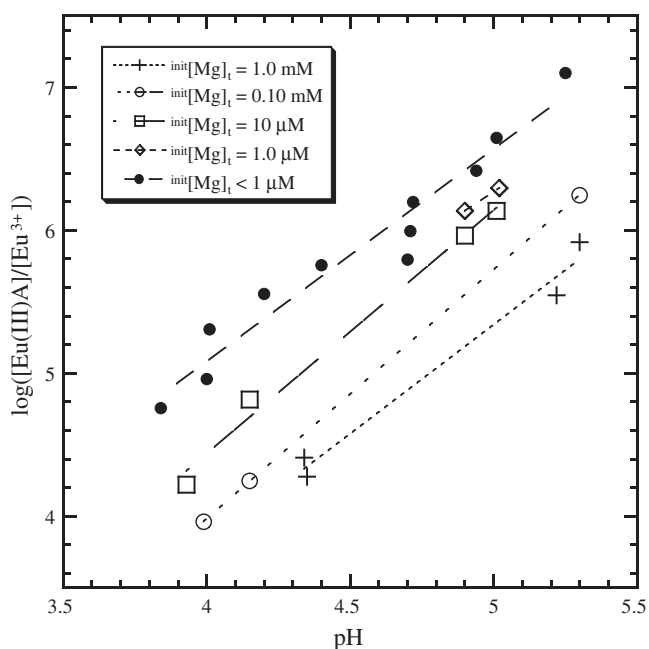


Figure 9. The pH dependence of log([Eu(III)A]/[Eu³⁺]) in the presence of various initial concentrations of Mg²⁺ ion (= [Mg]_i) when the concentration of humic acid was fixed at 100 mg/dm³.

ence of polyvalent cations inhibits the formation of humate complexes with trace metal ions.

5. Conclusions

The stability of Eu(III)-humate complexes at various pH in the presence of Na⁺, Mg²⁺, and Ca²⁺ ions were evaluated. The dependences on pH and concentrations of added cations can be interpreted by considering the polyelectrolyte nature of humic acid. From the stabilities, speciation calculations were conducted for Eu(III) species dissolved in fresh water and seawater. The results showed that humate complex could be the predominant form for lanthanides(III) and actinides(III) in fresh water, where the effects of Mg²⁺ and Ca²⁺ ions are small. In seawater, however, carbonate complex may be more important than humate for the dissolved species of lanthanides(III)

and actinides(III), since Mg^{2+} and Ca^{2+} at 10^{-2} M level inhibit the formation of humate complexes with trace metal ions.

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