Direct observation of Cm(III)-fulvate species on fulvic acid-montmorillonite hybrid by laser-induced fluorescence spectroscopy

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Abstract—Particulate matter plays an important role in the removal of metal ions from water in natural aquifers. Some of the most important of these materials consist of associations of inorganic particles (clay minerals, oxides) with humic substances, associations that can form readily in such an environment due to the strong affinity between inorganic particles and humic substances. These associations are referred to in this paper as organic-inorganic hybrids. However, it is not clear whether the sorbed species of metal ions in such organic-inorganic hybrids are organic or inorganic species because of the complexity of such hybrids and the lack of appropriate methods for characterizing the trace metal ions incorporated in them. In this study, laser-induced fluorescence spectroscopy (LIF) was used successfully to characterize the Cm(III) species on an FA(fulvic acid)-montmorillonite hybrid, an example of such organic-inorganic hybrids. The LIF clearly showed that Cm(III) can be sorbed as Cm(III)-fulvate complex in the FA-montmorillonite hybrid. These results were consistent with those of experiments of solid-water partitioning of Cm(III) (or Eu(III) used as an analogue) and speciation calculations based on the stability constants of Cm(III)-fulvate complexes determined in this study. The results of LIF and the partitioning experiments showed that the solid-water distribution of humic substances governed that of Cm(III) under our experimental conditions. The Cm(III) preference for forming Cm(III)-fulvate complexes was also evident under a condition that would be found in a natural aquifer with a fairly low concentration of organic matter in freshwater (dissolved organic carbon: 2 mg/dm^3), as determined by our speciation calculations. These findings on the importance of humic substances in the migration of Cm(III) indicate that the clarification of the environmental behavior of humic substances is necessary to understand fully the behavior of Cm(III), or actinide(III) and lanthanide(III) ions, in natural aquifers. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

It is recognized that knowledge of the behavior of actinide(III) ions at the earth's surface is of great importance in the management of radioactive wastes containing long-lived actinide(III) ions such as ^{241}Am(III) and ^{244}Cm(III) (e.g., Brookins, 1984). Speciation studies of actinide(III) ions to identify the chemical species present at the earth's surface are indispensable in the clarification of their behavior (Turner, 1995). For this reason, their sorption on clay minerals and complexation with dissolved humic substances (humin, humic acid, and fulvic acid) have been studied widely (Choppin and Allard, 1985; Wimmer et al., 1992; Turner, 1995; Stumm and Morgan, 1996). In some cases it has been assumed that clay minerals play a major role in retaining actinide(III) ions in natural aquifers (e.g., Stumm, 1992; McKinley and Scholtis, 1993). However, this retention effect can be modified by the presence of organic matter such as humic substances. In consideration of the effects of humic substances, emphasis is sometimes placed on their role in extracting metal ions into the aqueous phase and making them more mobile, since humic acid and fulvic acid are water soluble and form stable complexes with metal ions in water. However, the high affinity between humic substances and inorganic particles (such as clay minerals and oxides) indicates

that treating the inorganic particles associated with humic substances as another important phase in the water-rock system would aid in the understanding of the processes governing migration of metal ions. Many studies have dealt with such a ternary system consisting of metal ions, humic substances, and inorganic particulate matter (Righetto et al., 1991; Schulthess and Huang, 1991; Zachara et al., 1994; Ticknor et al., 1996; Takahashi et al., 1998a, 1999a,b). According to Takahashi et al. (1998a, 1999a), who studied the effects of humic substances on the sorption behavior of more than 30 ions, humic substances affect solid-water distributions of lanthanide(III) ions and actinide(III) ions to a greater degree than they affect any other ions. At neutral pH, the solid-water distributions of these ions were similar to those of the humic substances. This suggests that the actinide(III) species sorbed on particulate matter were complexed with humic substances, since actinide(III) ions form stable complexes with humic substances in the aqueous phase and on mineral surfaces. However, little research has been performed on the sorption of actinide(III) ions on clay minerals as species complexed with humic substances. In particular, few studies have involved direct observation of the formation of metal complexes with humic substances at the solid-water interface using appropriate spectroscopic methods. The methods used thus far have been inadequate for identification of metal species in such complex materials as those consisting of clay minerals and humic substances.

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In this study, we used laser-induced fluorescence spectroscopy (LIF) to characterize the species of Cm(III) sorbed on clay minerals in the presence of fulvic acid. LIF is a useful method for investigating the local structure of Cm(III) and Eu(III) in various systems, since it is highly sensitive and selective for Cm(III) and Eu(III) species by the f-f transitions of Cm(III) and Eu(III) fluorescence, providing valuable information on their local structure (Horrocks and Sudnick, 1979; Kimura and Choppin, 1994; Kimura et al., 1996, 2001). With LIF, the number of water molecules in the inner sphere of Cm(III) or Eu(III) can be determined from the lifetime of the fluorescence, and the species can be determined by comparing fluorescence spectra. Moreover, the method can be applied to sorbed species at the solid-water interface even in the presence of water, i.e., samples do not need to be dried before analysis. This is an important advantage, since the drying process may alter the sorbed species on the solid surface. These features of LIF have enabled the estimation of local structures of lanthanide(III) ions and actinide(III) ions at solid-water interfaces in previous studies (Takahashi et al., 1997a, 1998b, 1999b, 2000).

In previous work, LIF was used to examine sorbed species of Eu(III) on montmorillonite in the presence of synthetic polycarboxylic acids (e.g., polyacrylic acid), which served as analogues of humic substances (Takahashi et al., 1999b). It was revealed that Eu(III) can be sorbed on a montmorillonite surface as part of an Eu(III)-polycarboxylate complex. This result suggests that metal ions complexed with humic substances may form an important component of actinide(III) species sorbed on the surface of clay minerals, since their chemical characteristics are similar to those of lanthanide(III) ions. However, it was difficult to identify the sorbed Eu(III) species complexed with natural humic substances in the system, probably due to absorption of light emitted from Eu(III) by the humic substances. In applications of fluorescence properties in speciation studies of actinide(III) and lanthanide(III) ions, Cm(III) is preferable to Eu(III) since the detection limit for Cm(III) is lower than that for Eu(III) by two orders of magnitude, allowing the use of concentrations of Cm(III) that are lower than the concentrations of Eu(III). Hence, the present study involved the use of LIF to examine sorbed species of Cm(III) in a ternary system consisting of Cm(III), montmorillonite, and natural fulvic acid. Montmorillonite was chosen as the natural inorganic adsorbent whereas fulvic acid was used as the humic substances. This study successfully used LIF to observe directly Cm(III)-fulvate formation on the montmorillonite surface. The role of humic substances in the migration of Cm(III) or actinide(III) ions in the environment is also discussed based on these LIF results and on data regarding Cm(III)-fulvate formation equilibrium and Cm(III) sorption on montmorillonite.

2. EXPERIMENTAL

2.1. Materials

Dando Fulvic Acid (DFA), the standard reference material fulvic acid prepared by the Japanese Humic Substances Society, was used in this study. Characterizations of the DFA sample were reported by Watanabe et al. (1989, 1994) and Miyajima and Mori (1996). The ratio of aliphatic carbon and aromatic and olefinic carbon is 0.59 analyzed by ^{13}C-NMR, based on the method recommended by the International Humic Substances Society (International Humic Substances Society, 1981; Watanabe et al., 1994). Stability constants of the Cm(III)-fulvate

complex are reported in this paper. The proton exchange capacity of the DFA was 6.1 meq/g, as determined by pH titration. Montmorillonite was obtained from Nacalai Tesque. The surface area of the montmorillonite was 5.5×10 m^2/g, determined by the BET method (N_2), and its cation exchange capacity (CEC) was 3.0×10^{-1} meq/g, determined by the modified Schöfield method (pH 8, NH$_4$Cl, 2.0 mmol/dm^3) (Takahashi et al., 1998b). Curium-244 (half life: 18.1 yr) supplied by C.E.A. (France) was purified from its daughter nuclide ^{240}Pu by passage through anion exchange resin (AG 1×8) with elution by 7 mol/dm^3 HNO$_3$. The Cm fraction in effluent was fumed to dryness after the addition of concentrated HClO$_4$. The residue obtained was dissolved in 0.01 mol/dm^3 HClO$_4$ to yield the Cm(III) stock solution. The concentration of the Cm(III) in the stock solution was determined by α-ray spectrometry and liquid scintillation counting.

2.2. Experimental Setup and Details of LIF Experiments

The montmorillonite-water ratio was kept constant at 4.0 g/dm^3 throughout the course of this study. The concentration of supporting electrolyte (C_s) was constant at 0.10 mol/dm^3, adjusted with NaCl. Although this salt concentration is rather high compared with normal environmental conditions of freshwater, the experimental condition was constructed to promote the sorption of fulvic acid on montmorillonite, which usually increases with an increase in salt concentration for humic substances (e.g., Takahashi et al., 1998a). In this study, it was intended to identify sorbed Cm(III) species at the time of sorption of humic substances, specifically, the sorption of fulvic acid on montmorillonite. The initial concentration of fulvic acid (before contact with montmorillonite) was 100 mg/dm^3.

We used LIF for the speciation of Cm(III) in three different systems. Two were binary systems consisting of Cm(III) and fulvic acid (Cm/FA system) or Cm(III) and montmorillonite (Cm/mon system). The third system was a ternary system consisting of Cm(III), fulvic acid, and montmorillonite (Cm/FA/mon system). Montmorillonite and/or fulvic acid was mixed with water, and concentrations of montmorillonite, fulvic acid, and NaCl were maintained as shown above. The pH was adjusted by adding a small amount of a NaOH or HCl solution, and each sample was shaken overnight. After remeasuring the pH, the sample was placed in a quartz tube. A small amount of ^{244}Cm(III) solution was injected ([Cm] = 2×10^{-6} mol/dm^3), and the sample was shaken for 2 h. To keep the pH close to the preadjusted value after the injection of the acidic Cm(III) solution, four buffers were added to the solution: sodium acetate (0.0020 mol/dm^3) for pH between 3.7 and 5.3, hydroxylammonium chloride (0.010 mol/dm^3) for pH between 5.5 and 6.7, tris(hydroxymethyl)aminomethane (0.010 mol/dm^3) for pH between 7 and 8.5, and ammonium chloride (0.010 mol/dm^3) for pH between 8.5 and 10.5. The final pH of the solution was not measured since it was necessary to seal the quartz tube right after the injection of the solution containing Cm(III) due to the high radioactivity of Cm(III) in the sample. It is probable that the use of buffers might cause some affect on Cm(III) behavior in the experiments; however, even with acetate, which forms most stable complex with Cm(III) among the buffers used, Cm(III)-acetate is <1% among the Cm(III) species due to the substantial stability of Cm(III)-fulvate complex when calculated from the stability constants of Cm(III)-acetate (Martell and Smith, 1982) and Cm(III)-fulvate. The aim of this study is to compare the Cm(III) species between aqueous and solid phases in the presence of fulvic acid in which the influence of acetate formation is small. This will be proved by the large effect of the addition of fulvic acid on the partitioning of Cm(III) in the batch experiments (Fig. 1.)

The quartz tube containing each sample was exposed to an incident laser beam (395 nm) emitted from a dye laser (PBBO, Lambda Physik SCANmate2) pumped by an XeCl excimer laser (Lambda Physik, COMPex201). For samples from the Cm/FA system, the solution was exposed to the incident laser beam. For the samples from the Cm/mon and Cm/FA/mon systems, the slurry centrifuged to the bottom of the tube was exposed to the beam. The fluorescence at 597 nm emitted from Cm(III) species was measured using a photomultiplier tube (Hamamatsu R3896) with a time-resolved digital oscilloscope (Hewlett-Packard 54510A). The decay curve was fitted by an exponential curve to give the decay constant k (ms^{-1}), the reciprocal of fluorescence decay lifetime τ (k = $1/\tau$). For some samples at higher pH regions, two components were observed in the time spectrum. The
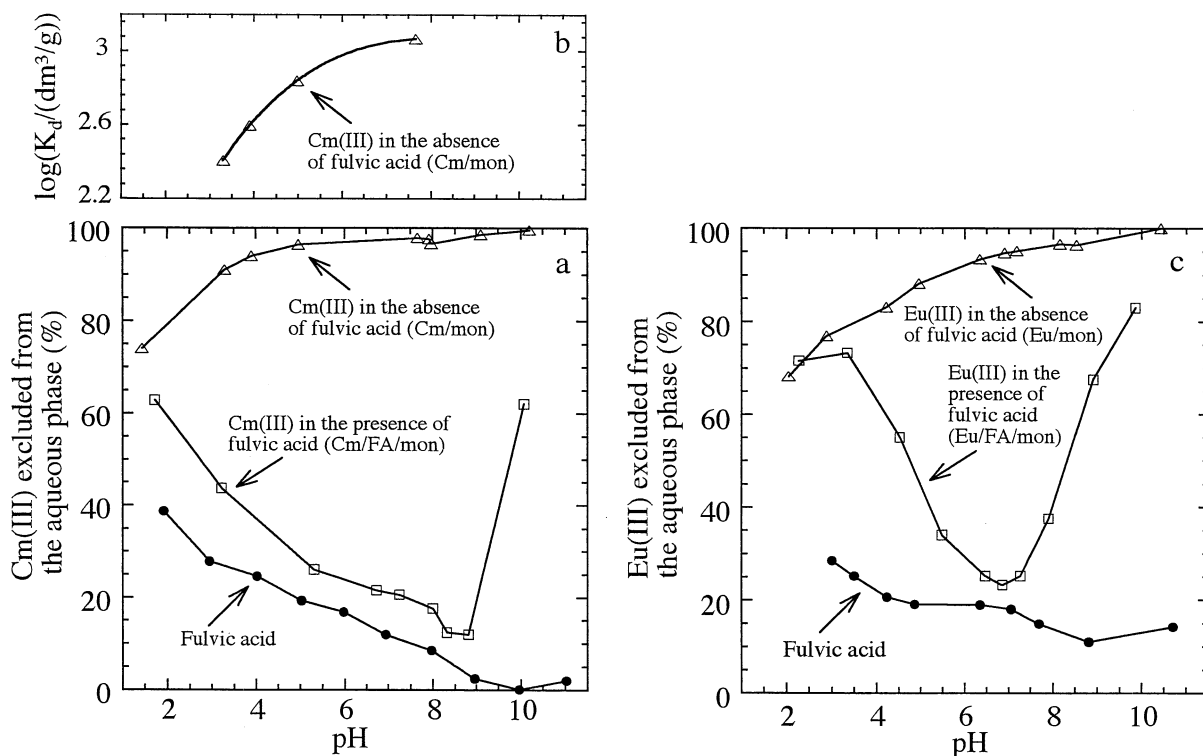
Fig. 1. (a) Fractions of Cm(III) and fulvic acid sorbed on montmorillonite at various pH (C_s = 0.10 mol/dm^3). The figure shows fractions of Cm(III) in the absence and presence of fulvic acid (100 mg/dm^3). Montmorillonite: 4.0 g/dm^3; [Cm(III)]$_{total}$: 2.0×10^{-8} mol/dm^3. (b) Figure 1a was replotted after conversion to log(K_d/(dm^3/g)) values according to Eqn. 1. (c) Fractions of Eu(III) and fulvic acid sorbed on montmorillonite at various pH (C_s = 0.10 mol/dm^3). The figure shows fractions of Eu(III) in the absence and presence of fulvic acid (100 mg/dm^3). Montmorillonite: 4.0 g/dm^3; [Eu(III)]$_{total}$: 2.0×10^{-6} mol/dm^3.

faster component can be assigned to inorganic Cm(III) precipitates, details of which are described under "Results and Discussion." Relative standard deviation of k was < 5%. The emission spectra were recorded using a multiple photodiode array (DIDA-512, Princeton Instruments). Detection of scattered light was avoided by using appropriately timed gate delays (e.g., 1–10 μs). Fulvic acid also has the character of fluorescence, but the lifetime of the fluorescence of humic material is quite small, ~20 ns (Senesi, 1989). The time delay techniques allowed us to obtain selectively the Cm(III) signal.

2.3. Batch Experiments

Samples of the Cm/mon and Cm/FA/mon systems prepared similarly to those used in the LIF experiments were placed in polypropylene test tubes. The Cm concentration was 2×10^{-8} mol/dm^3, which was lower than the LIF experiments, because it was preferred not use the high concentration of Cm in the filtration and measurement of DFA by absorption in the following procedures due to its high radioactivity. The sample was shaken for 48 h, and the aqueous phase of each sample was separated by filtration with a 0.45 μm teflon membrane filter to remove particulate matter. Radioactivity of Cm(III) in the aqueous phase (A_1) was determined with a liquid scintillation counting system. By comparing this value with the initial measured radioactivity of Cm(III) (A_0), the amount of the sorbed fraction of Cm(III) was obtained for samples from the Cm/mon and Cm/FA/mon systems, designated as K_d and K_d', respectively:

$$K_d \text{ or } K_d' \text{ (dm}^3\text{/g)} = (A_0 - A_1)/(R \, A_1), \qquad (1)$$

where R (g/dm^3) is the solid-water ratio, which was 4.0 g/dm^3 in this study. The quenching effect of fulvic acid in liquid scintillation count-

ing was reduced by dilution of the sample. The partitioning of fulvic acid (K_{FA}) was determined from absorbance at 360 nm before (B_0) and after (B_1) contact with montmorillonite as follows:

$$K_{FA} \text{ (dm}^3\text{/g)} = (B_0 - B_1)/(R \, B_1). \qquad (2)$$

To check the effect of difference in Cm concentration between LIF and batch experiments, similar batch experiments were conducted using [152]Eu tracers with a proper amount of Eu carrier ([Eu]$_{total}$ = 2.0×10^{-6} mol/dm^3), based on the analogy of actinide(III) and lanthanide(III). The distribution of Eu(III) was monitored by NaI scintillation counting of [152]Eu.

In the batch experiments, it may happen that some portion of Cm(III) or Eu(III) was sorbed to the polypropylene tube walls at high pH regions, though polypropylene is not active to sorb the inorganic species as glasses. We examined this point by measuring [152]Eu(III) before separation of the particulate matter. As a result, at least 10 to 30% of Eu(III) was removed from the suspension above pH 7. In this study, the batch experiments were conducted to compare Cm(III) behavior in the absence and presence of fulvic acid, in which the predominance of fulvate formation for Cm(III) or Eu(III) species will be shown due to the similarity of the distributions of fulvic acid and Cm(III) or Eu(III). The loss of Cm(III) or Eu(III) to the tube walls was not a serious problem in our aim to show the effect of fulvate formation on Cm(III) behavior. The effect of filtration is similar to this situation. Although filtration by the 0.45 μm filter did not prove to remove all precipitates and colloidal phases, which may have smaller sizes than the filter mesh, this did not pose a problem in comparing the distribution in the absence and presence of fulvic acid when using the same procedure through this work. Considering these limitations, however, the vertical axis of Figure 1a or Figure 1c was indicated as "Cm(III)

excluded from the aqueous phase (%)" to present the results of sorption experiments. Concomitantly, it was revealed that the sorption of fulvic acid by the equipment was little according to the absorbance measurement.

2.4. Stability Constants of Cm(III)-Fulvate Complex

Stability constants of Cm(III)-fulvate complexes, between pH 4.3 and 5.5 at $C_s = 0.10$ mol/dm^3, were determined by means of a solvent extraction method in which di(2-ethylhexyl)phosphoric acid (DEHP) was used as the extractant (Torres and Choppin, 1984; Takahashi et al., 1994). The aqueous phase was a fulvic acid solution containing a buffer reagent. The concentration of fulvic acid ranged from 0 to 50 mg/dm^3. Two buffer reagents were used to maintain the pH of the aqueous phase at the following pH regions: acetic acid (0.0010 mol/dm^3) between pH 4.3 and 5.2, and hydroxylammonium chloride (0.010 mol/dm^3) at pH ~5.5. The organic phase (DEHP/toluene solution) was preequilibrated with a buffer solution, so as not to alter the pH of the aqueous phase. The organic phase and aqueous phase were mixed and spiked with a ^{244}Cm tracer ([Cm] = ~2.0 × 10^{-8} mol/dm^3). The sample solution in a glass vial was shaken at room temperature for 2 d. After centrifugation, the aqueous and organic phases were separated, and the partitioning ratios of Cm(III) were obtained by measuring radioactivity using the scintillation counting system. The concentration of fulvic acid was determined from absorbance.

3. RESULTS AND DISCUSSION

3.1. Partitioning of Cm(III) and Fulvic Acid Between Montmorillonite and Water

Fractions of Cm(III) and fulvic acid sorbed on montmorillonite are shown in Figure 1a. In the absence of fulvic acid, at pH > 4, more than 90% of the Cm(III) was removed from the aqueous phase due to the soption on montmorillonite. In the presence of fulvic acid, less Cm(III) was sorbed, due to the formation of dissolved Cm(III)-fulvate complexes that kept Cm(III) in the aqueous phase. However, some fulvic acid was also sorbed on montmorillonite, although the amount of the fraction of fulvic acid sorbed on montmorillonite decreased with increasing pH. This pH dependence can be interpreted as due to electrostatic interaction between fulvic acid and montmorillonite. As pH increases, negative charges form on fulvic acid and montmorillonite, causing repulsion that inhibits sorption. Despite this repulsive force, a certain amount of fulvic acid was sorbed on montmorillonite even at neutral pH. Hybrid material composed of inorganic particulate matter (e.g., clay minerals, oxides) and polyorganic substances (e.g., fulvic acid) have been widely studied and have been found frequently in natural aquifers (Greenland, 1971; Sholkovitz et al., 1978; Tipping, 1981; Davis, 1982; Stumm, 1992; Stevenson, 1994; Hering, 1995). We refer to the hybrid particulate matter used in this study as FA-montmorillonite hybrid.

The percentages of fulvic acid and Cm(III) removed from the aqueous phase in the Cm/FA/mon system were compared. Between pH 5 and 8, the two values showed similar values. As mentioned above, Takahashi et al. (1998a, 1999a) compared the partitioning of humic substances and 30 different metal ions and observed different levels of stability between the metal ions and the humic substances. From those results, they concluded that lanthanide(III) and actinide(III) ions preferentially complex with humic substances, both as dissolved species in the aqueous phase and as sorbed species at the solid-water interface. Likewise, the similar values for sorbed fractions of fulvic acid and Cm(III) observed in the present study suggest that

Cm(III) exists as a fulvate complex, not only in the aqueous phase, but also on the montmorillonite surface. This estimation of the sorbed species of Cm(III) is supported by the results of batch experiments as described in Section 3.2.

In other pH regions (pH < 3 or 9 < pH), the percentage of sorbed fractions of fulvic acid and Cm(III) were not similar. Above pH 9, the discrepancy between the two percentages shows that Cm(III) species are not fulvate complex but other inorganic complex such as carbonate complexes. This situation is proved from speciation calculation that is found in Section 3.2. If Cm(III) does not form fulvate complex, the partitioning of Cm(III) would be discrepant from that of fulvic acid and should be closer to that of Cm(III) in the Cm/mon system, which is consistent with a point at pH 10 in Figure 1a. Similar behavior was found in other actinide(III) and lanthanide(III) ions (Takahashi et al., 1998a, 1999a). Below pH 3, the two percentages were also discrepant, since fulvate complexation becomes weaker for Cm(III) species as suggested below.

One problem remains in comparing the results of the batch experiments with the LIF data in Section 3.3. In the Cm(III) batch experiments, [Cm(III)] was 2 × 10^{-8} mol/dm^3, whereas it was necessary to employ [Cm(III)] = 2 × 10^{-6} mol/dm^3 for the LIF experiments to obtain a sufficient fluorescence signal. However, we avoided conducting the batch experiments at [Cm(III)] = 2 × 10^{-6} mol/dm^3 due to the safety requirement. To estimate the influence of metal loading on partitioning, similar batch experiments were conducted with ^{152}Eu tracer at [Eu(III)] = 2 × 10^{-6} mol/dm^3 by an analogy of lanthanide(III) and actinide(III). The partitioning of Eu(III) in the system was qualitatively similar except for the lower pH value (8) at which Eu(III) partitioning starts to deviate from that of fulvic acid (Fig. 1c). This is probably due to a decrease in the stability of fulvate complex with the increase in loaded metal ion (Eu) by the shielding effect of the electrostatic field in the vicinity of fulvate complex (e.g., Wilson and Kinney, 1977; Tipping and Hurley, 1992). The decrease in stability may be responsible for the deviation of sorbed Eu(III) fraction in the ternary system from fulvic acid fraction above pH 8. However, the sorbed fraction of Eu(III) was greatly influenced by fulvic acid between pH 5 and 8, suggesting that a considerable amount of Eu(III) is distributed as fulvate complex in the aqueous phase and at the montmorillonite surface even at the high loading of metal ion in the system. This condition may be similar to Cm(III), which reveals that the formation of Cm(III)-fulvate complex occurs in the aqueous phase and at the montmorillonite surface, which will be shown by LIF experiments.

3.2. Estimation of Cm(III) Species Sorbed on Montmorillonite from Results of Batch Experiments

Sorbed species of Cm(III) in the experimental solid-water system was estimated from the results of the simple batch experiments. This was considered from the stabilities of each Cm(III) species in this section. In the presence of fulvic acid, the total concentration of Cm(III) species in the water ([Cm$_t$]$_{aq}$) can be written as:

$$[Cm_t]_{aq} = [Cm^{3+}]_{aq} + \sum[Cm\text{-}L_i]_{aq} + [Cm\text{-}L_{FA}]_{aq}, \quad (3)$$

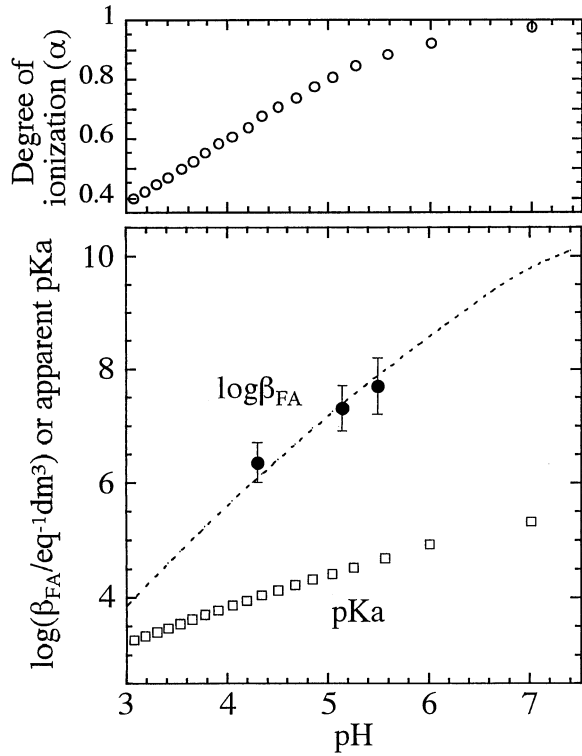where the second term on the right side represents the formation of hydroxide and carbonate complexes, that is,

Fig. 2. The pH dependence of stability constant of Cm(III)-fulvate ($\beta_{FA}/eq^{-1}dm^3$), apparent proton dissociation constant (pKa), and degree of ionization (α).

$\beta_{CmOH}[Cm^{3+}][OH^-], \beta_{CmCO3}[Cm^{3+}][CO_3^{2-}], \beta_{Cm(CO3)2}[Cm^{3+}]$ $[CO_3^{2-}]^2$ and $\beta_{Cm(CO3)3}[Cm^{3+}][CO_3^{2-}]^3$. β_{CmOH}, β_{CmCO3}, $\beta_{Cm(CO3)2}$, and $\beta_{Cm(CO3)3}$ are the stability constants of mono-hydroxide, monocarbonate, dicarbonate, and tricarbonate complexes, respectively. The third term on the right side of Eqn. 3, $[Cm-L_{FA}]_{aq}$, represents the Cm(III)-fulvate complex in the aqueous phase.

To determine the contribution of the Cm(III)-fulvate complex, among all dissolved Cm(III) species, we obtained conditional stability constants of the Cm(III)-fulvate complex ($^{FA}\beta$), according to the method of Torres and Choppin (1984). The $^{FA}\beta$ is defined as:

$$^{FA}\beta \ (eq^{-1}dm^3) = [Cm-L_{FA}]/([Cm^{3+}] [L_{FA}]), \qquad (4)$$

where L_{FA} (eq/dm^3) represents the ligand concentration of fulvic acid expressed as a mole equivalent and determined by pH titration. The relationship between pH and the degree of ionization (α) was determined by pH titration (Fig. 2). $[L_{FA}]$ was obtained by multiplying α by proton exchange capacity (6.1 meq/g) and the concentration of fulvic acid (g/dm^3) at each pH. The distribution ratio of the solvent extractions in the absence and presence of fulvic acid, D_1 and D_2, respectively, are defined as:

$$D_1 = [Cm-DEHP]_{org}/([Cm^{3+}]_{aq} + [Cm-L_a]_{aq}), \qquad (5)$$
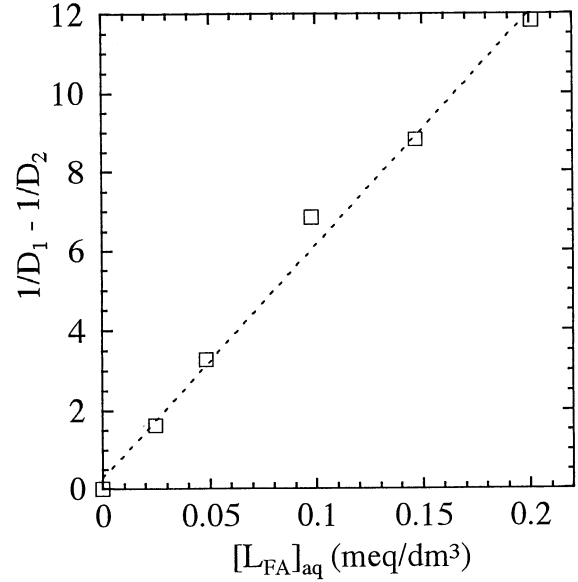
Fig. 3. The plot of $(1/D_2-1/D_1)$ against $[L_{FA}]$, at pH = 5.14. [(DEHP)$_2$]: 2.0×10^{-4} mol/dm^3; C$_s$: 0.10 mol/dm^3.

$$D_2 = [Cm-DEHP]_{org}/([Cm^{3+}]_{aq} + [Cm-L_{FA}]_{aq} + [Cm-L_a]_{aq})$$
$$= 1/(1/D_1 + [Cm-L_{FA}]_{aq}/[Cm-DEHP]_{org}), \qquad (6)$$

where L_a indicates ligands other than fulvate (such as OH^-, CO_3^{2-}, and buffer anions). Subscripts org and aq indicate organic (toluene) and aqueous phases, respectively. This leads to the following equation:

$$D_0 \ (1/D_2 - 1/D_1) = \sum{}^{FA}\beta \ [L_{FA}], \qquad (7)$$

where D_1 and D_2 at various $[L_{FA}]$ were obtained experimentally. In this study, the extraction of fulvic acid to the organic phase was negligible, as revealed by determining the concentration of fulvic acid in the aqueous phase by measuring absorbance. D_0 was obtained experimentally in this study, using the relation $D_0 = K_M \{[(DEHP)_2]/[H]\}^3$, where K_M is an extraction constant determined to be -1.01 (C$_s$ = 0.10 mol/dm^3). $^{FA}\beta$ for Cm(III) was determined at pH 4.30, 5.14, and 5.49, at α values of 0.65, 0.83, and 0.88, respectively. The plot of $(1/D_2-1/D_1)$ against $[L_{FA}]$, at pH = 5.14 and (DEHP)$_2$ concentration of 2.0×10^{-4} mol/dm^3, is shown in Figure 3. This relationship yielded the values of $^{FA}\beta$ shown in Figure 2, which shows that $^{FA}\beta$ increased with increasing pH. This is consistent with the fact that (conditional) stability constants of humic substances generally increase with increasing pH, due to the increase in negative charges on the molecules of humic substances (e.g., Wilson and Kinney, 1977; Torres and Choppin, 1984; Turner, 1995; Takahashi et al., 1994, 1997b). For the speciation calculation, $^{FA}\beta$ at other pH values was estimated based on simple electrostatic theory (Wilson and Kinney, 1977; Takahashi et al., 1997b). This treatment was necessary for estimating the stability constants in the neutral pH region, since it is usually difficult to obtain the stability constants for Cm(III) at neutral pH by the solvent extraction method due to its

Table 1. Thermodynamic data employed in the speciation calculation ($I = 0.10$ mol/dm^3).

Species	$\log\beta$ or $\log K_{sp}$	Ref.
Stability constants	$\log\beta$	
$Cm(OH)^{2+}$	6.67	Wimmer et al. (1992)
$Cm(OH)_2^+$	12.06	Wimmer et al. (1992)
$Cm(CO_3)^+$	6.65	Wimmer et al. (1992)
$Cm(CO_3)_2^-$	9.60	Wimmer et al. (1992)
$Cm(CO_3)_3^{3-}$	10.7	Wimmer et al. (1992)
Solubility product	$\log K_{sp}$	
$CmOHCO_3$	−18.70	Runde et al. (1992)

sorption of Cm(III) tracer on the glassware used in such experiments (Caseci and Choppin, 1983; Torres and Choppin, 1984). If we assume that the pH dependence is completely owing to the electrostatic effect at the vicinity of fulvic acid, the slope of $\log^{FA}\beta$ vs. pH reflects the effective charge of the ion. This assumption provides the relation between $\log^{FA}\beta(pH)$ and $\log^{FA}\beta_{int}$ ($^{FA}\beta_{int}$: the intrinsic stability constant):

$$\log^{FA}\beta(pH) = \log^{FA}\beta_{int} - 0.868\omega z_{Cm}Z, \qquad (8)$$

where ω is the electrostatic interaction factor, z_{Cm} is the effective charge of Cm(III), and Z is the average charge of humic acid at a given pH. A similar relation can be obtained for proton as

$$pKa(pH) = pK_{int} - 0.868\omega z_H Z, \qquad (9)$$

where pK_{int} is pKa and z_H is the effective charge of proton. If we assume that z_{Cm} is equal to k z_H (k: constant), these relations give the next relationship between $\log^{FA}\beta(pH)$ and apparent pKa:

$$\delta\{\log^{FA}\beta(pH)\}/\delta(pH) = k\ \delta\{pKa(pH)\}/\delta(pH). \qquad (10)$$

This allows us to estimate the pH dependence of $\log^{FA}\beta(pH)$, based on the relationship between apparent pKa and pH, which was fitted by a polynominal function. In Takahashi et al. (1997b), describing the stability constants between various metal ions and humic acid, the k value was 2.8 for lanthanide(III) ions, which was also employed in this study because of the chemical similarity of actinide(III) and lanthanide(III) ions. A least square iteration provided the pH dependence of $\log^{FA}\beta$ extrapolated in the range of pH 3 to 7.5 as shown by the dotted line in Figure 2. The increment of $\log^{FA}\beta$ was well fitted by its dependence on pKa using k = 2.8, which supports the validity of the present model. The increase of $\log^{FA}\beta$ vs. pH was assumed to terminate at pH 7.5, at which the fulvic acid was completely dissociated.

We can estimate the Cm(III) species in the aqueous phase in our experimental system based on values of β_{CmOH}, β_{CmCO3}, $\beta_{Cm(CO3)2}$, and $\beta_{Cm(CO3)3}$ reported in the literature (Table 1) and the $^{FA}\beta$ (Fig. 2). The concentration of FA remaining in the aqueous phase was used in the calculation. The contribution of carbonate formation was calculated by assuming an air-equilibrium condition (0.035% CO_2 partial pressure). The results show that the Cm(III)-fulvate complex is the dominant species in the aqueous phase of our experimental system below pH 9 (Fig. 4a):

$$[Cm_t]_{aq} \approx [Cm\text{-}L_{FA}]_{aq}, \qquad (3)'$$

Since it is not necessary to consider dissolved Cm(III) species other than fulvate in the pH region, the solid-water partitioning of Cm(III) in the presence of fulvic acid can be written as:
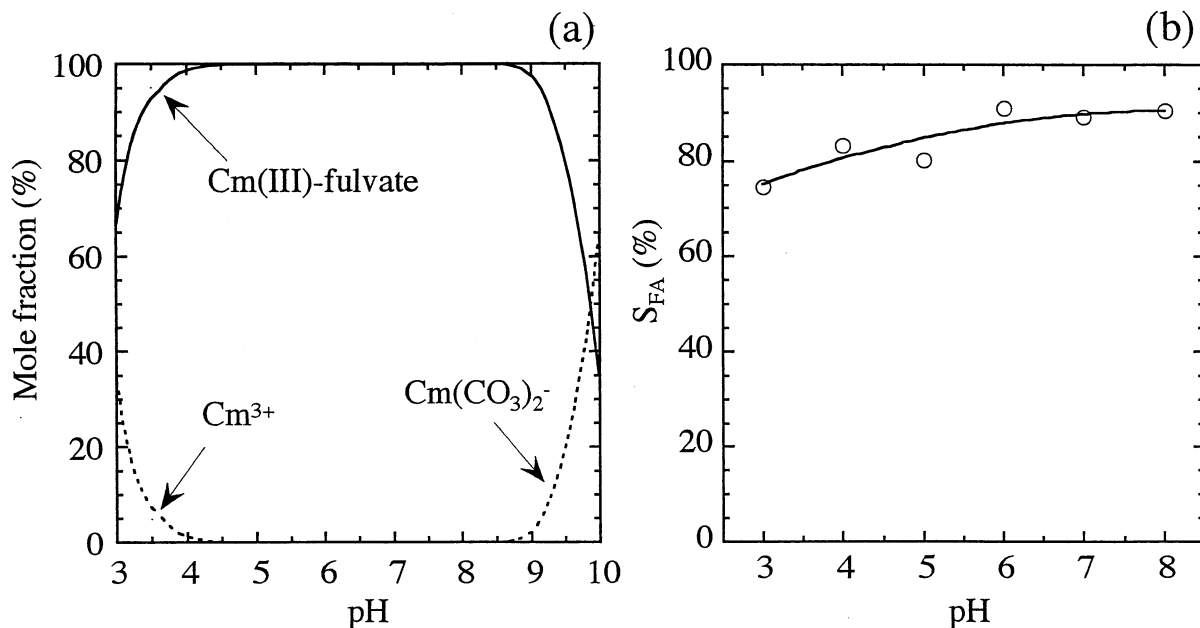

Fig. 4. (a) Dissolved Cm(III) species in the aqueous phase of our experimental system (fulvic acid: 100 mg/dm^3; $C_s = 0.10$ mol/dm^3), estimated from stability constants. (b) The pH dependence of the percentage of Cm(III) species sorbed on montmorillonite, which are in the form of Cm(III)-fulvate complexes, noted as S_{FA}, and based on Eqn. 13.

$$K'_d \ (dm^3/g) = [Cm\text{-}L_{FA}]_{aq}/\{R \ ([Cm\text{-}L_{FA}]_{sorb} + \sum[Cm\text{-}L_j]_{sorb})\}, \tag{11}$$

where $[Cm\text{-}L_j]_{sorb}$ is the concentration of inorganic Cm(III) species sorbed on the solid phase, and the subscript sorb indicates the species sorbed on the solid surface. If we assume that the stabilities of the Cm(III)-fulvate complex in the aqueous phase and at the montmorillonite surface are similar (Davis, 1984), the solid-water partitioning of Cm(III)-fulvate complex can be expressed as K_{FA}:

$$K_{FA} \ (dm^3/g) = [Cm\text{-}L_{FA}]_{aq}/(R \ [Cm\text{-}L_{FA}]_{sorb}). \tag{12}$$

From Eqn. 11 and 12, we could estimate the contribution of Cm(III)-fulvate among the sorbed Cm(III) species (S_{FA}) as:

$$S_{FA} \ (\%) = [Cm\text{-}L_{FA}]_{sorb}/([Cm\text{-}L_{FA}]_{sorb} + \sum[Cm\text{-}L_j]_{sorb})$$

$$= 100 \ K'_d/K_{FA}. \tag{13}$$

The pH dependence of S_{FA} was shown in Figure 4b, in which we see that the Cm(III)-fulvate complex accounts for > 80% of the sorbed species of Cm(III) on the montmorillonite surface. This figure also shows that the contribution of Cm(III)-fulvate complex is less at lower pH. These results suggest that the Cm(III)-fulvate complex is an important component of the sorbed species on montmorillonite, given the assumption that the stability of Cm(III)-fulvate complex on the solid surface is equal to its stability in the aqueous phase. The sorbed species of Cm(III) were directly observed by LIF, as described in the next section.

3.3. Speciation of Cm(III) Sorbed on Montmorillonite by LIF

From LIF measurements, decay constants of Cm(III) fluorescence (k/ms^{-1}) and fluorescence spectra of Cm(III) were deduced in the present study. k is the reciprocal of fluorescence lifetime, τ (i.e., $k = \tau^{-1}$). The pH dependence of the k values of Cm(III) species was plotted for the three systems (Cm/FA, Cm/mon, and Cm/FA/mon) in Figure 5. In the Cm/FA system, k decreases from 15 to 9.5 as pH increases from 2 to 9. When OH vibration of water molecules hydrated to Cm(III) is the main mechanism for the deexcitation of Cm(III), the number of water molecules in the inner sphere of Cm(III), N_{H2O} can be deduced using the following equation (Kimura and Choppin, 1994; Kimura et al., 1996):

$$N_{H2O} = 0.65 \ k - 0.88. \tag{14}$$

Using this equation, we found the value of N_{H2O} for Cm(III) to be ~9 at pH 2 in the Cm/FA system. This result indicates that Cm(III)-fulvate complex does not form at pH 2, since the aqua complex of Cm(III) has ~9 water molecules in the inner sphere (Kimura and Choppin, 1994). A decrease in N_{H2O} to a value < 9 above pH 3 (or an increase in fluorescence lifetime) indicates the formation of an inner-sphere Cm(III) complex with fulvic acid as a dissolved species in the Cm/FA system. Kim et al. (1991, 1993) extensively studied the complexation of Cm(III) with humic substances in the aqueous phase using LIF techniques, demonstrating increased Cm(III) fluorescence lifetime
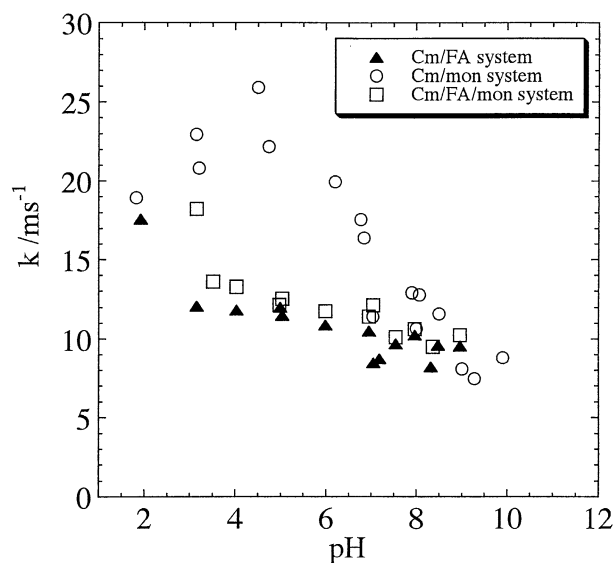

Fig. 5. The pH dependence of k values [= reciprocal of Cm(III) fluorescence lifetime] for Cm(III) species in three systems: Cm(III)-fulvate (Cm/FA), Cm(III) species sorbed on montmorillonite (Cm/mon); Cm(III) species sorbed on FA-montmorillonite hybrid (Cm/FA/mon). Total concentrations of Cm(III), fulvic acid, and montmorillonite are 2.0×10^{-6} mol/dm^3, 100 mg/dm^3, and 4.0 g/dm^3, respectively.

as a result of complexation with humic substances. Their results are similar to those observed in this study.

In the other binary system, Cm/mon, k increased with increasing pH from pH 2 to 4.5, whereas k decreased with increasing pH above pH 4.5. Below pH 7, the k value for Cm(III) sorbed on montmorillonite was > 15.2, meaning that N_{H2O} values for the Cm(III) species were greater than the hydration number of Cm(III), i.e., 9. This is an unlikely occurrence, and such relatively large k values may be caused by the quenching of Cm(III) fluorescence by montmorillonite. Similar phenomena of quenching by solid surfaces have been observed for Eu(III) sorbed on montmorillonite (Takahashi et al., 1998b) and Eu(III) sorbed on zeolite (Suib et al., 1984).

The k values in the ternary system, Cm/FA/mon, were compared with those in the systems Cm/FA and Cm/mon. The values in the ternary system were found to be similar to those in the Cm/FA system at pH values between 5 and 8. There is a possibility that the species we observed in the ternary system did not represent Cm(III) sorbed on the solid phase, but rather Cm(III) in fulvate complexes dissolved in a small amount of aqueous phase contained in the slurry of the solid phase. The amount of water in the slurry was estimated from the weight change of the slurry due to drying, and the solid/water ratio of the slurry was found to be > 250 g/dm^3. In our batch experiments (Fig. 1a), the solid/water ratio was kept at 4.0 g/dm^3. The increase of the solid/water ratio by the centrifuge indicates that > 90% of Cm(III) was sorbed in the slurry even if only 12% of the Cm(III) was sorbed in the batch experiments, which was the lowest value obtained for the ternary system in Figure 1a ([Cm] = 2.0×10^{-8} mol/dm^3). The loaded Cm(III) in LIF experiments ([Cm] = 2.0×10^{-6} mol/dm^3) is greater than that shown in Figure 1a, which would increase the sorbed fraction of Cm(III) in LIF experiments as suggested from the Eu(III)

batch experiments at $[Eu] = 2.0 \times 10^{-6}$ mol/dm^3 (Fig. 1c). Thus, the Cm(III) we observed in the slurry by LIF consisted of Cm(III) species sorbed on the solid surface.

The similarity of k values between the Cm/FA and Cm/FA/ mon systems (between pH 5 and 8) indicates that the Cm(III) species sorbed on the particulate matter were components of Cm(III)-fulvate complexes. Since it is to be assumed that the particulate matter consists of FA-montmorillonite hybrid, the present results indicate that in this hybrid, the complexing site for sorbed Cm(III) in fulvic acid is more stable than the complexing site in montmorillonite. This result is worthy of note, since few previous studies have identified the metal species sorbed on such organic-inorganic hybrids by direct spectroscopic methods. Our results clearly show that humic substances modify the sorption characteristics of inorganic particles by combining with them to form organic-inorganic hybrids. This points to a significant role for such organic material in the removal of metal ions from water by natural particulate matter, especially actinide(III) and lanthanide(III) ions.

The dominance of the Cm(III)-fulvate complex among the sorbed species, as revealed by LIF, is consistent with the results in the previous section regarding an estimation of the sorbed species (Fig. 4b). The estimation also indicates that 10 to 20% of Cm(III) is sorbed as inorganic species. This is probably related to the fact that k values in the ternary system are slightly greater than those in the Cm/FA system between pH 5 and 8. A relatively large difference in k between the Cm/FA/mon and Cm/FA systems at pH < 4 is due to an increase in the amount of inorganic Cm(III) species sorbed on montmorillonite as estimated in Figure 4b.

Similar results were obtained from fluorescence spectra (Fig. 6). At pH 3.2, the spectrum of the Cm/FA/mon system has a shoulder at the peak wavelength of the Cm/mon system, and its main peak coincides with that of the Cm/FA system. This indicates that Cm(III) sorbed directly on montmorillonite, and Cm(III) sorbed as fulvate complex coexist on the particulate matter. This is consistent with the fact that at pH 3.2, the k values are intermediate between those for Cm(III)-fulvate species and those for inorganic Cm(III) species sorbed on montmorillonite. At pH 7.3, no contribution from inorganic Cm(III) species sorbed on montmorillonite is detected, indicating that the Cm(III)-fulvate complex is the dominant Cm(III) species sorbed on the FA-montmorillonite hybrid.

There is a concern about the solubility of Cm(III) in the LIF experimental system at $[Cm] = 2.0 \times 10^{-6}$ mol/dm^3. Since there are no reliable data on the solubility product (K_{sp}) for Cm(III), the formation of Cm(III) precipitates was estimated based on Am(III) solubility data. Under 0.035% CO$_2$ partial pressure, CmOHCO$_3$ may be found as solid phase in oversaturation condition based on $\log K_{sp} = -18.7$ reported for AmO-HCO$_3$ (Runde et al., 1992). As a result, some portions of Cm(III) may form solid phase between pH 8.4 and 9.5 (Fig. 7). In LIF experiments, the formation of inorganic Cm(III) precipitates can be shown by the appearance of a Cm(III) emission component having a short lifetime. Estimated from similar behavior in Eu(III) fluorescence, this phenomenon is probably due to the quenching of Cm(III) fluorescence by energy transfer among Cm(III) ions when Cm(III)-Cm(III) distance is small as in inorganic precipitates (Takahashi et al., 1998b). In our ex-
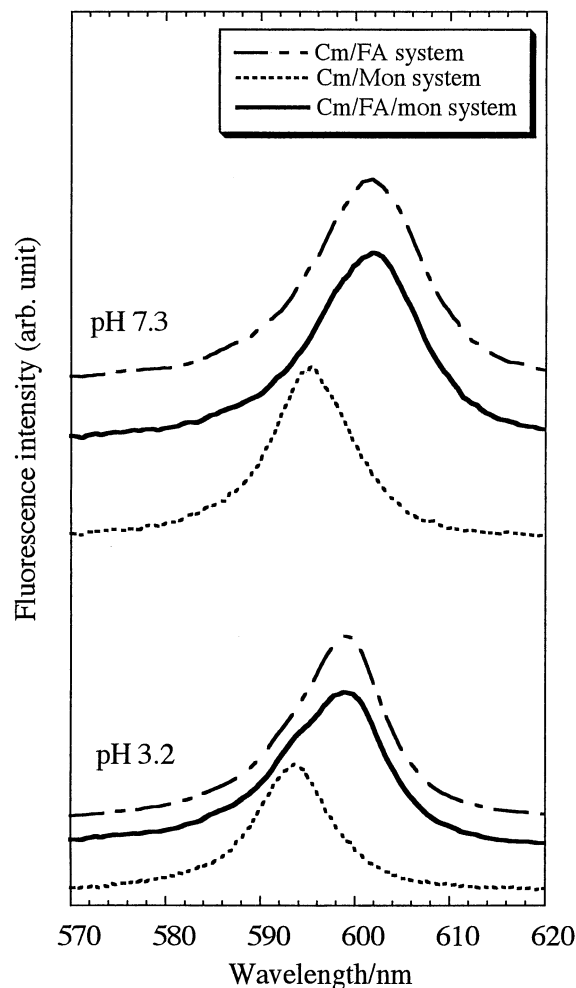

Fig. 6. Fluorescence spectra of Cm(III) species in three systems: Cm(III)-fulvate (Cm/FA), Cm(III) species sorbed on montmorillonite (Cm/mon), and Cm(III) species sorbed on FA-montmorillonite hybrid (Cm/FA/mon). Total concentrations of Cm(III), fulvic acid, and montmorillonite are 2.0×10^{-6} mol/dm^3, 100 mg/dm^3, and 4.0 g/dm^3, respectively.

perimental system, such a short lifetime was observed at $\sim$ pH 9 in the Cm/mon system (Fig. 8). The component can be separated from Cm(III) species showing a larger lifetime, which may be Cm(III) species at the water-montmorillonite interface. The component with a shorter lifetime in the Cm/FA/mon system was not observed clearly when compared with Cm/mon system at $\sim$ pH 8.4 to 8.5 (Fig. 8). This suggests that fulvate formation prevents the formation of inorganic Cm(III) precipitates in the Cm/FA/mon system, which also supports the idea that the fulvate complex is the dominant species in the Cm/FA/mon system.

3.4. Speciation of Cm(III) in a Solid-Water System

Based on calculation of equilibrium, we can estimate Cm(III) species in our experimental system and in the natural environment, taking into account the effects of solid media. From the results of batch experiments on the Cm/mon system, we can
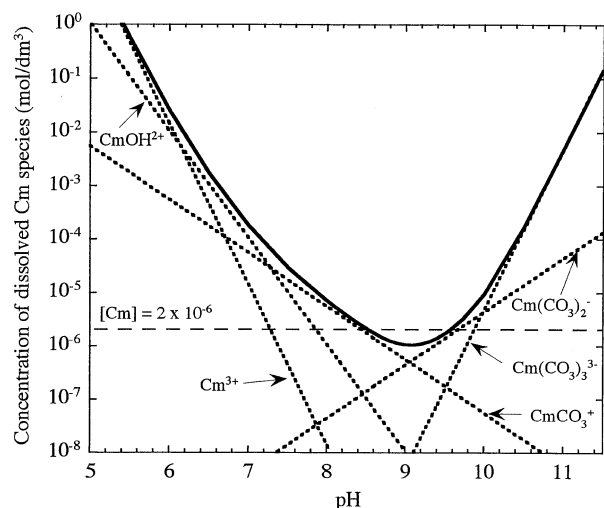
Fig. 7. Solubility of Cm(III) in our experimental system based on the stability constants and solubility product as shown in Table 1. The solid phase was assumed to be $CmOHCO_3$, whereas the partial pressure of CO_2 was fixed at 350 ppm.

obtain partitioning coefficients (K_d/dm^3g^{-1}) for the sorption reaction as follows:

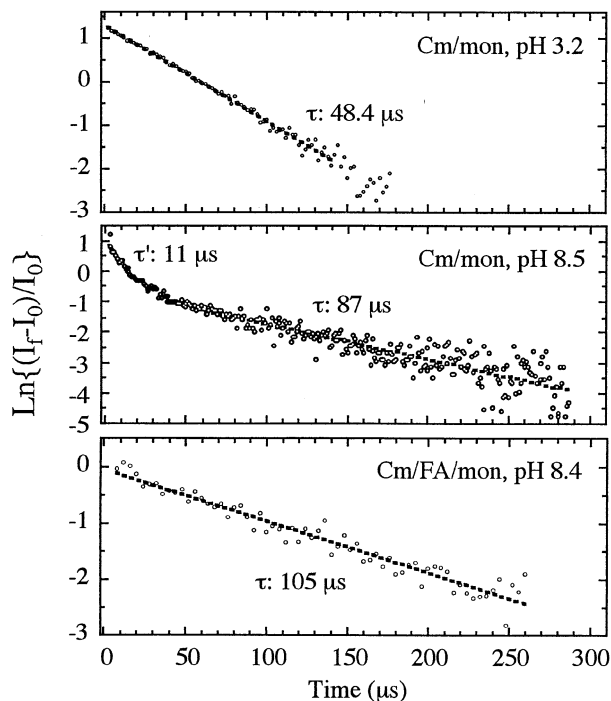$$K_d \, (g/dm^3) = ([Cm\text{-}L_j]_{sorb}/[Cm_t]_{aq})/R. \tag{15}$$

Fig. 8. Time spectra of Cm(III) in Cm/mon and Cm/FA/mon systems. I_0 is the background signal of the photomultiplier tube, whereas I_f is the fluorescence intensity (mV) detected by the photomultiplier tube. Total concentrations of Cm(III), fulvic acid, and montmorillonite are 2.0×10^{-6} mol/dm^3, 100 mg/dm^3, and 4.0 g/dm^3, respectively. Lifetime (τ) is shown, and shorter lifetime component found in Cm/mon system at pH 8.5 was also shown as τ'.
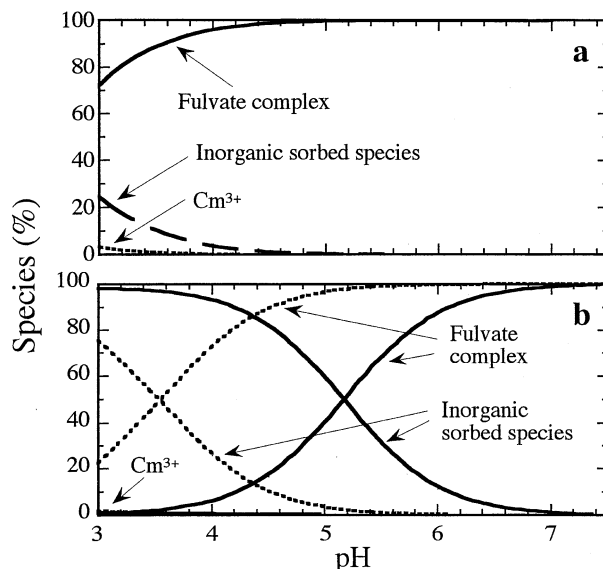

Fig. 9. Speciation calculations for Cm(III) in the ternary system containing Cm(III), fulvic acid, and montmorillonite, assuming the following: (a) the conditions of the partitioning experiments in this study ([fulvic acid]: 100 mg/dm^3; [montmorillonite]: 4.0 g/dm^3); (b) assuming two natural aquifers: [DOC] = 51 mg/dm^3 and [SPM] = 19 g/dm^3 or [DOC] = 2 mg/dm^3 and [SPM] = 38 g/dm^3. DOC, dissolved organic carbon; SPM, suspended particulate matter. In these calculations, we assumed that DOC and SPM have similar characteristics (e.g., proton exchange capacity, affinities to cations) to fulvic acid and montmorillonite employed in this study, respectively. It is also assumed that the concentrations of DOC and SPM are equal to those of fulvic acid and montmorillonite.

The pH dependence of the K_d value is shown in Figure 1b for pH lying between 3 and 8. Using Eqn. 3 and 15, we can estimate the concentration of inorganic sorbed species, [Cm-$L_j]_{sorb}$, as follows:

$$[Cm\text{-}L_j]_{sorb} = K_d \, R \, (1 + \sum \beta_i [L_i]_{aq})[Cm^{3+}]_{aq}. \tag{16}$$

Eqn. 3, 4, and 16 allow us to estimate the concentration ratios of Cm(III) species (free ions, fulvate complex, dissolved inorganic complexes, and inorganic sorbed species) in a solid-water system under our experimental conditions and in a natural aquifer system. In this estimation, we do not distinguish between fulvate species in the aqueous phase and those sorbed on the montmorillonite surface. In addition, we consider the stability constants of Cm(III)-fulvate complex in the aqueous phase and the solid phase to be identical as a first approximation (Davis, 1984). Hence, if the speciation calculation shows that fulvate complex is the dominant species in the system, then Cm(III) exists as fulvate complex in the aqueous phase or on the montmorillonite surface.

Figure 9a shows the results of speciation calculation for the present experimental system. The figure shows that the fulvate complex is the dominant Cm(III) species above pH 5, whereas other inorganic species (free ions and inorganic sorbed species) make significant contributions below pH 5. This is consistent with the LIF results, i.e., k values for the Cm/FA/mon and Cm/FA systems are similar above pH 5, whereas k values for the Cm/FA/mon system lie between those for the Cm/FA and Cm/mon sys-

tems below pH 5. The latter result shows that the Cm(III) species on the FA-montmorillonite hybrid consist of a mixture of fulvate complex and inorganic species interacting directly with the montmorillonite surface. A similar finding was suggested by the results of an estimation of sorbed species (Fig. 4b).

Since the results of the speciation calculation agreed well with the results of the present partitioning experiments, a similar calculation was used to estimate Cm(III) species in a natural aquifer. Turner (1995) reported the concentration ranges of dissolved organic matter (DOC) and suspended particulate matter (SPM) as 2 to 100 mg/dm^3 and 0.08 to 38 g/dm^3, respectively, in freshwater. In this calculation, we assume that DOC and SPM mainly consist of fulvic acid and montmorillonite, respectively. Using the medians of these values (DOC, 51 mg/dm^3; SPM, 19 g/dm^3) as representative of the environment, we obtained the speciation calculation shown in Figure 9b by setting the concentrations of fulvic acid and montmorillonite equal to those of DOC and SPM, respectively. This figure shows that fulvate complex can be the dominant species of Cm(III) in a natural aquifer with characteristics that conform to those of this calculation. Even when we set the ratio of DOC to SPM at the lowest value within the range of Turner's data (DOC, 2 mg/dm^3; SPM, 38 g/dm^3), complexation with humic substances was still found to be the source of the dominant Cm(III) species in a natural aquifer at neutral pH (Fig. 9b). These results suggest that the solid-water distribution of Cm(III), or other trivalent actinides, is affected greatly by the activity of humic substances, even in the presence of a solid phase like montmorillonite. Furthermore, the present study indicates that species complexed with humic substances are not only important as dissolved species but also as species sorbed on particulate matter in the environment.

3.5. Geochemical Implications for Cm(III) Migration

The results obtained here, using LIF, clearly show that Cm(III) can be sorbed as a component of fulvate complex onto particulate matter composed of fulvic acid and montmorillonite, which we refer to as an organic-inorganic hybrid. In other words, fulvic acid and other humic substances (such as humin and humic acid) play significant roles in the sorption of metal ions on particulate matter in natural aquifers. This finding is consistent with estimations from partitioning experiments and speciation calculations in this study, which show that Cm(III) can exist as a component of fulvate complex in the aqueous phase and on the solid surface. This situation may be independent of the concentration of humic substances. The sorption of humic substances on the solid media can be Langmuir-type in which the maximum sorption is attained at rather low concentration of humic substances in the aqueous phase (e.g., 5 mg/dm^3) (Murphy et al., 1992; Schlautman and Morgan, 1994; Takahashi et al., 1998a). This means that the solid media can accumulate the humic substances until the maximum sorption is reached. Therefore, the sorption of Cm(III) as the complex with humic substances is possible even in an environment with low concentrations of humic substances.

This means that the distribution of humic substances can determine the solid-water distribution of Cm(III) if the concentration of humic substances in the natural system is large enough. For example, sorption of Cm(III) or other actinide(III)

or lanthanide(III) ions is promoted in an environment where there is a high degree of sorption of humic substances onto active mineral surfaces. This situation is depicted in Figure 10, where we take into account the influence of solid media on the fate of Cm(III), based on the results of laboratory studies and speciation calculations in the present study. In a system without humic substances, the solid-water distribution of Cm(III) would be determined by the degree of aqueous complexation with carbonate and hydrolysis and sorption on "neat" mineral surfaces not coated with humic substances (Fig. 10a). However, even in a freshwater system with a very low concentration of humic substances, complexation with humic substances would still have an important effect on the distribution of Cm(III) species, as shown in the speciation calculations in this study (Fig. 10c). One theoretical possibility is the system shown in Figure 10b, in which there is competition between humate formation in the aqueous phase and sorption on the mineral surface. The present results, however, indicate that a more accurate model is shown in Figure 10c, in which the distribution of humic substances governs the distribution of metal ions such as actinide(III) and lanthanide(III) ions, depending on the affinity of humic substances with various solid media. Thus, to estimate the environmental behavior of actinide(III) and lanthanide(III) ions, we need to study the behavior of humic substances in the environment. The behavior of humic substances is controlled by various factors. The composition of humic substances at each site, i.e, the ratio of humin, humic acid, and fulvic acid fractions, is likely to be an important factor, since different humic substances show quite different behavior in water-rock interactions. Other factors may include properties of humic substances in various environments (molecular weight, origin of the humic substances, etc.), affinities of humic substances for various minerals and oxides, and the characteristics of the water at each site (pH, salinity, redox conditions). For example, differences in flocculation behavior among various humic substances can result in different effects on the solid-water distribution of lanthanide(III) ions (Takahashi et al., 1998c). The present results indicate that a fuller characterization of the behavior of humic substances will, in turn, contribute to a better understanding of the behavior of actinide(III) and lanthanide(III) ions in the environment. Information about the behavior of lanthanide elements in natural water-rock systems (particularly the relationship with solid-water partitioning of humic substances) will likely be important in developing methods for assessing the environmental behavior of actinide(III) ions.

4. SUMMARY

Laser-induced fluorescence spectroscopy (LIF) was used successfully to characterize the Cm(III) species sorbed on a fulvic acid-montmorillonite hybrid (organic-inorganic hybrid). It is worth noting that the Cm(III) species sorbed on the montmorillonite as fulvate complex were identified directly using LIF. These results show that the species complexed with humic substances are important not only as dissolved species but also as species sorbed on particulate matter. The results of the Cm(III) partitioning experiments, in which the partitioning of Cm(III) was observed to be similar to that of fulvic acid, and the speciation calculations suggest that the solid-water distri-

In the presence of humic substances

b Humic substances

Complexation with humic substances in the aqueous phase

Cm(III)

Sorption on mineral surface

Mineral surface

Competitive

In the absence of humic substances

a Carbonate, hydrolysis

Complexation in the aqueous phase

Cm(III)

Sorption on mineral surface

Mineral surface

Competitive

c Humic substances

Complexation with humic substances in the aqueous phase

Cm(III)

Sorption on mineral surface as complexed species with humic substances

Mineral surface

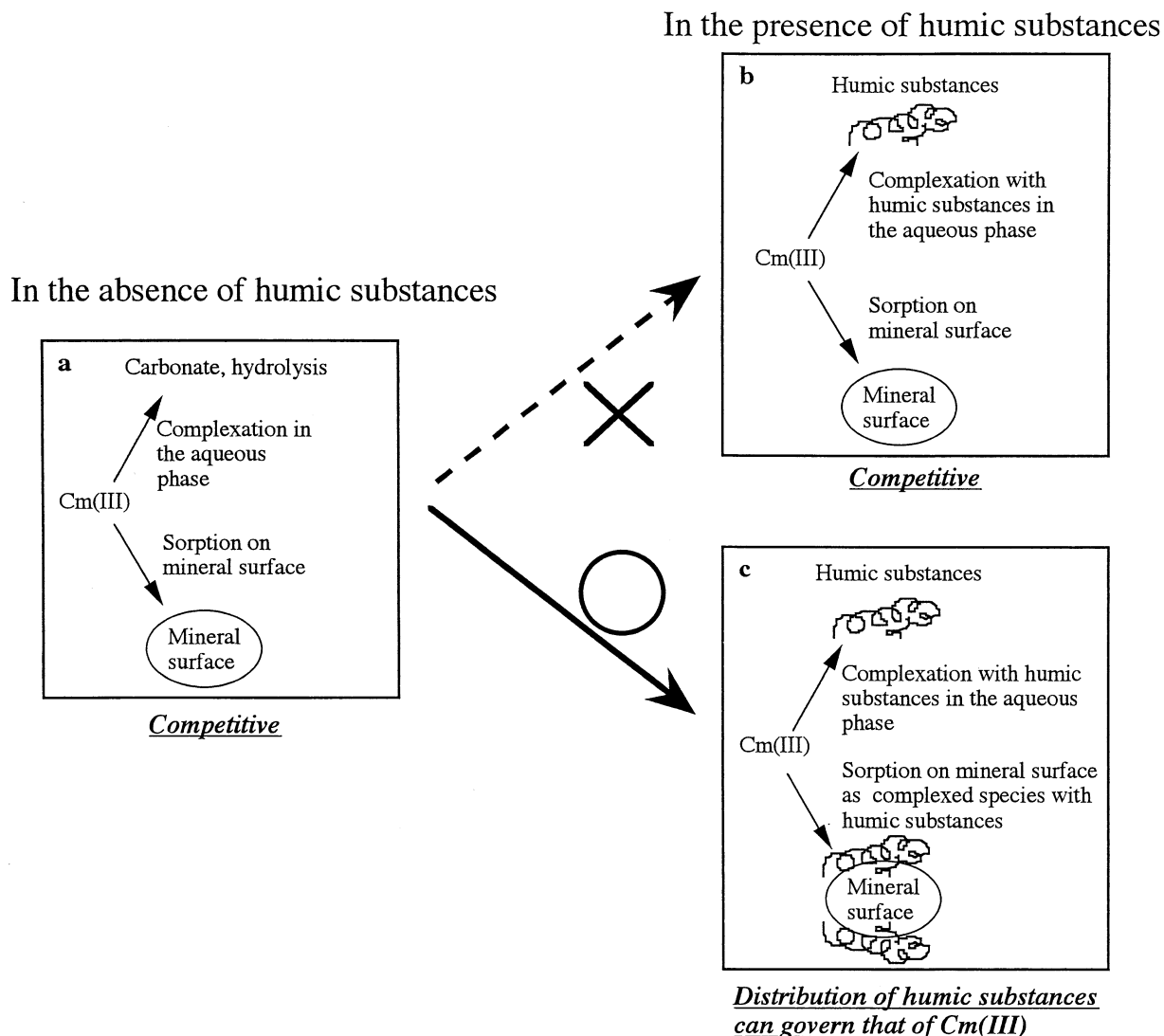*Distribution of humic substances can govern that of Cm(III)*

Fig. 10. Schematic figure for the distribution of Cm(III) in the ternary system containing Cm(III), humic substances, and inorganic mineral surfaces. (a) In the absence of humic substances, the distribution of Cm(III) between solid and aqueous phases can be determined by competition between aqueous complexation with carbonate and hydroxide and sorption on a "neat" mineral surface not coated with humic substances. (c) In the presence of humic substances, the distribution of Cm(III) can be determined by the distribution of humic substances. (b) Competition between complexation with aqueous humic substances and sorption on inorganic mineral surfaces is unlikely to occur in the ternary system.

bution of Cm(III) can be governed by the behavior of humic substances, even in environments where the concentration of organic material is relatively low. Therefore, understanding the environmental behavior of humic substances is quite important in predicting the solid-water distribution of trivalent actinide(III) ions in the environment and should be particularly useful in the field of radioactive waste management. Knowledge of the characteristics of humic substances, such as their composition (humin, humic acid, and fulvic acid), solubility, flocculation behavior, and affinities with various solid media in natural aquifers, will help us understand the behavior of actinide(III) ions and lanthanide(III) ions at the earth's surface.

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