

## Sorption of Eu(III) on Kaolinite in the Presence of Humic Acid: Effects of Ionic Strength

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The effects of ionic strength on the sorption of Eu(III) on kaolinite in the presence of humic acid (HA) were examined using a batch method. Eu(III) sorption increased with increased ionic strengths in the pH range of 6 to 10, but was insensitive to ionic strength in the pH range below 5. Adsorption of HA onto kaolinite also increased in the pH range of 6 to 10, indicating that the increase in adsorption of Eu(III)-humate complexes is a predominant process for the increase in Eu(III) sorption.

Humic acid (HA) is common organic matter occurring widely in environments<sup>1</sup> and is well recognized as having an affinity for both metal ions<sup>1,2</sup> and mineral surfaces.<sup>1,3</sup> Thus, it is quite possible that HA plays an important role in speciation and migration of radiotoxic cations, which are essential safety aspects of radioactive waste disposal. Sorption behavior of metal ions on a mineral has been widely studied in ternary systems consisting of metal ions, HA, and a mineral.<sup>4-8</sup> Murphy and Zachara<sup>4</sup> concluded that metal ion sorption is enhanced in the lower pH region and is depressed in the relatively higher pH region in comparison with sorption in the absence of HA. The influence of HA increased with increasing HA concentrations.<sup>5</sup> Since groundwaters might be originated from seawater or brine in a salt dome, study on sorption at high ionic strengths, which will play an essential role on colloidal nature of HA, is of pivotal importance for migration modeling of actinides(III) in saline systems. However, there is no systematic study of the ionic strength effects on the metal ions sorption in ternary systems. Namely, a few data as to ionic strength effects on Eu(III) sorption can be found in the literatures,<sup>6,7</sup> and were limited below 0.1 M.

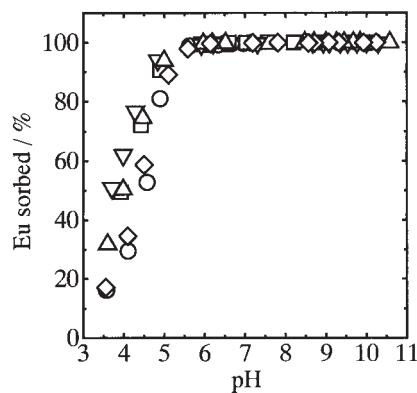
This paper is intended to clarify the effects of ionic strength on the sorption of Eu(III) in ternary systems consisting of Eu(III), HA, and kaolinite. Eu(III) serves as an analogue for trivalent actinides, especially for Am(III). Tracer Eu-152 was purchased from the Japan Radioisotope Association as EuCl<sub>3</sub> in 0.1 M HNO<sub>3</sub>. Kaolinite is a typical secondary mineral and was obtained from the Iwamoto Mineral Co. (particle size, 2–5  $\mu$ m). No contaminant minerals were detected in the kaolinite by X-ray diffraction. Aldrich humic acid, widely used among researchers, was purified. Following the purification, the carboxylic group capacity and ash content of the HA were determined, 4.7 eq/kg and less than 1 percent, respectively.

Experiments were performed by a batch method. Suspensions of 0.20 dm<sup>3</sup> (1.0 g kaolinite/dm<sup>3</sup>) were prepared with HA concentrations of 0 and 10 ppm, ionic strengths from 0.05 to 1.0 M (NaClO<sub>4</sub>), and an Eu concentration of  $1 \times 10^{-7}$  M (activity, 52.5 kBq) in an N<sub>2</sub> atmosphere (CO<sub>2</sub>-free) at a pH of 10. Aliquots of  $5.0 \times 10^{-3}$  dm<sup>3</sup> were transferred from the stirred suspensions to polypropylene vials with airtight caps. Repeated decreases in pH values in steps of about 0.3 units allowed the removal of additional aliquots until the pH values reached about 3.5. The aliquots were shaken for 48 h in a 298 K water bath. When

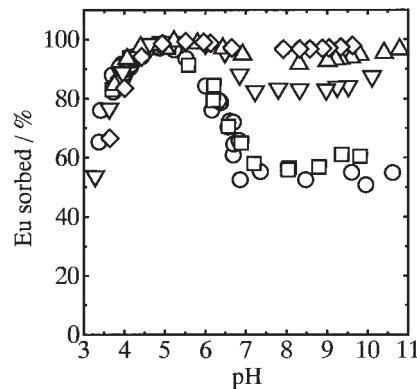
equilibrium was achieved, the final pH was measured after separation by centrifugation at 3000 rpm for 10 min. The sorbed Eu on kaolinite was eluted by 3 M HCl. The radioactivity of liquid and solid phase samples was measured with a NaI(Tl) well-type scintillation counter (Aloka ARC-380), and the percentage of sorbed Eu was obtained. The adsorption of HA onto kaolinite was also determined by measuring the HA concentrations of the supernatant using a UV/Vis spectrophotometer (Shimadzu UV-160A). The experimental details can be found in the literature.<sup>5</sup>

Figure 1 shows the effect of ionic strength on the sorption of Eu(III) on kaolinite in the absence of HA. The sorption of Eu(III) rapidly increases in the pH region from 3 to 5 and reaches almost 100% above a pH of 5.5. This increase in trivalent cation sorption on kaolinite with increasing pH was observed previously.<sup>5,8</sup> Throughout the entire pH region, the change in ionic strengths does not affect the sorption. This suggests that site-specific (inner-sphere type) binding, rather than electrostatic interactions, is dominant in this system.

Figure 2 shows the effects of ionic strength on the sorption of Eu(III) in a ternary system consisting of Eu(III), HA, and kaolinite. In the presence of HA, the Eu(III) sorption no longer continues to increase with increases in pH. At the sorption peak, around a pH of 5, the sorption behavior greatly changes. In the lower pH regions, the sorption increases rapidly with pH and is distinctly independent of varying ionic strengths. In the higher pH regions, the percentage of sorbed Eu(III) decreases as pH increases to 7 and is constant over the pH region of 7 to 10. Moreover, in the pH region beyond the peak, the percentage of sorbed Eu(III) markedly increases with increasing ionic strengths above 0.2 M. At a pH of 10 and an ionic strength of 0.1 M, the sorbed Eu(III) is approximately 50%. This percentage increases to more than 95% at 1.0 M. Below 0.1 M ionic strengths, changes in ionic strengths do not affect the Eu(III) sorption in this system.



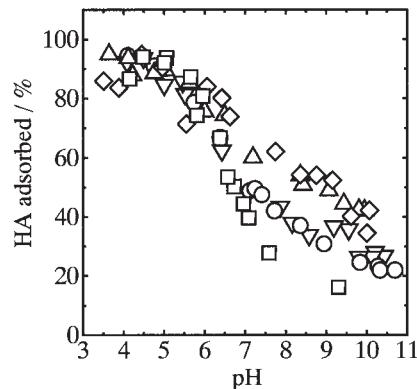
**Figure 1.** Effect of ionic strength on the sorption of Eu(III) on kaolinite as a function of pH in the absence of humic acid. Ionic strengths: 1.0 M (◊), 0.5 M (△), 0.2 M (▽), 0.1 M (○), and 0.05 M (□).



**Figure 2.** Effects of ionic strength on the sorption of Eu(III) on kaolinite as a function of pH in the presence of humic acid. Ionic strengths: 1.0 M ( $\diamond$ ), 0.5 M ( $\triangle$ ), 0.2 M ( $\nabla$ ), 0.1 M ( $\circ$ ), 0.05 M ( $\square$ ), and 0.01 M ( $\bullet$ ).

Figure 3 shows the adsorption of HA alone onto kaolinite as a function of pH at different ionic strengths. The adsorbed HA, which is about 90% at a pH below 5, decreases as the pH increases. This may be attributed to the electrostatic repulsion arising from dissociation of both the HA functional groups and kaolinite surface hydroxyl groups. When ionic strengths in the systems increase above pH values of 6, the adsorption increases. At a pH of 10, the percentage adsorbed HA at a 1.0 M ionic strength is about 20% more than at a 0.05 M ionic strength. Takahashi et al.<sup>7</sup> also observed an increase in HA adsorption with ionic strength. By nature, van der Waals attraction forces between HA and mineral surfaces may be effective and may be one of the primary causes for HA accumulation on minerals.<sup>9</sup> Although an increase in pH gives rise to the electrostatic repulsion, the increase in NaClO<sub>4</sub> concentration plays a screening role and may make the attraction be effective.

In ternary systems, inorganic Eu(III) and Eu(III)-humate complexes are expected to be sorbed on kaolinite. The inorganic fraction is not affected by ionic strength, as seen in Figure 1. On the other hand, adsorption of HA onto kaolinite is markedly affected by ionic strength, as seen in Figure 3, and shows a behavior similar to Eu(III) sorption in ternary systems. This indicates that Eu(III) is sorbed on kaolinite as Eu(III)-humate complexes in the ternary systems. In an attempt to elucidate the increase in Eu(III) sorption with ionic strengths, the additivity model applied by Samadfam et al.<sup>5</sup> was tested using the results obtained from the binary systems mentioned above and using distribution of Am(III) for HA obtained by an ion exchange method.<sup>10</sup> The additive hypothesis neglects any effect of the interaction between kaolinite and the adsorbed HA on the Eu(III) binding. The differences in Eu(III) sorption with different ionic strengths on bare kaolinite were assumed to be equal and were treated identically in this model calculation. The calculated percentage of Eu(III) sorbed at 0.1 M ionic strength was



**Figure 3.** Effect of ionic strength on the adsorption of humic acid on kaolinite as a function of pH. Ionic strengths: 1.0 M ( $\diamond$ ), 0.5 M ( $\triangle$ ), 0.2 M ( $\nabla$ ), 0.1 M ( $\circ$ ), and 0.05 M ( $\square$ ).

approximately 80% at a pH of 9, which is inconsistent with the measured value, 50%. This deviation may arise from the fact that the HA is not fractionated. Furthermore, nonadditive effects would arise from the modification in the surface charge density of kaolinite and HA due to the overlap of the respective double layers. However, an increase in the calculated percentage with ionic strengths from 80% (0.1 M) to over 95% (0.5 M) was obtained in this model, indicating that the increase in HA adsorption is a predominant process for the increase in Eu(III) sorption in the ternary systems.

These Eu(III) sorption experiments were performed at the Central Institute of Isotope Science, Hokkaido University.

## References

- 1 F. J. Stevenson, "Humus Chemistry," 2nd ed., Wiley & Sons, New York (1994).
- 2 V. Moulin, J. Tits, and G. Ouzounian, *Radiochim. Acta*, **58/59**, 179 (1992).
- 3 E. Tipping, *Geochim. Cosmochim. Acta*, **45**, 191 (1981).
- 4 E. M. Murphy and J. M. Zachara, *Geoderma*, **67**, 103 (1995).
- 5 M. Samadfam, T. Jintoku, S. Sato, H. Ohashi, T. Mitsugashira, M. Hara, and Y. Suzuki, *Radiochim. Acta*, **88**, 717 (2000).
- 6 M. Norden, J. H. Ephraim, and B. Allard, *Radiochim. Acta*, **65**, 265 (1994).
- 7 Y. Takahashi, Y. Minai, T. Kimura, and T. Tominaga, *J. Radioanal. Nucl. Chem.*, **234**, 277 (1998).
- 8 A. J. Fairhurst, P. Warwick, and S. Richardson, *Radiochim. Acta*, **69**, 103 (1995).
- 9 M. A. Schlautman and J. J. Morgan, *Geochim. Cosmochim. Acta*, **58**, 4293 (1994).
- 10 T. Sakuragi, S. Sawa, S. Sato, and T. Kozaki, to be submitted for publication.