



## EFFECT OF pH ON STABILITY CONSTANTS OF Am(III)- AND Cm(III)- HUMATE COMPLEXES

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### Abstract

The apparent stability constants of Am(III)- and Cm(III)-humate complexes were determined by dialysis method at ionic strength 0.1 in the pH range from 3.3 to 5.7 under N<sub>2</sub> bubbling. The Am(III) and Cm(III) loadings were about 10<sup>-7</sup> and 10<sup>-10</sup> mol/dm<sup>3</sup>, respectively. The concentrations of Am-241 and Cm-242 tracers were measured by  $\alpha$ -spectrometry.

It was found that the apparent stability constants were almost identical for both the Am(III)-humate and Cm(III)-humate complexes, although the Am(III) loading was 3 order of magnitudes larger than the Cm(III) loading. The apparent stability constants showed a small pH-dependence, increasing from 10<sup>4.6</sup> at pH 3.3 to 10<sup>5.1</sup> at pH 5.7. The ionization of acidic functional groups of humic acid is possibly the primary factor, responsible for the observed pH-dependence of the apparent stability constant.

Above pH 6, the dialysis membrane was no longer permeable to Am(III) and Cm(III) ions and the apparent stability constant could not be experimentally obtained. The apparent stability constants between pH 6 and pH 8.5 were evaluated by considering that both binary metal-humate and ternary metal-hydroxo-humate complexes exist at pHs above 6. It was assumed that mono-hydroxo-humate complex Am(OH)HA and Cm(OH)HA are the major ternary complexes that exist below pH 9. The overall stability constants for Am(III)- and Cm(III)-humate complexes increased from 10<sup>5.7</sup> at pH 6 to 10<sup>7.2</sup> at pH 8, because of the formation of ternary metal-hydroxo-humate complexes. This implies that the formation of metal-hydroxo-humate species is preferred over the formation of hydroxide species.

The apparent overall stability constants, determined in this study can be easily incorporated into geochemical modeling of trivalent actinide migration. The results of the present study show that the apparent stability constants determined experimentally at pH  $\leq$  6 do not represent the complexation properties at higher pHs and the formation of ternary complexes should be considered in speciation calculations of radionuclides at terrestrial environment.

## I. Introduction

It has unambiguously been demonstrated that humic substances, naturally existing organic compounds in soil and groundwater, interact with metal ions by forming rather stable and often soluble complexes<sup>(1)</sup>. One possible consequence of the complexation of radionuclides with humic substances would be a change in the migration behavior of radionuclides<sup>(1)-(3)</sup>. Therefore, the interaction of radionuclides with humic substances has been the subject of extensive investigations<sup>(4)-(17)</sup>.

Obviously, actinide ions are the most concerned radionuclides in safety assessment of radioactive waste management. Although a rather substantial amount of literature on the complexation of metal ions by humic substances is available, it must be concluded that the number of publication of direct relevance to the actinide ions is limited. Furthermore the literature appears to be rather scattered, and it is apparently difficult to obtain consistent data.

Due to the poly-electrolytic nature of HA, it is generally expected that its binding with metal ion will be dependant on pH, as well as to other factors such as ionic strength and metal loading<sup>(1), (18)</sup>. Such a claim is supported by numerous experimental results<sup>(1), (7)-(12)</sup>. The main purpose of the present study is to determine the pH-dependence of the apparent stability constant for complexation of Am(III) and Cm(III) with humic acid (HA), one of the humic substances.

## II. Experimental

### 1. Materials

Humic acid (HA), obtained from Aldrich Co., was purified and its ash content was less than 1%. The carboxylic group capacity of the purified HA sample was 4.9 milli-equivalents per gram of HA, determined by direct titration of 0.2 g/l of HA solution at 298 K. The maximum slope of the titration curve was chosen as the end point of dissociation of the carboxylic groups<sup>(18)</sup>. More detailed preparation and characterization of the HA sample is provided elsewhere<sup>(4)</sup>.

Commercially available 10 µg of Am-241 foil (about 1.26 MBq) in its oxide

form ( $\text{AmO}_2$  deposited on a thin silver foil and sealed by vacuum deposition of palladium) was obtained from Japan Radioisotope Association. The foil was irradiated in the hydraulic power rabbit-1 of the Japan Material Testing Reactor (JMTR) for 5 days at an average thermal neutron flux of  $1 \times 10^{14}$  n/cm<sup>2</sup>s. About 94.5% of the thermal neutron capture of Am-241 leads to the formation of short life ( $t_{1/2} = 16.02$  h) Am-242 and, 5.0% to long life ( $t_{1/2} = 152$  y) isomer Am-242m. Majority of Am-242 undergoes  $\beta^-$ -decay and transform into Cm-242. Part of Am-242 ( $\sim 16\%$ ) undergoes electron capture decay and transforms into Pu-242. Curium-242 has a half life of 162.8 d and transforms into Pu-238 by  $\alpha$ -decay process.

The irradiated specimen was let to be cooled for one year during which the inventories of most of the short-lived radionuclides including Am-242 were substantially decreased and the radioactivity of the Cm-242 became approximately equal to that of the Am-241. Then, the irradiated specimen was dissolved in aqua regia and, the Am-241 and Cm-242 were extracted according to the separation scheme described in Appendix 1, Ref. 19. A mixed solution of Am-241/Cm-242 (in 0.1 M  $\text{HClO}_4$ ) was used as a stock solution in the various stages of experiments.

All other chemicals including HCl, NaOH, NaF,  $\text{NaClO}_4$ ,  $\text{HClO}_4$  and NaOAc, used in the different experimental stages, were reagent grade chemicals and obtained from Wako Chemical Industries Ltd. or Kanto Chemical Co. Inc.

## 2. Procedure

The dialysis method was used to determine the stability constants of Am(III) and Cm(III)-humate complexes. The stability constants were determined at humic acid concentrations of 5, 10, and 20 ppm, and at the ionic strength 0.1 (prepared with  $\text{NaClO}_4$ ) in the pH range from 3.3 to 5.5 under  $\text{N}_2$  bubbling. Each experimental batch used seven cellulose ester dialysis tubes (Spectra Pore Sterile DispoDialyzer 1000 MWCO); six with  $2.0 \times 10^{-3}$  dm<sup>3</sup> of the humic acid solution (three pairs of 5, 10, 20 ppm humic acid solution), and one containing  $2.0 \times 10^{-3}$  dm<sup>3</sup> of the humic acid-free blank solution with 0.1 mol/dm<sup>3</sup>  $\text{NaClO}_4$ . The blank solution was used to establish if the Am/Cm(III) ions permeate freely through the dialysis tube. The dialysis tubes were

immersed in  $3.5 \times 10^{-1} \text{ dm}^3$  of  $0.1 \text{ mol/dm}^3$   $\text{NaClO}_4$  solution in a polypropylene flask. The Am-241/Cm-242 solution was added to the exterior solution in the separable flask to yield final Am (III) and Cm(III) concentrations of about  $10^{-7}$  and  $10^{-10} \text{ mol/dm}^3$  over the entire (interior + exterior solutions) volume, respectively. Then, the pH of the solution was adjusted to a desired value by the addition of  $0.1 \text{ mol/dm}^3$  or  $1 \text{ mol/dm}^3$  solutions of  $\text{HClO}_4$  or  $\text{NaOH}$ . The exterior solution was gently stirred for at least 3 days in a  $\text{N}_2$  atmosphere at 298 K. Preliminary kinetic experiments revealed that the equilibrium was established within this period.

After equilibration, the pH of the solutions were measured and duplicate  $1.0 \times 10^{-3} \text{ dm}^3$  samples of both the interior and exterior solutions were removed for radiometry of  $^{241}\text{Am}$  and  $^{242}\text{Cm}$ . The  $^{241}\text{Am}$  and  $^{242}\text{Cm}$  were co-precipitated by  $\text{SmF}_3$  and collected on a  $0.22 \text{ }\mu\text{m}$  filter. The filters were vacuum-dried and the radioactivity of thin precipitated layer over the filters was measured by an alpha-spectrometry system. Co-precipitation and radiometry of  $^{241}\text{Am}$  and  $^{238}\text{Cm}$  were described in detail in Appendix 2, Ref. 19.

The concentration of humic acid in both the interior and the exterior solutions were measured to establish the extent of the humic acid transfer from the interior to the exterior solution during the dialysis. The concentration of humic acid was measured at 365 nm with a Shimadzu (UV-160) UV-VIS spectrophotometer. Some correction of the stability constant might be necessary due to the slight transfer of humic acid to the exterior solution.

### III. Results and Discussion

The interaction between the Am(III) and Cm(III) ions with humic acid and the apparent stability constant of the Am(III)-humate and Cm(III)-humate complexes are defined by the following equations:



$$\beta = \frac{[\text{M(III)HA}]}{[\text{M(III)}][\text{HA}]}, \quad (2)$$

where, M(III) represents Am(III) and Cm(III). Implied in Eqs. (1) and (2) are that (1) the concentration of M(III) ions is much smaller than that of humic acid and, (2) only 1:1 complexes are formed. The term M(III) in equation (2) stands for the free  $M^{3+}$  ions, and hydrolyzed ions like  $MOH^{2+}$  that may form at high solution pH. Since the experiments were carried out under  $N_2$  atmosphere, no carbonate species exist. In equation (2), [HA] is the concentration of free humic acid ligands capable of binding with M(III), and is substantially equal to the initial concentration of humic acid functional ligands, because the concentration of M(III) is much smaller than that of humic acid ( $[M]/[HA] < 0.01$ ). A carboxylate capacity of 4.89 milliequivalents per one gram of humic acid, obtained from titration data, was used to operationally define the humic acid concentration. It must be emphasized that potential binding sites on humic acid are not limited to carboxylic groups, although these are likely to be responsible for most of the metal ion binding.

Equation (2) can be rewritten as:

$$\log \beta = \log \frac{[M(III)HA]}{[M(III)]} - \log[HA] . \quad (3)$$

The values of  $\log \beta$  can be obtained from equation (3), provided that  $[M(III)HA]/[M(III)]$  is known. The term  $[M(III)HA]/[M(III)]$  can be obtained from the equation,

$$\frac{[M(III)HA]}{[M(III)]} = \frac{C_{in} - C_{ex}}{C_{ex}} , \quad (4)$$

where  $C_{in}$  and  $C_{ex}$  are the concentrations of HA-bound and non-bound M(III) ions in the interior and exterior solutions, respectively.

The [HA] in equation (3) is the final concentration of humic acid in the interior solution which may differ slightly from the initial concentration due to the transfer of humic acid to the exterior solution or sorption on the dialysis tubes and container wall.

In Fig. 1, the apparent stability constants of Am(III)-humate at three different HA concentrations are given as a function of pH. Each point on Fig. 1 is the average of two measurements (one from each of the two dialysis tubes containing HA solutions of

same concentration). Data for the dialysis tubes where the final concentration of HA in the interior solutions decreased more than 5%, were discarded. Each data set shows little dispersion with a standard derivation of less than  $\pm 0.10$ .

The experimental results given in Fig. 1 were slightly corrected for the transfer of humic acid to the exterior solution by the following procedure: The concentration of HA-bound M(III) in the exterior solution,  $[M(III)HA]_{ex}$ , was calculated by the equation,

$$[M(III)HA] = (C_{in} - C_{ex}) \times \frac{[HA]_{ex}}{[HA]_{in}} \quad / \text{ mol dm}^{-3} . \quad (5)$$

Once the  $[M(III)HA]_{ex}$  was known, it was used to correct  $C_{ex}$  as;

$$C_{ex}^{corr} = C_{ex} - [M(III)HA]_{ex} . \quad (6)$$

The  $C_{ex}^{corr}$  was then used to estimate the  $[M(III)HA]/[M(III)]$  term in equation (4). The first estimates of  $C_{ex}^{corr}$  caused changes up to 5% in the values of  $[M(III)HA]/[M(III)]$ . The data points in Fig. 1 are based on the first estimated values of  $C_{ex}^{corr}$ , as the second estimates of  $C_{ex}^{corr}$  were not more than 0.5% different from the first estimates. The data did not corrected for the sorption of M(III) ions onto the membrane and container wall, because the concentration change resulting from the sorption does not affect the value of  $[M(III)HA]/[M(III)]$ . Meanwhile, the mass balance over M(III) showed that no more than 10% of the total M(III) ions were adsorbed on dialysis tube and container walls.

Despite the fact that the Am(III) loading was four order of magnitudes larger than the Cm(III) loading, the apparent stability constants were almost identical for both the Am(III)-humate and Cm(III)-humate complexes, as shown in Fig. 2. The immediate conclusion is that in actual repository condition where the radionuclides concentration are supposed to be very small, the effects of other predominantly existing competing ions (such as Ca(II) and Fe(III)) on the apparent stability constants of radionuclides are likely more important than the effect of radionuclide loading itself.

The apparent stability constants seems to be slightly dependent on humic acid concentration, as shown for the Am(III)-humate in Fig. 1. They are slightly decreased with increasing humic acid concentration. However, the standard deviation from an

average value (obtained by least squares method) is less than  $\pm 0.17$ . The decrease in apparent stability constants with increasing humic acid concentration is attributed to the decrease in activity coefficient of the humic acid at higher concentrations.

The apparent stability constants also show a gradual increase with pH. One should expect that the apparent stability constants show a significant pH-dependence because, (1) a change in pH affects the ionization of acidic groups and thereby the number of binding sites on HA<sup>(18), (20)</sup> and, (2) a change in the ionization of acidic groups due to a change in pH may affect the structural configuration of HA molecules<sup>(18), (21)</sup>. Unfortunately, major difficulties are encountered in quantitative assessment of the individual contributions of the ionization of acidic functional groups of HA to the overall stability constant. Because, determination of the types and concentrations of functional groups of HA is not usually straightforward and there are many discussions in the literature regarding this point<sup>(21)</sup>. In addition, the ionization of various functional groups may overlap significantly. It is generally accepted that carboxylic and phenolic groups are two major acidic groups of HA (the content of carboxylic groups is likely higher than that of phenolic groups)<sup>(2), (18)</sup>. However, due to the poly-electrolytic nature of HA, it is very unlikely that any two binding sites (even of same type) will be exactly identical in a given sample<sup>(21)</sup>. In actual practice, the concentrations of functional groups are operationally defined and only a portion of the titration curve is analyzed<sup>(22)</sup>. The following discussion is limited to the effect of ionization of the carboxylic groups and it is assumed that the ionization of the carboxylic groups does not overlap with that of the phenolic groups.

The ionization of a carboxylic group functional group of humic acid may proceed as;

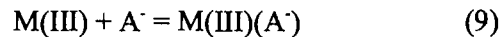


$$\alpha = \frac{[A^-]}{[HA]_0} \quad (8)$$

Where  $[HA]_0$  is the total concentration of the acidic group and,  $\alpha$  is the degree of dissociation of the acidic group and can be obtained from titration data. The reaction



between the ionized acidic groups and Sr(II) ions can be expressed by,



$$K_M = \frac{[M(\text{III})(A^-)]}{[M(\text{III})][A^-]} \quad (10)$$

Combining Eqs. (2-28) and (2-39) finally leads to the equation,

$$\log \beta = \log K_M + \log \alpha \quad (11)$$

Equation (11) clearly shows the pH-dependence of the apparent stability constant. An increase in pH from 4 to 6 corresponds to an increase in  $\alpha$  from 0.2 to 0.8, and, if  $K_M$  does not change with pH, then  $\log \beta$  would increase about 0.6, which is somehow larger than 0.4 obtained from the experiment. Therefore, the increase in apparent stability constant with pH can be mainly attributed to the increase in the number of binding sites due to ionization of the acidic functional groups of humic acid.

Given the hydrolysis constants of americium and curium ions, the free americium and curium ions,  $M^{3+}$  are the only form of M(III) that exist below pH 6 and, binary  $M^{3+}$ HA complex is the only actinide-humate complex that can form.

Above pH 6, the dialysis membrane was no longer permeable to M(III) ions and the apparent stability constant could not be experimentally obtained. It is likely that the stability constant of  $M^{3+}$ HA complex will no further increase at  $\text{pH} > 6$ , because the dissociation of carboxylic groups of humic acid is substantially completed at pH 6. It does not mean that the apparent stability constant (defined by equation 2) does not change with pH. Note that the term M(III) in equation (2) stands not only for free  $M^{3+}$  ions, but for hydrolyzed M(III) ions like  $\text{MOH}^{2+}$  that may form at high solution pH. The apparent stability constant may change due to a change of chemical form of inorganic M(III) species.

It is argued that trivalent actinide and lanthanide ions may form mixed complexes with humic acid and an additional ligand such as  $\text{OH}^-$  or  $\text{CO}_3^{2-}$ <sup>(23)-(25)</sup>. Under our experimental conditions where no  $\text{CO}_3^{2-}$  exists,  $\text{OH}^-$  is the only competing ligand that may participate in the formation of ternary complexes with  $M^{3+}$  and humic acid.

Contrary to the results of Dierckx et al.<sup>(24)</sup> who postulated that mixed

complexes with hydroxyl ions only occur beyond pH 8.5, Panak et al.<sup>(25)</sup> reported that mixed complexes with hydroxyl ions may considerably form at pH lower than 8.5 (but above pH 6). Panak et al.<sup>(25)</sup> argued that mono-hydroxo humate complex  $M(OH)HA$  is the major ternary complex below pH 9.

In the presence of ternary humate complexes the apparent stability constant, defined by equation (2), can be rewritten as:

$$\beta = \frac{[M(III)HA]}{[M(III)][HA]} = \frac{[M^{3+}HA] + [M(OH)HA]}{([M^{3+}] + [M(OH)^{2+}])[HA]} \quad (2^*)$$

$M(OH)^{2+}$  is the only hydroxylated species of  $M(III)$  that may considerably form below pH 9.  $[M(OH)HA]$  and  $[M(OH)^{2+}]$  are given by the equations:

$$[M(OH)HA] = K^{M(OH)HA} \times [M^{3+}HA][OH^-] \quad (12)$$

$$[M(OH)^{2+}] = \beta_1^{OH} \times [M^{3+}][OH^-] \quad (13)$$

By substituting of Eqns. (12) and (13) in eqn. (2\*),

$$\beta = \frac{(K^{M(OH)HA} \times [OH^-] + 1)}{(\beta_1^{OH} \times [OH^-] + 1)} \times \beta_{pH=6}^{M^{3+}HA} \quad (2^{**})$$

where  $\beta_{pH=6}^{M^{3+}HA} = \frac{[M^{3+}HA]}{[M^{3+}][HA]}$  is the apparent stability constant of  $M^{3+}HA$  at  $pH > 6$ . If the values of  $\beta_{pH=6}^{M^{3+}HA}$ ,  $\beta_1^{OH}$  and  $K^{M(OH)HA}$  are known, then the apparent stability constant of  $M(III)-HA$  at  $pH > 6$  can be estimated by Eqn. (2\*\*). We assumed that the apparent stability constant of  $M^{3+}HA$  at  $pH > 6$  is constant and equal to that at pH 6 ( $10^{5.1}$ , determined from Fig. 1). The value of  $\log K^{M(OH)HA}$  has already reported by Panak et al. (1996) to be  $6.94 \pm 0.04$ . The hydrolysis constant for  $M^{3+}$  has been reported as:  $\beta_1^{OH} = 6.0^{(26)}$ . The apparent stability constant at  $pH > 6$ , estimated by Eqn. (2\*\*), is shown in Fig. 2. The fitting curve is a second-order polynomial function obtained by the least squares method with a standard derivation of  $\pm 0.1$ . The correlation was made only for the sake of easy incorporation of data into geochemical modeling codes and has no chemical significance.

The apparent stability constant given by Eqn. (2) quantitatively describes the strength of metal-humate binding in the simplest way. It was assumed that humic acid

behaves as well-defined low-molecular-weight monomer ligands. In reality, humic acid is an extremely heterogeneous ligand with respect to molecular weight and content of functional groups. Although the apparent stability constants may not be particularly representative of reality, they can be easily incorporated into geochemical modeling codes. Fish et. al.<sup>(27)</sup> and Turner et. al.<sup>(28)</sup> concluded that they may be the best for quantitative analysis.

#### IV. Conclusions

The pH dependence of the apparent stability constants of Am(III)-humate and Cm(III)-humate complexes at the ionic strength of 0.1 M (prepared by NaClO<sub>4</sub>) were studied by the dialysis method. The apparent stability constant for Am(III)-humate and Cm(III)-humate complexes were almost identical and, were increased from 10<sup>4.6</sup> at pH 3.3 to 10<sup>5</sup> at pH 5.5. It is likely that the observed pH-dependence of the stability constant is caused by the ionization of acidic functional groups of HA with increasing pH.

The apparent stability constants between pH 6 and pH 8.5 were evaluated by considering that both binary metal-humate and ternary metal-hydroxo-humate complexes exist at pHs above 6. It was assumed that mono-hydroxo-humate complex Am(OH)HA and Cm(OH)HA are the major ternary complexes that exist below pH 9. The overall stability constants for Am(III)- and Cm(III)-humate complexes increased from 10<sup>5.7</sup> at pH 6 to 10<sup>7.2</sup> at pH 8, because of the formation of ternary metal-hydroxo-humate complexes. This implies that the formation of metal-hydroxo-humate species is preferred over the formation of hydroxide species.

The values of the stability constants indicate that in most of natural aquifer system where pH is 5~9 and humic acid concentration is less than 10<sup>-4</sup> M, in the absence of other complexing ligands and at tracer level concentrations of radionuclide ions, the majority of trivalent radionuclide ions are associated with humic acid.

The results of the present study show that the apparent stability constants determined experimentally at pH ≤ 6 do not represent the complexation properties at

higher pHs and the formation of ternary complexes should be considered in speciation calculations of radionuclides at terrestrial environment.

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