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Colloidal α-Al_2O_3, Europium(III) and Humic Substances Interactions: A Macroscopic and Spectroscopic Study

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ABSTRACT Eu(III) sorption onto α-Al_2O_3 in the presence of purified Aldrich humic acid (PAHA) is studied by batch experiments and time-resolved laser-induced luminescence spectroscopy of Eu(III). Experiments are conducted at varying pH, at 0.1 mol/L $NaClO_4$, 10^{-6} mol/L Eu(III), 1 g/L α-Al_2O_3 and 28 mg/L PAHA. Adsorption of Eu(III) presents the expected pH-edge at 7, which is modified by addition of PAHA. Presence of Eu(III) slightly increases PAHA sorption throughout the pH range. The evolutions of luminescence spectra and decay times of the binary systems, i.e. Eu(III)/α-Al_2O_3 and Eu(III)/PAHA, indicate a progressive surface- and humic-complexation with increasing pH. The typical bi-exponential luminescence decay in Eu(III)/PAHA system is also recorded; the fastest deactivation depending barely on pH. In ternary Eu(III)/PAHA/α-Al_2O_3 system, the existence of a luminescence bi-exponential decay for all pH means that Eu(III) is always in the direct neighborhood of the humic substance. Below pH 7, the spectra of the ternary system (Eu(III)/PAHA/α-Al_2O_3) are not different from the ones of Eu(III)/PAHA system, implying the same complex symmetry. Nevertheless, the increase of luminescence decay time points to a change in PAHA conformation onto the surface.

KEYWORDS

Humic acid; Europium; Alumina; Luminescence; Sorption; Ternary complex

BRIEFS

Influences of humic acid and pH on retention and speciation of Eu(III) in contact with colloidal α-Al_2O_3 are analyzed by macroscopic batch experiments and time-resolved laser luminescence spectroscopy.

Introduction

Natural organic matter (NOM) interactions with mineral colloids in soils partly control the speciation and migration of heavy metals as well as nanoparticles in the environment, and notably of lanthanides and actinides[1,2]. The modeling of ternary systems consisting of metal-NOM-mineral surface has often led to discrepancies. Particularly, the additivity of the binary systems was not fulfilled[3,4]. In some examples, successful modeling exercises were proposed for fulvic acids[5,6]. These samples can be assumed to be more or less similar to simple organic molecules[7]. Fulvic acids (FA) sorption is stable or decreases with increasing ionic strength[8–10], whereas sorption of humic acids (HA) onto oxides increases with ionic strength[8,10,11]. Hence, it is still difficult to propose interpretations of HA effects on the modeling of ternary systems in a wide parametric space[4,12]. Moreover, heterogeneous composition and nature of HA[13,14], and constant modification of HA aggregates with physico-chemical conditions of the solution[15] or due to sorption[16,17] do not ease the modeling of these systems. The accurate understanding and description of the HA-containing systems are still under discussion. A better description of these systems is still needed to improve the understanding of the behavior of metals and nanoparticles in the environment.

One way to obtain both macroscopic and spectroscopic information on Ln/An(III) sorption onto mineral surfaces is through time-resolved laser-induced luminescence spectroscopy (TRLS). Due to their luminescence properties, one can have a direct insight on speciation of the ions in solution, in contact with humic substances[18–23] as well as sorbed onto mineral surfaces[24,25] or in ternary systems[26]. Measurements can be made at low metal ion concentration, to get as close as possible to environmental concentrations. TRLS has been used in either combination of the ternary systems, but up to now no direct comparison has been done between the two binary systems and the corresponding ternary system in a whole range of pH.

The aim of this study was to investigate the influence of Aldrich humic acid on the behavior and the speciation of a lanthanide, Europium(III), as a chemical analog of An(III), in presence or absence of α-Al_2O_3. Aluminum oxides are not the more frequent mineral surfaces found in the environment, but their aluminol surface sites are part of aluminosilicates reactive sites, very abundant in natural systems. Besides, its transparency for light allows spectroscopic measurements with mineral in solution, contrary to iron oxides[24]. Macroscopic and spectroscopic experiments have been carried out to see the influence of pH on the evolution of the different systems.

Experimental Section

Materials Commercial Aldrich humic acid was purified (PAHA) according to ref 27. Stock suspension at 1 g/L has been prepared by diluting PAHA in NaOH (pH around 10) in order to completely dissolve the sample. The solution was then stored in the dark under N_2. Proton exchange capacity was determined by potentiometry and found at 6.12 eq/kg[28]. Alumina (α-Al_2O_3) was purchased from Interchim (pure 99.99%, size fraction 200–500 nm). The solid was washed thrice with carbonate-free NaOH and thrice with Millipore water before drying and storage at room temperature under N_2 atmosphere according to ref 29. The specific surface area measured by N_2-BET method was 15 m²/g. Point of zero charge was determined by acid-base titrations and found at pH = 9.4 (data not shown). Europium(III) stock solution (10^{-3} mol/L) was obtained from the dissolution of Eu_2O_3 (Johnson Matthey, 99.99%) in $HClO_4$. All solutions were prepared using freshly boiled milli-Q water.

Methods Batch contact experiments were conducted in 10.4 ml Beckman centrifugation tubes (355603). The different concentrations of compounds were 1 g/L of α-Al_2O_3, 10^{-6} mol/L of Eu(III) and 28 mg/L of PAHA, which assured a complete complexation of Eu(III) by PAHA (see refs 23 and 30 confirmed by Supporting Information (SI) Figure S1). First solid α-Al_2O_3, then PAHA and Eu(III) stock solutions and finally freshly degazed electrolyte solutions were weighed, with no specific contact time applied between additions. To minimize carbonation of the systems, nitrogen was swept on the top of the solution before closing the tubes. Ionic strength was fixed at 0.1 mol/L $NaClO_4$. The pH values of the solutions were adjusted by addition of fresh 0.1 mol/L $HClO_4$ and NaOH solutions. They were measured using one combined glass electrode (Radiometer Analytical) connected to a Radiometer Analytical pH Meter. To prevent $KClO_4$ precipitation in the electrode frit, the electrode filling solution was modified with NaCl at 0.1 mol/L. The pH electrode was calibrated using buffer solutions (pH 4.01, 7.01, and 10.00). The solutions were applied to three dimensional stirring for 3 days of equilibration at room temperature before pH measurements and analyses.

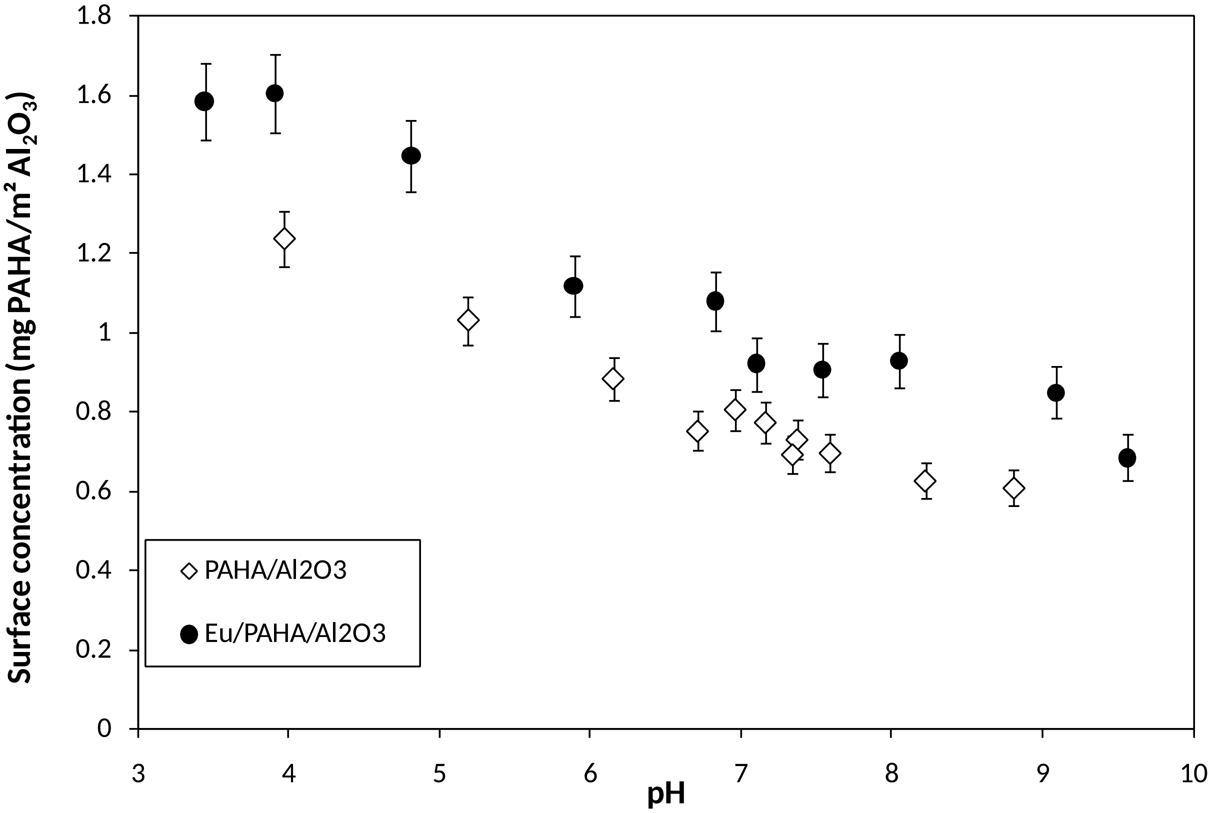
After equilibration, subsamples (2.4 ml) were taken from the centrifugation tubes and analyzed in quartz cuvettes (10 mm). Preliminary experiments showed no significant differences between aliquots taken from one same tube. Eu(III) laser-induced properties were studied in contact with either PAHA, or α-Al_2O_3, or both components using TRLS. The excitation laser beam was generated by a 355 nm tripled output of a Continuum Nd-YAG laser, coupled to an optical parametric oscillator system (Panther II, Continuum, USA). The time-resolved luminescence signal is collected at 90° and focused into an Acton spectrometer (slit 1 mm) equipped with 600 lines/mm grating. For the time-resolved detection, the luminescence signal was collected during a gate width L = 300 µs, at an initial gate delay D = 10 µs after the excitation by a laser flash. To increase the signal to noise ratio, 1000 accumulations were performed for each spectrum. To avoid the aggregation and settling of the samples occurring in α-Al_2O_3-containing systems, these samples were manually shaken between two measurements. All luminescence measurements were performed at ambient temperature (21°C ± 2). The excitation wavelength was set at $\lambda_{exc} = 393.8$ nm. The observed luminescence corresponds to the transitions of the $^5D_0$ excited state to the ground ^7F_j manifold[31]. They are the $^5D_0 \rightarrow ^7F_0$ forbidden for magnetic and electric reasons ($\lambda_{max} \approx 580$ nm), the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition ($\lambda_{max} \approx 593$ nm), and the $^5D_0 \rightarrow ^7F_2$ "hypersensitive" transition ($\lambda_{max} \approx 615$ nm), [32,33] (SI Figures S1 and S2).

To characterize adsorbed amounts of PAHA and Eu(III) onto α-Al_2O_3, after equilibration the solutions were ultra-centrifuged at 60 000 rpm during 2 h. Concentration of PAHA in the supernatant was measured by a Shimadzu TOC-VCSH analyzer, calibrated in concentration of PAHA between 0 and 50 mg_{HA}/L. The quantification of non-sorbed Eu(III) was made using TRLS using the standard addition method[34], diluting an aliquot of the supernatant in K_2CO_3 3 mol/L. This method allow determination of Eu(III) concentration down to 10^{-9} mol/L.

Results and Discussion

Macroscopic Adsorption Experiments Figure 1 shows the influences of pH and Eu(III) on PAHA adsorption onto α-Al_2O_3. The humic acid sorption is typically decreasing when pH increases and α-Al_2O_3 surface becomes less positively charged, as for other oxides[8,35,36]. Adsorption is nevertheless significant throughout the pH range, going from 1.24 mg_{HA}/m^2 at pH 4.0 (i.e. 76% of initial amount of PAHA) to 0.61 mg_{HA}/m^2 at pH 8.8 (i.e. 37%).

Figure 1. Surface concentration of PAHA on α-Al_2O_3 depending on pH, with (●) or without (◊) Eu(III). C(Alumina) = 1 g/L, $C(PAHA)_{initial} = 26.5 \pm 2$ mg/L, $[Eu(III)]_{initial} = 10^{-6}$ mol/L, $I = 0.1$ mol/L $NaClO_4$. Error bars correspond to 2σ.



The presence of Eu(III) seems to homogeneously increase the retention of the humic substance onto α-Al_2O_3 surface throughout the pH range studied. For the ternary system, PAHA sorption goes from 1.60 mg_{HA}/m^2 at pH 3.9 (i.e. 88%) to 0.69 mg_{HA}/m^2 at pH 9.6 (i.e. 38%).

Schlautman and Morgan reported an increase of HA sorption onto γ-Al_2O_3 in presence of Ca^{2+} between pH 4 and 10 for different coverage rates (from 0.1 to 5.6 mg_{HA}/m^2) in 0.1 mol/L NaCl, but did not observe this increase in their Ca/FA/alumina system[8]. Krepelova et al. also noticed this increase in sorption of HA in a U(VI)/HA/kaolinite system (initial ratio of 0.32 mg_{HA}/m^2), but only at 0.01 mol/L $NaClO_4$ and not at 0.1 mol/L[37]. The same trend was reported by Christl and Kretzschmar when studying fulvic acid sorption in a Cu/FA/hematite system in 0.01 $NaNO_3$ media (initial ratio of 0.68 mg_{FA}/m^2), but not at 0.03 and 0.1 mol/L[3]. Weng et al. observed an increase of FA sorption in a Cu/FA/goethite system at 0.1 mol/L $NaNO_3$ for two initial FA concentrations, i.e 0.13 and 0.80 mg_{FA}/m^2 [5]. This latter value is closer to our organic matter-to-mineral ratio, i.e. 1.86 mg_{HA}/m^2. However, the direct comparison between HA and FA may not be straightforward regarding the influence of ionic strength on FA and HA sorption[8–11].This increase of HS adsorption in ternary systems is often interpreted as the formation of a metal bridge between the negatively charge surface and humic binding sites, which is unlikely at pH 4, i.e. before the sorption edge of Eu(III). Schlautman and Morgan attribute this increase at low to neutral pH to hydrophobic bonding, polyvalent ions screening the repulsive charges of the humic molecule at the mineral surface and thus enhancing HA adsorption[8]. One could also propose the variation of humic conformation induced by ionic strength[38,39] or agglomeration induced by complexation of Ln(III)[40,41]. The ratios between the different components, as well as the metal charge, may also play a major role.

Figure 2 shows the influence of pH and PAHA on Eu(III) adsorption onto α-Al_2O_3. In the binary Eu(III)/α-Al_2O_3 system, the adsorption curve shows the expected sorption-edge around pH 7 for Ln/An(III)[29,42–44], increasing from 3.5×10^{-6} $mmol_{Eu}/m^2$ retained at pH 4.4, that is, 5% of initial amount of Eu(III), to 6.4×10^{-6} $mmol_{Eu}/m^2$ at pH 9.8 (i.e. ≈ 100%). Inorganic speciation of Eu(III) using data from Hummel et al.[45] is shown in SI Figure S3a. Eu^{3+} is predominant up to pH 7, and then hydrolyzed species become the predominant ones. Eu(III) adsorption increases just before its first hydrolysis, as previously observed by Bradbury and Baeyens onto illite[46]. They have shown that surface complexation of metals is closely related to their first hydrolysis constants[47]. As expected, presence of HA changes Eu(III) behavior: at pH < 6, PAHA enhances Eu(III) retention onto the surface[42,43]. Around their first acidity constants, PAHA molecules, negatively charged, adsorb onto the positively charged oxide surface at low pH values, and Eu(III)-PAHA complexes adsorb onto the surface. The Eu(III)-PAHA speciation under our experimental conditions determined by ECOSAT[48] software and generic data from Milne[30] is shown in SI Figure S3b.

At pH greater than 7, the presence of PAHA is slightly decreasing Eu adsorption compared to the binary system, as previously observed in other metal-oxide systems[26,35,42,43,49]. This is commonly thought to be due to the progressive decrease of HA sorption with increasing pH and the resulting competition for Eu(III) between adsorbed HA and HA in solution. At pH ≥ 8, the adsorption of Eu(III) onto the surface increases slightly again, resulting from the competition of Eu(III) between α-Al_2O_3 surface, surface-adsorbed PAHA and dissolved PAHA.

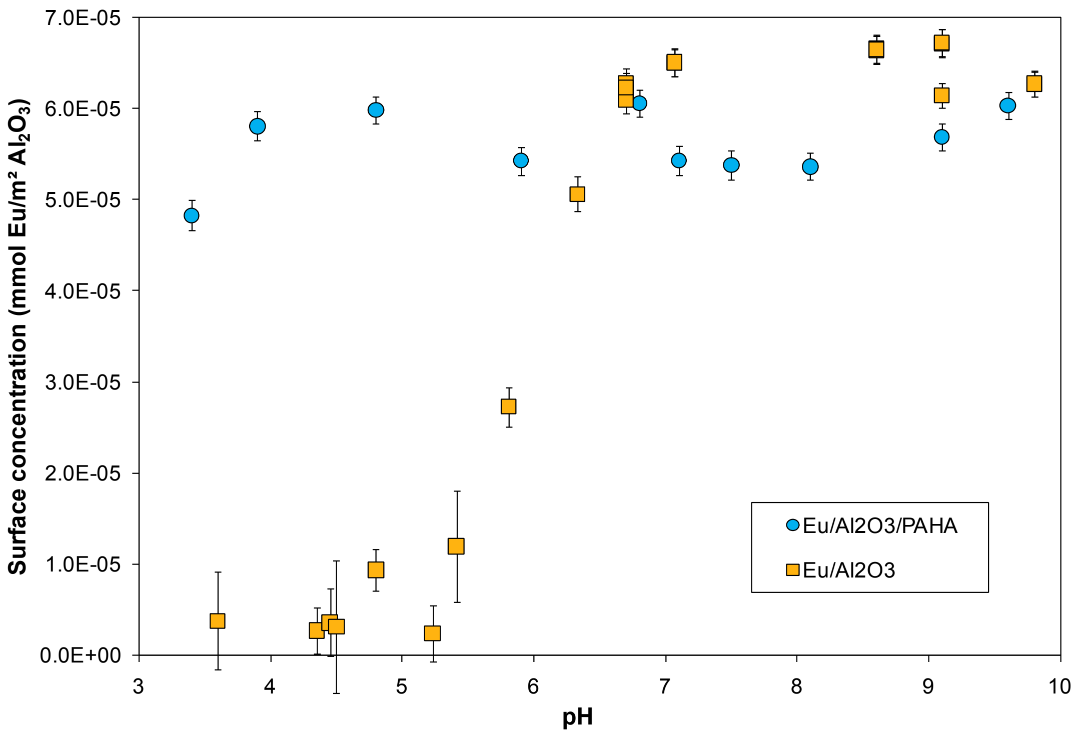


Figure 2. Surface concentration of Eu(III) on α-Al_2O_3 depending on pH, with (●) or without (□) PAHA. C(Alumina) = 1 g/L, $C(PAHA)_{initial}$ = 28 mg/L, $[Eu(III)]_{initial} = 10^{-6}$ mol/L, I = 0.1 mol/L $NaClO_4$. Error bars correspond to 2σ.

Eu(III) Speciation Analysis Eu(III) luminescence spectra and decay times in the different systems were analyzed by TRLS at different pH. The peak shapes and asymmetry ratios, i.e. $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ ($^7F_2/^7F_1$), provide information on Eu(III) speciation[31]. The calculation of ratios avoids us the necessity to take into account light attenuation for comparing the different systems, as this information is independent from the total luminescence recorded. The evolution of these ratios depending on pH is shown in Figure 3 for the different systems. Luminescence decay times have been measured with delay steps of 10 to 25 µs. They are plotted against pH for the different systems in Figure 4. They have been adjusted to the decay of $^5D_0 \rightarrow {}^7F_1$ transition area (between 585 and 600 nm)[19,20,22], as it is less sensitive to solution conditions[32,33].

<u>*Binary Systems*</u>. As seen in Figure 3, the $^7F_2/^7F_1$ ratio in Eu(III)/α-Al_2O_3 system increases from 0.6 at pH 4.4 to 2.0 at pH 8.8. When pH increases, the possibility for Eu(III) to form surface complexes on α-Al_2O_3 is also increasing, as seen in macroscopic data. The $^5D_0 \rightarrow {}^7F_0$ transition appears for pH > 5.5, indicating a loss of symmetry in the ion environment above this pH value, which corresponds to the beginning of Eu(III) adsorption (Figure 2).

Mono-exponential luminescence decay time (τ) of Eu(III) ions in binary Eu(III)/α-Al_2O_3 system increases with pH, from τ = 120 ± 3 µs at pH 4.4 to τ = 277 ± 5 µs at pH 8.8 (Figure 4). A greater luminescence decay time means that there is a higher probability for an excited Eu ion to emit a photon than to lose energy through other non-radiative pathways, i.e. quenching by water molecules, -OH groups, and -NH groups. The increase of τ is interpreted as the substitution of water molecules in the first coordination sphere of the luminescent ion[50,51]. Here, the increase of τ from 120 µs to 277 µs would correspond to the

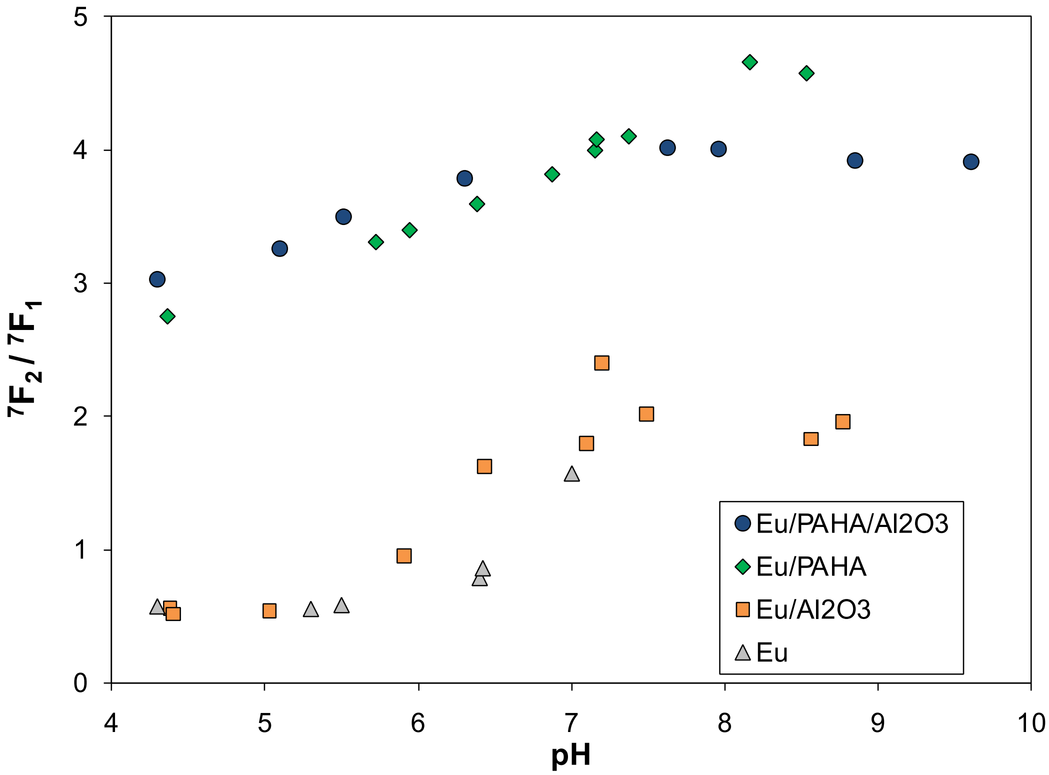


Figure 3. Evolution of $^5D_0 \rightarrow {}^7F_2/^5D_0 \rightarrow {}^7F_1$ ratio depending on pH: C(α-Al_2O_3) = 1 g/L, C(PAHA)$_{\text{initial}}$ = 28 mg/L, [Eu(III)]$_{\text{initial}}$ = 10^{-6} mol/L, I = 0.1 mol/L $NaClO_4$.

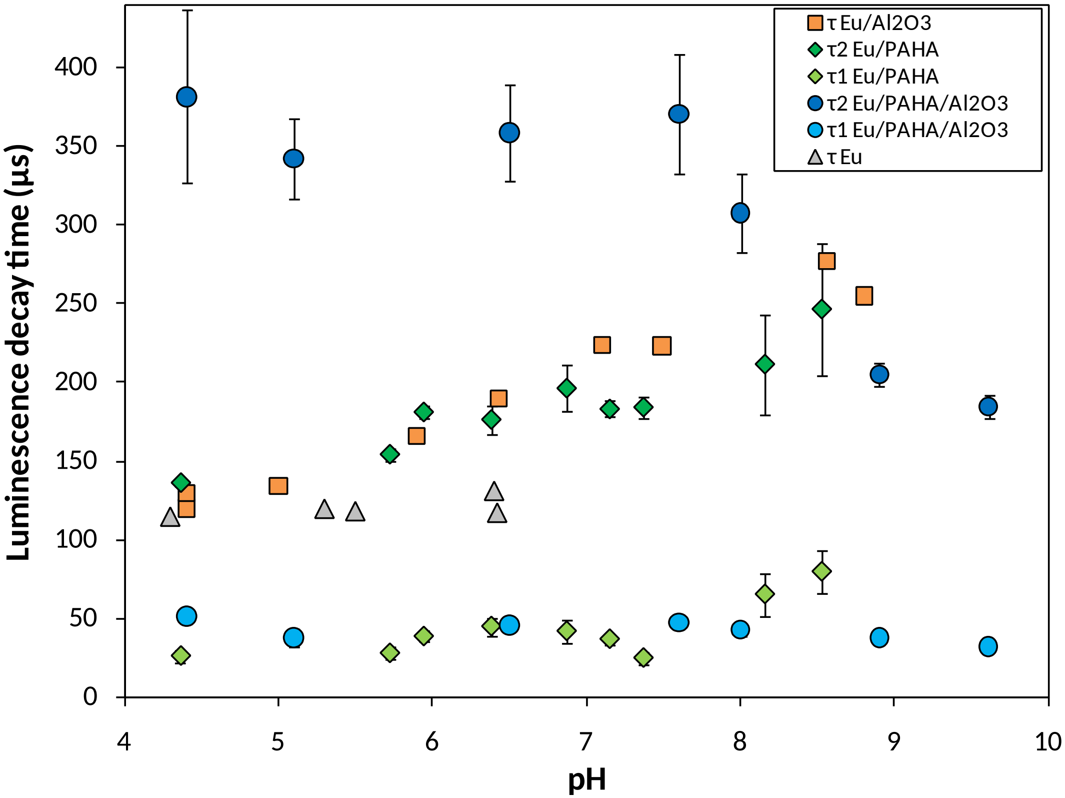


Figure 4. Evolution of Eu(III) luminescence decay times in contact with PAHA, α-Al_2O_3 or both compounds depending on pH; C(Alumina) = 1 g/L, $C(PAHA)_{initial}$ = 28 mg/L, $[Eu(III)]_{initial}$ = 10^{-6} mol/L, *I* = 0.1 mol/L $NaClO_4$; Error bars correspond to 2σ.

loss of 5 water molecules according to ref 52. Water molecules are supposed to be excluded from the first coordination sphere of Eu(III) when it forms surface complexes onto α-Al_2O_3. Nevertheless, this number must be taken carefully, as previous studies have shown that the relationship between luminescence decay time and the number of surrounding water molecules may depend on the system studied[53]. One should better consider the more complete relationship determined otherwise[50,51], which requires the measure of the decay time in D_2O in all the three systems, which was out of the scope of this study.

In Eu(III)/PAHA systems, $^7F_2/^7F_1$ increases from 2.6 at pH 4.1 to 4.6 at pH 8.5 (Figure 3). There is apparently a continuous evolution of the chemical environment of Eu(III) throughout the pH range. This could be linked to the increase of Eu(III) binding to PAHA with increasing pH and the evolution of the type of bonding of Eu(III) within the humic structure[54]. The evolution parallels the Eu(III)/α-Al_2O_3 system at a different magnitude, with $^7F_2/^7F_1 > 1$ at all pH. In presence of PAHA, the $^5D_0 \rightarrow {}^7F_0$ transition is always present (as in SI Figure S2a at pH 4.1). Together with the fact that the $^5D_0 \rightarrow {}^7F_2$ peak is the most prominent one at all pH, this means that Eu(III) is always bound to the humic acid.

A typical bi-exponential luminescence decay is recorded throughout the pH range, with a short luminescence decay time ($\tau_1 < 70$ µs) and a longer one ($120 < \tau_2 < 250$ µs), as previously seen[19–22] (Figure 4). The first decay time is shorter than free aqueous Eu^{3+} (τ ≈ 114 µs)[50] and independent of pH, which suggests that this phenomenon barely depends on the chemical environment of Eu(III) and may be due to a fast exchange between Eu(III) and humic acid[22,55]. When pH increases, τ_2 continuously increases, from 137 ± 2 µs at pH 4.4 to 246 ± 42 µs at pH 8.5, which means that water molecules are progressively excluded from the coordination sphere of Eu(III) when pH increases.

Ternary System. A comparable ternary system was studied by Tan et al. by TRLS at pH 6.3 on hydrous alumina (mixture of bayerite, boehmite, and diaspore) and Chinese soil HA/FA[26]. The direct comparison of the $^7F_2/^7F_1$ ratios may not be done[20], but the trends can be compared. Recalculated $^7F_2/^7F_1$ from Tan et al.[26] are equal to 2.0 in their Eu/hydrous alumina system and 5.0 in their Eu/HA system. In their ternary system, this value is equal to 4.8, which is similar to the Eu/HA binary system. Therefore, no change in Eu(III) environment is expected between the HA-containing systems.

Here this behavior is probed for a wider pH range. The $^7F_2/^7F_1$ ratios of ternary Eu(III)/PAHA/α-Al_2O_3 system are much more important than in Eu(III)/α-Al_2O_3 system, and are slightly increasing from 3.0 at pH 4.3 to 4.0 at pH 7.6 (Figure 3). Above pH 7.6, the peak ratio is constant, but there is a shift from 615 to 617 nm of $^5D_0 \rightarrow {}^7F_2$ maxima accompanied with a change in peak shape (SI Figure S4), indicating a further change in Eu(III) chemical environment. At pH < 7, the $^7F_2/^7F_1$ ratios of binary Eu(III)/PAHA or ternary Eu(III)/PAHA/α-Al_2O_3 systems are very close, as it was for Tan et al. at pH 6.3[26]. It seems that Eu(III) has a very similar environment in both systems, whether it is in binary Eu(III)/PAHA or sorbed with PAHA onto α-Al_2O_3 in ternary system. This would suggest that throughout this pH range Eu(III) is directly linked to sorbed humic aggregates and has a limited access to the aluminol surface sites. Conversely, Tan et al.[26] reported based on XPS that Eu(III) was fixed to both components in the ternary system. This is not apparent here, as it was not in their TRLS spectra.

As shown in Figure 4, there is a bi-exponential decay in the ternary system (see SI Figure S5), which first decay time is directly comparable to the one in Eu(III)/PAHA system. This fast de-excitation is another direct indication that Eu(III) is strongly linked to sorbed humic aggregates. These results also suggest that sorbed Eu(III) in the ternary system is always bound to the sorbed humic acid entities, even at high pH when humic acid sorption is the lowest (Figure 1).

The values of the longer decay time τ_2, from 382 ± 55 μs at pH 4.4 to 308 ± 25 μs at pH 8.0, are more important for the ternary system than for both binary systems, i.e. between 120 and 212 μs. This is not directly comparable to the results from Tan et al.[26] who observed a decrease in the decay time between the binary Eu/hydrous alumina, i.e. 219 μs, and ternary, i.e. 163 μs; and an increase between the binary Eu/HA, i.e. 111 μs, and ternary. These authors did not report the typical bi-exponential decay in the presence of HA, maybe because of too long delay step (*viz.* 15 μs for Eu/HA, and 35 μs for Eu/HA/hydrous alumina), which already had precluded the determination of bi-exponential decay in past studies[56]. Nevertheless, the increase of luminescence decay time between the binary Eu/HA and ternary Eu/HA/hydrous alumina system was observed both in Tan et al.[26] and in this study. One can also compare the results on the basis of the mass of HA per surface of oxide in both systems. Tan et al.[26] used 0.02 mg_{HA}/m^2 (10 mg_{HA}/L for 4.4 g/L hydrous alumina with specific area of 105 m^2/g) when we were using 1.86 mg_{HA}/m^2. The lesser amount of mineral surface could be an explanation for these differences, as well as for the interaction with alumina evidenced by XPS[26].

Assuming that τ_1 is due to a fast exchange mechanism and τ_2 is due to complexation environment, according to reference 52 it would mean that there is only 2 water molecules remaining in the first coordination sphere of Eu(III) in Eu(III)/PAHA/α-Al_2O_3 system at pH 4.4, when there would be 7 in the Eu(III)/PAHA system at the very same pH. Knowing the reserves on the applicability of this relationship to this particular case we cannot take this value for granted.

At low pH, the spectrum in the ternary system is almost the same as the spectrum of Eu-PAHA complex, and very different from the one of Eu(III) in contact with α-Al_2O_3 (SI Figure S2a). The spectroscopic and macroscopic data lead us to think that, at pH < 7, Eu-PAHA complexes are sorbed onto α-Al_2O_3 surface. The increase in τ_2 may then be due to a more constrained environment of Eu(III), but of the same symmetry, in the sorbed humic structure, which may decrease the probability of the Eu(III) ions to lose energy through quenching moieties.

When pH is increasing, the slower decay time τ_2 decreases from 382 µs at pH 4.4 to 185 µs at pH 9.6, which means that there is a greater probability of Eu(III) to be submitted to quenching process when PAHA is less sorbed onto the surface, or that Eu is progressively more exposed to quenching groups. One can also consider the fractionation of humic acid during sorption. After the pH-edge there is a small decrease in Eu(III) sorption in the ternary system (Figure 2). This is in fact reflecting the progressive change in the structure of Eu(III)/PAHA sorbed onto the surface and the competition of Eu(III) with dissolved PAHA. At pH greater than 8.5, the $^5D_0 \rightarrow {}^7F_1$ transition of the binary Eu(III)/α-Al_2O_3 and the ternary systems are the same (SI Figure S2b), giving indication that alumina has a direct influence on Eu(III) environment. Above pH 8, influence of the mineral surface and possible ternary complexes should be taken into account when trying to model such a system.

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Supporting Information Available

Five figures show Eu(III) luminescence spectra in contact with different concentration of PAHA at pH ≈ 4, Eu(III) luminescence spectra in the different systems at pH ≈ 4.2 and 8.7, inorganic and humic Eu(III) speciation in solution as a function of pH, evolution of Eu(III) luminescence spectra in the ternary system at three different pH, and luminescence decay of Eu(III) in the ternary system at pH 4.4. This material is available free of charge via the Internet at http://pubs.acs.org.

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