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Modelling Eu(III) speciation in a Eu(III)/PAHA/ α -Al₂O₃ ternary system

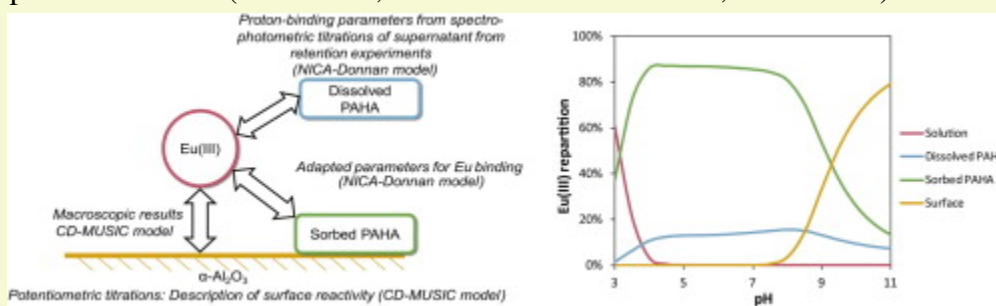
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ABSTRACT. In this work, modelling of Eu(III) speciation in a ternary system, i.e., in presence of purified Aldrich humic acid (PAHA) and α -Al₂O₃, is presented. First, the mineral surface charge is measured by potentiometric titrations and then described using the CD-MUSIC model. This model is also used to describe Eu(III) binding to the α -Al₂O₃ surface at different pH values, ionic strength and mineral concentrations. Time-resolved luminescence spectroscopy (TRLS) is then used to study the binding of Eu(III) to PAHA at pH 4 with different humic acid concentrations. The spectra are used to calculate a spectroscopic “titration curve”, used to determine Eu(III)/PAHA binding parameters in the NICA-Donnan model. Following a previous study (Janot et al., Water Res. 46, 731–740), modelling of the ternary system is based upon the definition of two PAHA pools where one fraction remains in solution and the other is adsorbed onto the mineral surface, with each possessing different proton and metal binding parameters. The modification of protonation behaviour for both fractions is examined using spectrophotometric titrations of the non-adsorbed PAHA fraction at different organic/mineral ratios. These data are then used to describe Eu(III) interactions in the ternary system: Eu(III) repartitioning in the ternary system is calculated for different pH, ionic strength and PAHA concentrations, and results are compared to experimental observations. The model is in good agreement with experimental data, except at high PAHA fractionation rates. Results show that organic complexation dominates over a large pH range, with the predominant species existing as the surface-bound fraction. Above pH 8, Eu(III) seems to be mostly complexed to the mineral surface, which is in agreement with previous spectroscopic observations (Janot et al., Environ. Sci. Technol. 45, 3224–3230).



HIGHLIGHTS

- Eu(III) behaviour is described under a various range of environmental conditions.
- CD-MUSIC and NICA-Donnan models are used to calculate Eu(III) speciation.
- Modifications of HA reactivity due to its fractionation are taken into account.
- Model shows that Eu(III) is preferentially bound to adsorbed humic acid fraction.

KEYWORDS Complexation; Adsorption; Fractionation; Modelling; Natural organic matter

1. Introduction

Interactions between humic substances (HS) and mineral surfaces have a great influence on contaminant behaviour in the environment. Presence of humic substances greatly modifies the adsorption of metals onto minerals, and may enhance their solubility and potential transport [1,2]. Several models can describe the different binary systems: Model VI [3] or NICA-Donnan [4] for metal complexation to humic substances, CD-MUSIC for metal adsorption onto surfaces [5,6], Ligand and Charge Distribution (LCD) model for humic substances retention onto oxides [7,8]. However, the additivity of the binary systems - i.e., metal/HS, metal/surface, and HS/surface is often not respected for the ternary systems metal/HS/surface [9,10]. Some studies have succeeded in describing ternary systems containing fulvic acids [11,12], but the larger size and higher heterogeneity of humic acid makes it more difficult to describe [13]. In fact, like real polymers [14], humic acids adsorption onto minerals increases with ionic strength [9,15–17], which is not observed for fulvic acids [18], and is often different from the behaviour of small organic molecules [19]. Recently, Weng et al. [20] succeeded to describe the behaviour of arsenate in a humic acid-containing ternary system; however, arsenate has a different behaviour towards colloids than metallic ions.

Despite numerous studies of these ternary systems, it is still difficult to predict the speciation of metal ions [21,22], a major reason being the fractionation of humic substances constituents when they adsorb onto mineral surfaces [23–27]. This phenomenon has been characterized by several techniques, including UV–visible spectroscopy, size-exclusion chromatography, time-resolved luminescence spectroscopy (TRLS), and asymmetric flow-field flow fractionation. These techniques have been applied to different ternary systems, with contrasting results depending on the mineral surface, the HS origin, and the solution parameters such as pH and ionic strength. The adsorption of HS onto mineral surfaces induces a mass/size fractionation, as noted by several authors [23,24,28,29], but chemical fractionation is also occurring. Spectrophotometric studies show preferential adsorption of the most aromatic moieties

[25–27,29]. The two HS fractions – the one in solution and the one onto the surface – present different composition and affinity towards protons and ions [11,26,27].

A new major step to successfully describe a metal/HA/surface system is to characterize the reactivity of HA fractions created upon adsorption. However, this is difficult due to the low concentrations of HA in the supernatant from adsorption experiments. Recently, the use of spectrophotometric titrations has facilitated the measurement of environmentally relevant humic acid concentrations, i.e., less than 10 mg/L [30,31]. In Janot et al. [27], we applied this method to determine the modification of proton-binding behaviour of HA fractions after adsorption onto α -Al₂O₃. Here, Eu(III) speciation is studied in presence of the same purified Aldrich humic acid (PAHA) and α -Al₂O₃ surface. Eu(III) is considered to be (i) a representative of the lanthanides, which use is increasing in modern industry and which are important for understanding geochemical processes; and (ii) as an analogue of some actinides(III). We have already described the evolution of the Eu(III) chemical environment in the binary and ternary systems using time-resolved luminescence spectroscopy (TRLS) [32], which guides our modelling hypotheses. Aluminium oxides are not the most common minerals in the environment, but their surface sites are used here as an analogue of the aluminol surface sites of clays [15], which are ubiquitous in natural systems. Here, we use the CD-MUSIC and NICA-Donnan models to construct a model describing the repartitioning of Eu(III) within the different compartments of the system (solution, surface, adsorbed-PAHA, and dissolved-PAHA).

2. Materials and methods

2.1. Materials

The α -Al₂O₃ sample was purchased from Interchim (pure 99.99%, size fraction 200–500 nm). As in previous studies [27,31–33], the solid was washed thrice with carbonate-free NaOH and thrice with milli-Q water before drying and storage at room temperature under N₂(g) atmosphere. Specific area was measured by N₂-BET method and found to be 15 m²/g.

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.

Commercial Aldrich humic acid was purified (PAHA) according to Kim et al. [34]. Stock suspension at $5 \text{ g}_{\text{PAHA}}/\text{L}$ was prepared by diluting PAHA in NaOH (pH around 10) overnight to completely dissolve the sample.

2.2. Potentiometric titrations of $\alpha\text{-Al}_2\text{O}_3$

Potentiometric titrations were performed in a computer-controlled system under $\text{N}_2(\text{g})$ atmosphere in a thermostatic vessel (25°C) equipped with a stirrer using 50 mL solutions at 100 g/L $\alpha\text{-Al}_2\text{O}_3$. Ionic strength I was fixed using KNO_3 (for 0.01 M and 1 M titrations) or NaClO_4 (0.1 M titration). The quoted ionic strengths are the initial values before the addition of any titrant. Experimental values of I were calculated for every data point, accounting for both background electrolyte ions and free H^+ and OH^- . The pH values of the solutions were controlled during titrations by addition of 0.1 mol/L acid and base solutions. Base titrant (titrisol for 0.1 mol/L solution) was prepared with degassed Millipore water. The pH values were recorded with two pH Metrohm 6.0133.100 glass electrodes and a single Metrohm 6.0733.100 reference electrode. The pH electrodes were calibrated by performing a blank titration of the background electrolyte prior to the sample titration. The aqueous suspension was purged with $\text{N}_2(\text{g})$ at pH 4 for 90 min. The suspension was then titrated by adding small volumes of titrant, and pH was recorded as a function of the titrant volume added to the suspension. After each addition, a drift criterion for pH was used ($\Delta\text{mV}/\text{min} < 0.1$) and a maximum waiting time of 60 min was set for acquiring each data point. Usually stabilization of pH took less than 2 min. A similar procedure was followed for the blank solution titration. Two forward and backward titrations were performed to eliminate the hysteresis effect.

2.3. Adsorption experiments

The methodology of these experiments have been described in a previous study [33]. Briefly, batch experiments were carried out at ambient

temperature with 10^{-6} mol/L Eu(III) concentration at different pH, ionic strengths (0.01 M and 0.1 M NaClO_4) and various concentrations of organic and/or inorganic compounds. To minimize carbonation of the systems, and formation of $\text{Eu}(\text{CO}_3)_n^{3-n}$ complexes, headspace was purged with nitrogen prior to closing the tubes. The pH values of the solutions were adjusted by addition of fresh 0.01 or 0.1 mol/L HClO_4 or 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, and to minimize junction potential, the electrode filling solution was modified to use 0.1 M NaCl. The pH electrode was calibrated using buffer solutions (pH 4.01, 7.01, and 10.00), yielding σ_{pH} of 0.05–0.08. After 3 days of equilibration, the final pH was checked and samples were ultracentrifuged at 60,000 rpm during 2 h. Eu(III) concentration in the supernatant was measured by ICP-AES or by standard addition method in TRLS, diluting an aliquot of the supernatant in 3 mol/L K_2CO_3 [35].

2.4. Spectroscopic measurements

We studied Eu(III) speciation in binary and ternary systems by TRLS. A detailed description of the installation can be found elsewhere [33]. Briefly, a luminescence signal was collected after a gate delay $D = 10 \mu\text{s}$ after the excitation by a laser flash, during a gate width $W = 300 \mu\text{s}$. To increase the signal to noise ratio, 1000 accumulations were performed for each spectrum. To avoid aggregation and settling of samples in the $\alpha\text{-Al}_2\text{O}_3$ -containing systems, samples were manually shaken between two measurements. All luminescence measurements were performed at ambient temperature ($21 \pm 2^\circ\text{C}$). The excitation wavelength was set at $\lambda_{\text{exc}} = 393.8 \text{ nm}$, which corresponds to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition of Eu(III). The observed luminescence corresponds to the transitions from the ${}^5\text{D}_0$ excited state to the ground ${}^7\text{F}_j$ manifold [36]. They are the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition, forbidden for magnetic and electric reasons

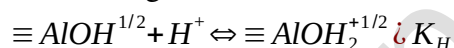
($\lambda_{\max} \approx 580$ nm), the ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition ($\lambda_{\max} \approx 593$ nm), and the ${}^5D_0 \rightarrow {}^7F_2$ hypersensitive electric dipole transition ($\lambda_{\max} \approx 615$ nm) [37–39]. Photo-degradation [40] of the humic acid can be neglected due to the relatively low amount of energy provided to the system, as described previously [33,41–43].

3. Results and Discussion

3.1. Surface charge of $\alpha\text{-Al}_2\text{O}_3$

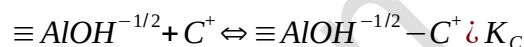
The experimental charging curves are presented in Fig. 1, together with the results of the fits obtained using CD-MUSIC model [5,6]. Calculations were done using the ECOSAT software [44]. The pH_{PZC} was found to be 9.6, meaning that the storage procedure managed to avoid carbonation of the surface. The oxide surface is positively charged below pH_{PZC} , with charge increasing with ionic strength.

The application of Pauling valence rules to $\alpha\text{-Al}_2\text{O}_3$ structure, in which the Al ions distribute their charge to the six surrounding O atoms, results in a charge of -0.5 per $\equiv\text{AlOH}$ site. Those singly coordinated surface groups can be protonated following the reaction



in which K_H is the protonation constant.

In the $\alpha\text{-Al}_2\text{O}_3$ structure, doubly coordinated surface sites $\equiv\text{Al}_2\text{OH}$ also exist, but they are uncharged in the pH range studied and are not taken into account for the description of surface charging behaviour [45]. The fitted parameters are summarized in Table 1. The electrostatic double layer of the water–oxide interface was described using the Basic Stern model [46]. Ion pair formation of surface groups with electrolyte ions is taken into account, and described with the following equations



where C^+ and A^- are the cation and the anion from the electrolyte, respectively.

The electrolyte ions were all positioned in the outer plane of the Stern layer. Evidence of asymmetric binding of electrolyte ions on gibbsite has been previously reported [45], so different affinity constants have been determined for the different electrolyte used. Their values were derived from those found for the charging of goethite [47]. The values obtained for cation pair formation are in accord with the ones of Rietra et al. [47]. However, NO_3^- ions were found to have very weak interaction with the alumina surface ($\log K_{\text{NO}_3^-} = -1.6$), which is much lower than the observations made by Rietra et al. [47] who found ($\log K_{\text{NO}_3^-} = -1$) with goethite. The affinity constants for ClO_4^- are

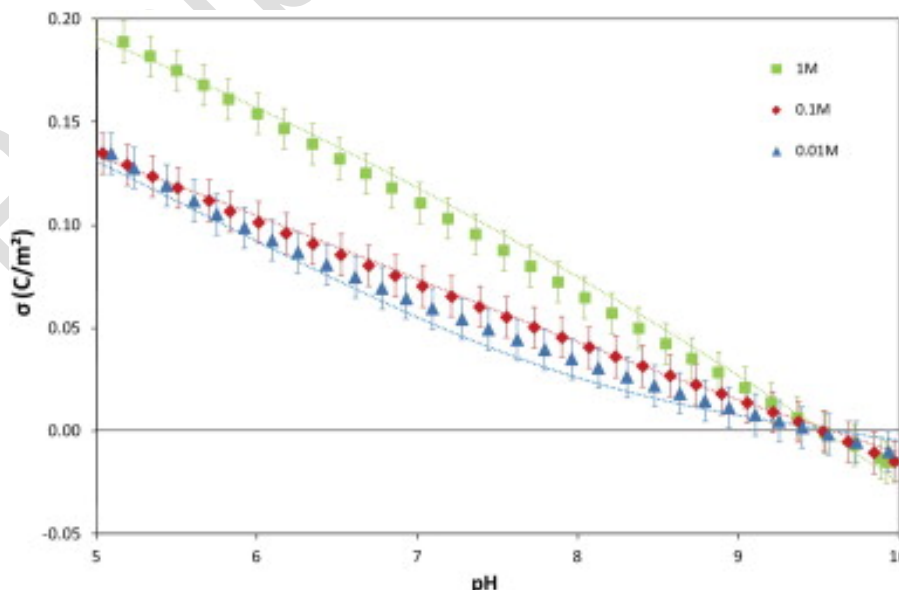


Figure 1. Surface charge of $\alpha\text{-Al}_2\text{O}_3$ at different pH and ionic strengths. The dotted lines are the results of modelling.

Table 1. Fitted parameters used for describing the charging behaviour of $\alpha\text{-Al}_2\text{O}_3$ surface.

| | |
|---|------|
| Specific area (m^2/g) | 15 |
| Site density (sites/nm^2) | 8 |
| Stern layer capacitance (F/m^2) | 2.2 |
| $\log K_{\text{H}^+}$ | 9.6 |
| $\log K_{\text{Na}^+}$ | -0.8 |
| $\log K_{\text{K}^+}$ | -1.5 |
| $\log K_{\text{NO}_3^-}$ | -1.6 |
| $\log K_{\text{ClO}_4^-}$ | -1.4 |

coherent in the two studies: -1.4 in our case, -1.7 for Rietra et al. [47].

The obtained capacitance ($C = 2.2 \text{ F}/\text{m}^2$) is quite high compared to the values proposed by Hiemstra and van Riemsdijk [48] for metal (hydr)oxides surfaces ($C \approx 1 \text{ F}/\text{m}^2$). It is however similar to the value found by Rabung et al. [49] in the case of hematite ($C = 2.24 \text{ F}/\text{m}^2$). A previously observed surface transformation of $\alpha\text{-Al}_2\text{O}_3$ occurred after hydration, which leads to a surface structure closer to gibbsite – $\text{Al}(\text{OH})_3$ – surface [50]. After 10 h titrations in solution, our sample of $\alpha\text{-Al}_2\text{O}_3$

may develop gibbsite-like, or hydroxide-like, surface properties.

3.2. Eu(III) adsorption onto $\alpha\text{-Al}_2\text{O}_3$

Eu(III) adsorption onto $\alpha\text{-Al}_2\text{O}_3$ has been measured in Janot et al. [32] at different pH and two ionic strengths, 0.01 M and 0.1 M NaClO_4 (Fig. 2). As expected, it shows a great dependency to pH and a low dependency to ionic strength. Together with TRLS data showing a loss of water molecules in the first coordination sphere of the ion when surface complexes are formed [32], this indicates inner-sphere complexation [49,51,52]. The influence of metal/surface ratio has also been studied at $\text{pH} = 6.2 \pm 0.2$ by changing $\alpha\text{-Al}_2\text{O}_3$ concentration in the system (see Figure S1 of Supplementary Information). At high Eu(III)/ $\alpha\text{-Al}_2\text{O}_3$ ratio, with 0.5 g/L $\alpha\text{-Al}_2\text{O}_3$, 58% of initial Eu(III) is retained onto the surface. The proportion of adsorbed Eu(III) increases with $\alpha\text{-Al}_2\text{O}_3$ concentration, and reaches 100% at approximately 5 g/L $\alpha\text{-Al}_2\text{O}_3$.

Modelling in the framework of the CD-MUSIC model has been done using ECOSAT software. Data for Eu(III) speciation in solution has been taken from Hummel et al. [53]. Spectroscopic re-

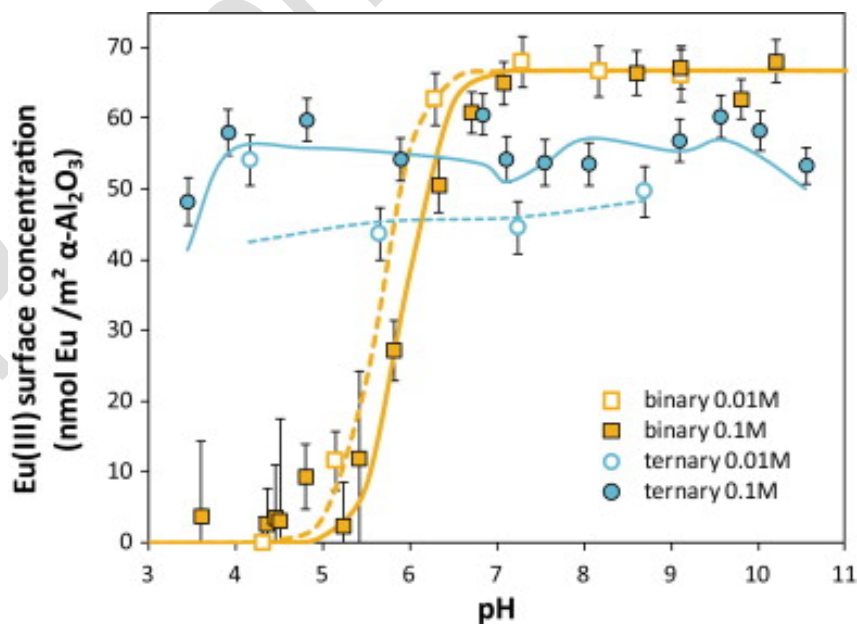


Figure 2. Surface concentration of Eu(III) in the binary Eu(III)/ $\alpha\text{-Al}_2\text{O}_3$ (squares) and ternary (circles) systems depending on pH and I [adapted from 32]. Lines are the results of modelling. $[\text{Eu(III)}] = 10^{-6} \text{ mol}/\text{L}$; $C(\alpha\text{-Al}_2\text{O}_3) = 1 \text{ g}/\text{L}$; Error bars correspond to 2σ .

sults showing the presence of one Eu(III) adsorbed species [33], the formation of only one complex $\equiv\text{AlOHEu}^{+5/2}$ was taken into account. The charge of the ion was distributed between the inner and outer planes of the Stern layer. The best fitting parameters ($r^2 \geq 0.90$) are displayed in [Table 2](#).

Table 2. Fitted CD-MUSIC parameters for Eu(III) complexation to $\alpha\text{-Al}_2\text{O}_3$.

Δz_0 and Δz_1 represent the charge distribution on the inner and outer planes of the Stern layer, respectively.

| | Δz_0 | Δz_1 | logK |
|---|--------------|--------------|------|
| $\equiv\text{AlOH}^{-1/2} + \text{E}^{3+} \leftrightarrow \equiv\text{AlOHEu}^{+5/2}$ | 1.93 | 1.07 | 13.5 |

To confirm the accuracy of this model, the parameters were then used to describe independent data sets from literature of Eu(III) binding to hydrous alumina [21] and $\gamma\text{-Al}_2\text{O}_3$ [22]. [Fig. 3](#) shows that the results of modelling are in good agreement for Eu(III) concentrations close to our conditions, i.e., between 6×10^{-6} and 6×10^{-7} mol/L, even if the mineral surfaces used in these studies were different from our surface, especially with higher specific area (above $100 \text{ m}^2/\text{g}$ compared to our $15 \text{ m}^2/\text{g}$ surface). For higher concentrations of Eu(III) (above 10^{-5} mol/L), the model is slightly overestimating Eu(III) adsorption, with pH-edges found at lower pH values than in experiments (see blue line on [Fig. 3a](#) and blue, red and green lines on [Fig. 3b](#)). The ability of our model to describe literature data then validates a range of concentrations in which this model can be used.

3.3. Eu(III) binding to humic acid

Eu(III) binding to PAHA has been studied by TRLS at pH 4 and different PAHA concentrations. Eu(III) luminescence spectra present an hypersensitive transition, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, the intensity of which is enhanced in the metal-ligand complex relative to its intensity for the aquo ion [39]. Consequently, the change of relative intensities of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions indicates a change in Eu(III) environment symmetry. This asymmetry ratio

$^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ (noted $^7\text{F}_2 / ^7\text{F}_1$) evolves with the relative concentration of metal and humic acid [32]. Above 20 mg/L of PAHA in the system, the asymmetry ratio is constant, suggesting that all the Eu(III) is complexed to humic acid. When PAHA is absent from the system, the asymmetry ratio value is the value corresponding to free Eu(III). It is then possible to use this evolution as a spectral titration curve [54] (see Figure S2 of SI).

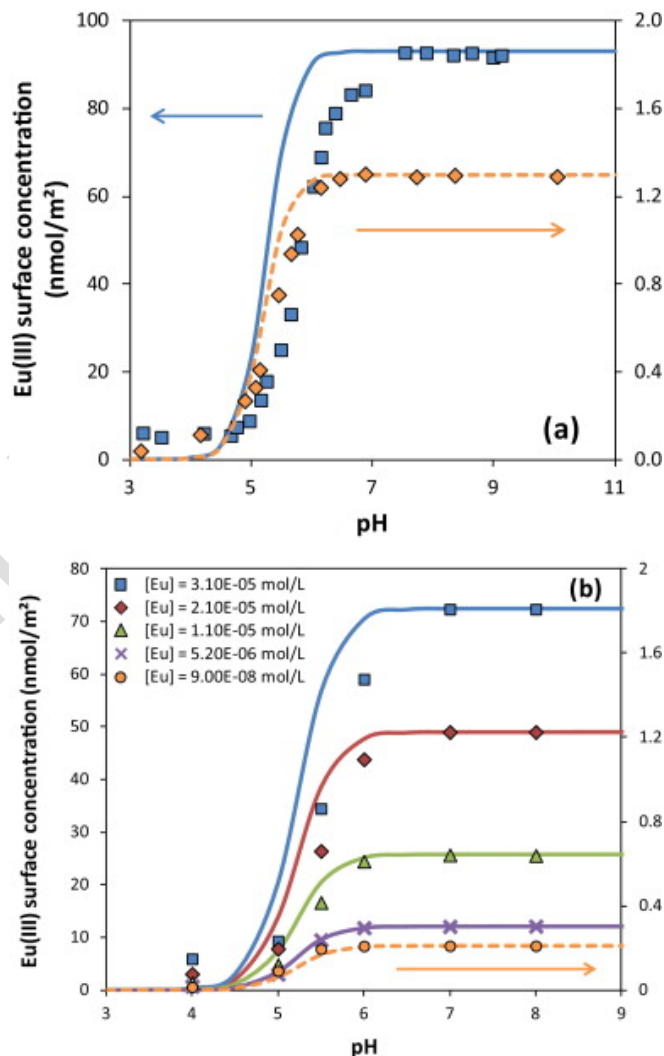


Fig. 3. Eu(III) surface concentration on (a) 4.4 g/L hydrous alumina ($105 \text{ m}^2/\text{g}$), for $I = 0.1 \text{ M KNO}_3$ and $[\text{Eu(III)}] = 4.3 \cdot 10^{-5} \text{ mol/L}$ (squares) and 0.1 M NaClO_4 and $[\text{Eu(III)}] = 6.0 \cdot 10^{-7} \text{ mol/L}$ (diamonds) [21]; (b) 3.6 g/L $\gamma\text{-Al}_2\text{O}_3$ ($119 \text{ m}^2/\text{g}$) for $I = 0.1 \text{ M NaClO}_4$ and various Eu(III) concentrations [22]. Symbols are the data from literature, and lines are the results of our modelling.

We used these asymmetry ratios as indicators of the proportion of Eu(III) complexed, to adjust the NICA-Donnan parameters for Eu(III)/humic acid binding [55,56], as shown in Fig. 4. Modelling has been done using ECOSAT software. The NICA-Donnan equation for metal binding to humic substances can be found elsewhere, together with the definition of the different parameters [55].

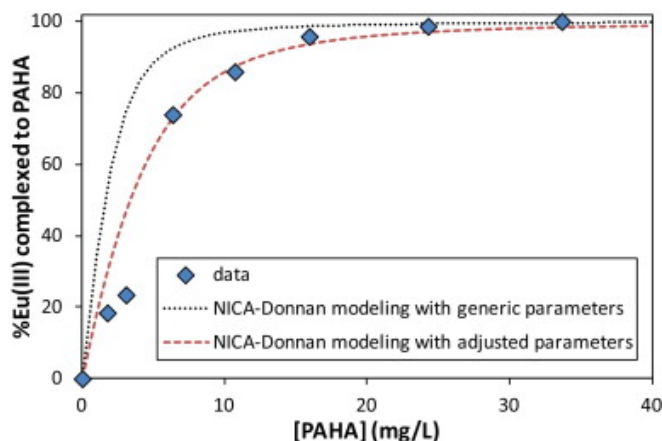


Fig. 4. Results of adjustment of NICA-Donnan parameters for Eu(III)/PAHA binding at pH 4; $[Eu]_{total} = 10^{-6} \text{ mol/L}$; $I = 0.1 \text{ M NaClO}_4$. The generic parameters come from Milne et al. [55].

The adjustment of Eu(III)-binding parameters was done at pH 4 only, because 100% complexation was immediately reached when PAHA was added in the system at pH 6. At higher pH, due the presence of hydrolyzed species of Eu(III) in solution, it is impossible to have the asymmetry ratio value corresponding to the absence of complexation. Thus, we only adjusted the parameters for the low affinity sites (S1). Results are given in Table 3.

Table 3. Adjusted NICA-Donnan parameters used for Eu(III) binding to PAHA and PAHA fractions after contact with mineral surface (dissolved and adsorbed). ^aMilne et al. [55].

| | $\log K_{Eu,1}$ | $n_{Eu,1}$ | $\log K_{Eu,2}$ | $n_{Eu,2}$ |
|---------------------|-----------------|------------|-------------------|-------------------|
| PAHA | 1.05 | 0.50 | 3.43 ^a | 0.36 ^a |
| PAHA _{sol} | 0.9 | 0.50 | 4.07 | 0.36 ^a |
| PAHA _{ads} | 1.13 | 0.50 | 3.43 ^a | 0.36 ^a |

3.4. Eu(III) speciation in the ternary system

A ternary system is difficult to describe due to HA fractionation and modification of reactivity after adsorption onto the mineral surface [23-26]. In this work, spectrophotometric titrations of PAHA supernatants presented in previous studies [27], [31] are used to quantify proton-binding behaviour of humic fractions. Two pools of PAHA are defined: one staying in solution after centrifugation of the suspension (PAHA_{sol}) and one adsorbed onto the mineral (PAHA_{ads}), each fraction showing different NICA-Donnan parameters. Titrations of original PAHA material and modelling of its charge before fractionation using the NICA-Donnan model have been published elsewhere [31]. In a previous study on the binary PAHA/ α -Al₂O₃ system, we used spectrophotometric titrations of supernatant from adsorption experiments to determine modifications of the proton binding parameters of the two PAHA fractions [27]. Here, we take these modifications into account for modelling the behaviour of Eu(III) in presence of both PAHA and α -Al₂O₃.

In our conditions – at 0.1 M NaClO₄ and an initial PAHA concentration of 28 mg/L – between 90 and 30% of PAHA is adsorbed onto α -Al₂O₃ in the ternary system, depending on pH [27]. Except at pH < 4, fractionation rate of PAHA is therefore moderate. In order to test the validity of our approach, we then chose to modify the proton-binding parameters of the two fractions to values corresponding to a moderate fractionation rate.

Spectrophotometric titrations of the dissolved fraction after adsorption did not show any change of the proton-binding site density of high-affinity sites Q₂, neither of the apparent heterogeneity parameters m₁ and m₂ compared to the initial material [27]. Therefore, we did not change these parameters. However, the proton-binding site density of the low affinity sites Q₁ and the median values of the affinity distribution for proton for both types of sites $\log K_{H,1}$ and $\log K_{H,2}$ were modified: Q₁ and $\log K_{H,1}$ were lowered, and $\log K_{H,2}$ increased compared to the original compound, as seen by spectrophotometric titrations of non-sorbed fractions [27]. The same calculation was performed for PAHA_{ads}: from spectrophotometric titrations and mass balance calculations, we ob-

Table 4. NICA-Donnan proton-binding intrinsic parameters for PAHA before contact with the oxide (PAHA), PAHA fraction in solution (PAHA_{sol}), and adsorbed PAHA fraction (PAHA_{ads}), determined from spectrophotometric titrations [27], [31].

In bold are the modified parameters used to model the PAHA fractions compared to PAHA_i.

| | Q ₁ | logK _{H,1} | m ₁ | Q ₂ | logK _{H,2} | m ₂ |
|------------------------------|----------------|---------------------|----------------|----------------|---------------------|----------------|
| PAHA _i [27], [31] | 3.63 | 2.80 | 0.66 | 1.77 | 6.41 | 0.45 |
| PAHA _{sol} [27] | 2.00 | 2.40 | 0.66 | 1.77 | 7.60 | 0.45 |
| PAHA _{ads} [27] | 4.40 | 3.00 | 0.66 | 1.77 | 6.41 | 0.45 |

served an increase in Q₁ and logK_{H,1} values regarding the values fitted for non-fractionated PAHA [27]. The calculated parameters for both fractions PAHA_{sol} and PAHA_{ads} are reported in Table 4.

The logK_{H,1} values for protonation varied for the two fractions compared to the original material. Consequently, the logK_{Eu,1} values for Eu(III)/PAHA binding determined previously (see Table 3) were modified in the same proportions. Following the same reasoning, the logK_{Eu,2} value for Eu(III) binding to PAHA_{sol} was updated as well. The NICA-Donnan parameters taken into account for modelling Eu(III) binding to dissolved and adsorbed PAHA fractions are given in Table 3. For metal binding to humic acid, generic values of intrinsic heterogeneity parameters p₁ (0.62) and p₂ (0.41) were used [57]. The m_i values for proton binding were the same in original PAHA and fractions, so values of the non-ideality ion-binding parameters n_{Eu,i} for Eu(III) binding were kept unchanged.

Using these parameters, the surface concentration of Eu(III) in each batch experiment was calculated, using as inputs of the model the values of pH, Eu(III) and α-Al₂O₃ concentrations, as well as amounts of both PAHA fractions. Eu(III) and α-Al₂O₃ concentrations may slightly vary between two experiments due to modifications of solution volume when adjusting the pH value. These differences within a series explain the otherwise apparently peculiar variations of model for some data. Model values were calculated for the experiments performed at different pH and I (see circles in Fig. 2), and for experiments performed at constant pH and various initial PAHA concentrations (see Fig. 5). They show theoretical and actual surface con-

centration of Eu(III), i.e. Eu(III) bound to the surface and to adsorbed PAHA.

Under these modelling hypotheses, the behaviour of Eu(III) is well described in a ternary Eu(III)/PAHA/α-Al₂O₃ system depending on pH, especially at 0.1 M. Modification of PAHA binding parameters with fractionation are determined from adsorption experiments performed at pH ≈ 7 and I = 0.1 M [27], thus results of the modelling provide better fits to experimental data at this ionic strength value and neutral pH. The trends of Eu(III) behaviour depending on initial PAHA concentration are captured, but the values are not always accurate. The isotherm at pH ≈ 6.2 is well described, whereas the Eu(III) adsorption at pH ≈ 7.4 seems underestimated. The behaviour of Eu(III) at pH 4 is less well described, even if the general trend is present. These conditions corre-

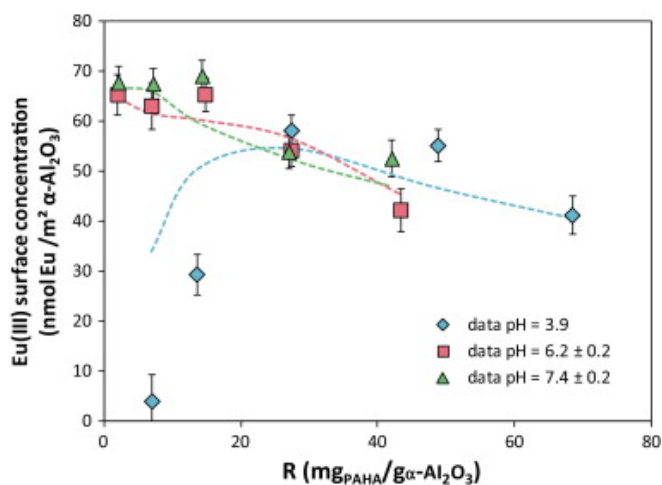


Fig. 5. Eu(III) surface concentration in the ternary system depending on pH and coverage ratio. Lines are the results of modelling. [Eu(III)] = 10⁻⁶ mol/L; C(α-Al₂O₃) = 1 g/L; I = 0.1 M NaClO₄. Error bars correspond to 2σ.

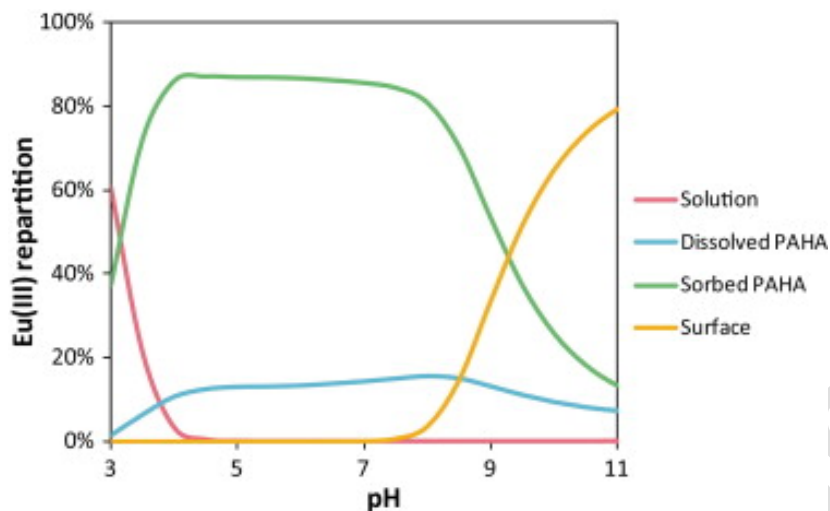


Fig. 6. *Eu(III) speciation in the ternary system depending on pH.*

$$I = 0.1 \text{ M NaClO}_4, [\text{PAHA}] = 28 \text{ mg/L}, C(\alpha\text{-Al}_2\text{O}_3) = 1 \text{ g/L}, [\text{Eu(III)}] = 10^{-6} \text{ mol/L}.$$

spond to a high fractionation rate, with a large percentage of PAHA being adsorbed and PAHA reactivity being greatly modified [27], [31]. The disagreement between experimental and calculated concentrations under these conditions may be due to the values chosen for adapted protonation parameters of both PAHA fractions, which correspond to a median fractionation rate (around 70%).

Fig. 6 shows the model results of pH-dependent Eu(III) speciation. It is observed that between pH 4 and 8, Eu(III) is mainly bound to PAHA_{ads}. The influence of the mineral surface becomes significant only above pH 9, which is in agreement with spectroscopic observations [33]. TRLS spectra of Eu(III) in the ternary system showed an apparition of surface-like features for pH values higher than 8: decrease of asymmetry ratio, broadening of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, shifting of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ apparent maximum towards higher wavelengths [32].

At 0.01 M NaClO₄, macroscopic observations showed less adsorbed PAHA, so the surface concentration of Eu(III) is lower, but Eu(III) repartitioning is similar (data not shown). Eu(III) repartitioning at different surface coverage ratios is shown in Figure S3 of SI. At pH 6.2 and 7.4, Eu(III) is partially complexed to the surface for surface coverage ratios below 10 mg_{PAHA}/g_{α-Al₂O₃}. When PAHA concentrations increase, Eu(III) is totally bound to PAHA, mostly to the adsorbed fraction. At pH 4, the surface has no influence, in

agreement with binary Eu(III)/α-Al₂O₃ observations. Eu(III) surface concentration is only due to its complexation with adsorbed PAHA. Below 20 mg_{PAHA}/g_{α-Al₂O₃}, a significant proportion of Eu(III) is free in solution, which is not seen at higher pH values.

4. Conclusions

In this model of contaminant behaviour in a ternary metal/HA/mineral system, we took into account the modification of humic acid reactivity due its fractionation after adsorption onto a mineral surface. We used results from spectrophotometric titrations of PAHA supernatants from adsorption experiments performed at pH ≈ 7 and I = 0.1 M. The results of our approach show a good description of experimental observations at different pH, ionic strength and humic acid concentration values, thus providing model validation. However, the description is less accurate when fractionation rate of the humic acid is high, such as at low pH. Performing spectrophotometric titrations of supernatants from adsorption experiments at other pH values would allow a better characterization of PAHA reactivity modifications. Moreover, the protonation parameters used for the modelling were calculated from titrations made on supernatant from binary PAHA/α-Al₂O₃ system. The presence of Eu(III) may have an influence on the fractionation of humic moieties as complexation presumably primarily involves the carboxylic

groups at low pH values [58]. Still, the results of this study show the importance of the reactivity modifications of the humic substances, and provide a step towards a better understanding and description of these complex ternary systems.

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Supporting Information Available.

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