Effect of aqueous Acetic, Oxalic and Carbonic Acids on the adsorption of Americium onto α-Alumina

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Summary

The prediction of the migration for radionuclides in geologic media requires a quantitative knowledge of retardation phenomena. For this purpose, the sorption of Am(III) onto a model mineral -α-alumina- is studied here, including the effects of groundwater chemistry: pH and concentrations of small organic ligands (acetate, oxalate and carbonate anions). This work presents some experimental evidences for the synergic sorption mechanism of americium-ligand cationic complexes onto the alumina. As, its anionic complexes were not sorbed, Am(III) cations were desorbed as a result of the formation of anionic complexes in the aqueous phase. By using the ion-exchange theory, and a corresponding restricted set of parameters – exchange capacities and thermodynamic equilibrium constants - the whole set of sorption experiments of Am(III) cationic species onto the α-alumina was modelled in various chemical conditions.

Keywords

Alumina, americium (III), oxalate, acetate, carbonate, sorption, synergic, ion-exchange theory

Introduction

The chemistry of f-block elements at the +III oxidation state is very important for nuclear waste management. Indeed, isotopes of lanthanides are fission products of ^{235}U, while isotopes of transuranic actinides –mainly Pu, Am and Cm- are activation products of ^{238}U. Moreover, lanthanides(III) are used as non-radioactive analogues of Pu(III), Am(III) and Cm(III). In order to understand the chemical behaviour of these elements in geological and environmental context for future nuclear waste disposals, it is necessary to understand their interaction mechanisms with natural solids such as oxides or clays. These mechanisms consist in chemical retention -partition of the metallic element between aqueous solution and mineral surface-. This is the key phenomenon for modelling the resulting limitations in the migration of radionuclides.

Complexing agents, such as anions $CH_3CO_2^-$, $C_2O_4^{2-}$ and CO_3^{2-} of respectively acetic, oxalic or aqueous carbonic acids can decrease the retention of metals as a result of competitive complexation reactions in the aqueous phase [1, 2] conversely synergic effects *–i.e.* adsorption of a metal-ligand complex– can increase their retention [3].

In the present study we first investigate the sorption of Am(III) on α-alumina as a function of pH and ionic strength, without any complexing agent. Then, we shall study the effect of ligands (acetate, oxalate and carbonate anions) on the sorption of the actinide. This work is a preliminary study allowing to compare Eu(III) and Am(III) behaviour and so to verify their analogy. POURQUOI TU ECRIS CA ? SI TU l'AS FAIT DANS TA THESE, METS LA EN REF. SINON, JE NE PENSE PAS QUE TU PEUX LE METTRE.

Even though Al_2O_3 does not occur frequently as a pure mineral in natural systems, its surface characteristics are known to be similar to those of iron oxides with respect to metal ion sorption [4]. In contrast to iron oxides, it is transparent for visible exciting laser light, and so α-Al_2O_3 is an appropriate model sorbent for studies by Time Resolved Laser Fluorescence Spectroscopy (TRLFS), a technique that we used in a near paper for Eu(III) sorption. Moreover the crystallographic structure of Al_2O_3 is known.

Experimental details

Alumina (α-Al_2O_3) from Interchim (pure 99.99%) was washed by NaOH 0.1M to remove adsorbed carbonate, and equally for saturating the solid surface with Na^+ ions. The solid was washed with de-ionised water to remove salt excess. It was then centrifuged and stocked in vacuum. It was characterised by X-ray diffraction methods (XRD). No change in the crystalline structure of the solid was detected after the washings. However, the XRD method is not appropriate to see possible modifications in the solid-solution interface. Thus the solid was analyzed by X-ray photoelectron spectroscopy (XPS) using a VG Escalab MKII spectrometer with an unmonochromated AlK_α (hν = 1486.6 eV) radiation to confirm crystalline form of α-alumina at interface.

The measurement of point zero net proton charge was used to control the presence of adsorbed carbonate. We obtain a PZNPC equal to 9.1 which confirmed that no carbonate was adsorbed on our alumina [5]. (12(±0.2) m²/g) is the measurement of the specific area useful for this study and was made using a Coulter SA3100 apparatus from Beckman Coulter. This surface area is indicated to be able to compare our results with others studies, but in this study the results of Kd are expressed in term of mass.

Solutions of ^{241}Am isotope (α emitter, half life 432 years) were purchased from CERCA. Counting were carried out using Ultima gold AB and a Tri-Carb 2700-TR Packard radio counter.

CO_2 free solutions were prepared with limited volumes of gas over the aqueous solutions in order to limit CO_2 in batches. Total carbonate concentrations were controlled and always found to be below 10^{-5}M. The solutions of NaCl or HCl were prepared by weighting Suprapur products from Aldrich, and diluting them with Millipore water purged by Argon. NaOH solutions were prepared similarly with weighted amounts of NaOH 50% from Aldrich. The ligand solutions were prepared by weighting amounts of Suprapur (Aldrich) NaCl and $NaCH_3COO$, $Na_2C_2O_4$ and $NaHCO_3$ that were dissolved in Millipore water purged with Argon for 2 hours.

pH was adjusted with carbonate free HCl or NaOH solutions, and controlled with a combined pH microelectrode (Mettler Toledo). The outer reference cell was filled with saturated NaCl/KCl solutions and calibrated with solutions of known $[H^+]$, *i.e.* in $-\log[H^+]$ units, not in $-\log(a_{H+})$ units. The buffers (acetic acid / acetate 10^{-3}M; hydrogenocarbonate / carbonate 10^{-3}M) used for calibrating the glass electrode had the same ionic strength as the working solutions.

Preliminary sorption measurements

Preliminary measurements showed, that equilibrium conditions were achieved within one day for the sorption of Am(III) on α-Alumina in different chemical conditions. Sorption measurements (sorption at trace radionuclide concentrations $<10^{-8}$ M) were carried out as a function of pH in 10 mL polycarbonate centrifuge tubes. After spiking with ^{241}Am, and shaking for at least 2 days, the samples were centrifuged for 2 hours at 60000 rpm before sampling the supernatant solutions, and pH measurements. The samples were counted a time long enough time to obtain an error of less than 1 percent on radiochemical measurements. Uncertainty was estimated as the maximum absolute error calculated by considering the maximum error in each operation in batch sorption experiments. Sorption on batch walls was checked, and found not significant.

Preliminary measurements showed that oxalic, acetic and aqueous carbonic acids did not specially change the time needed for achieving equilibrium conditions of Am(III) sorption on α-alumina. The influence of ligand concentrations was studied by sorption experiments of metal at fixed other chemical conditions. Sorption isotherms were determined as a function of ligand concentrations.

Treatment of data

Aqueous speciation is classically modelled with mass balance and mass action laws using published equilibrium constants (Table 1). The uptake of aqueous metal species on alumina was modelled using the same type of equations, including electroneutrality for the interface phase, *i.e.* the ion-exchange theory (IXT) as already described and justified elsewhere [6, 8]. Sorption was attributed to surface sites i, of stoichiometry $\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}$, when pure alumina is originally in contact with pure water. This notation includes charge compensation at the interface as postulated by the model (IXT), and it can very well be an ion pair –*i.e.* an outer-sphere sorbed species- since surface sites are ionized by water. Site i, can be saturated with any of the major species from the solution: H^+, OH^-, Cl^-, Na^+, and carboxylic acid LH_2 or AcH and their ionized forms L^{2-}, LH^- or Ac^-. Using notations that include charge compensation, the following stoichiometries of site i, were taken into account: $\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}$, $\left\{\overset{(i)}{\equiv}\text{Al-O}^-\text{,Na}^+\right\}$, $\left\{\overset{(i)}{\equiv}\text{Al-OH}_2^+\text{,Cl}^-\right\}$ and $\left\{\overset{(i)}{\equiv}\text{Al-OH}_2^+\text{,CH}_3\text{COO}^-\right\}$ (or $\left\{\overset{(i)}{\equiv}\text{Al-OH}_2^+\text{,HL}^-\right\}$) and $\left\{\overset{(i)}{\equiv}(\text{Al-OH}_2^-)_2^{2+}\text{,L}^{2-}\right\}$. The later sorbed species can equivalently be written as dehydrated species $\left\{\overset{(i)}{\equiv}\text{Al-Cl}\right\}$ $\left\{\overset{(i)}{\equiv}\text{Al-OOCCH}_3\right\}$ (or $\left\{\overset{(i)}{\equiv}\text{Al-HL}\right\}$) and $\left\{\overset{(i)}{\equiv}(\text{Al})_2\text{L}\right\}$ respectively, for ideal systems in water solvent, which is the case for IXT model at constant ionic strength as here used. These types of species are widely used in literature; however, not always with notations that include charge compensation. The above species are merely the result of ionic exchanges: cations H^+ and Na^+ are exchanged between $\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}$ and $\left\{\overset{(i)}{\equiv}\text{Al-O}^-\text{,Na}^+\right\}$, typically from $\left\{\overset{(i)}{\equiv}\text{Al-OH}_2^+\text{,Cl}^-\right\}$, anions CH_3COO^-, LH^- or $0.5\,L_2^-$ can be exchanged with Cl^-, while its sorbed species of stoichiometry $\left\{\overset{(i)}{\equiv}\text{Al-Cl}\right\}$ can be obtained from species $\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}$ by OH^- / Cl^- anion exchange. In the model (IXT), these ionic exchange equilibria are associated with equilibrium constants, also often named selectivity coefficients. In Table 2, we give the definitions and notations of those for which we estimated a numerical value in a previous work [6].

The exchange capacities (mass balance on the solid) and the equilibrium constants provide a set of equations that were analytically solved for speciation in both phases, as classically done for ionic exchanges on clayed materials [6-8]. The modelled aqueous and surface speciation were used to identify the stoichiometries of the sorption equilibria, and finally for fitting the numerical values of the exchange capacities and corresponding equilibrium constants, when feasible, or a product of these parameters as explained below.

The relative uncertainty was constant on the measured activities A (see above), hence on C_{Am} (mol.L^{-1}), the total concentrations of Am in the aqueous solution. Consequently the uncertainty was constant for $\log C_{Am}$: $\log C_{Am}$ should rather be used for curve fitting and graphical representations. Furthermore, the log-log plot of K_d *v.s.* concentration is an usual and convenient graphical representations, since classical slope analysis provide the corresponding stoichiometry of the partition reaction, when written with the major species, where

$$K_d = \frac{C_{\overline{Am}}}{C_{Am}} = \left(\frac{A°}{A} - 1\right)\frac{V}{m} \text{ (L.kg}^{-1}\text{) or equivalently (mL.g}^{-1}\text{)} \tag{1}$$

is the distribution coefficient of Am between solid and liquid phases, $C_{\overline{Am}}$ (mol.kg^{-1}) is the total concentrations of Am on the solid, V is the volume (L) of solution, and m the mass (kg) of solid. A° and A are the initial and final activities (Bq) of the solution respectively, which were measured. However, when A and A° are of the same order of magnitude *–i.e.* for small K_d values- big uncertainties are associated with $C_{\overline{Am}}$, and consequently with K_d determinations.

For simplifying the presentation and the qualitative interpretation of the experimental data, the effect of aqueous speciation was eliminated from the sorption results; for this

$$K_{d_{Am^{3+}}} = \frac{C_{\overline{Am}}}{[Am^{3+}]} = K_d\, \alpha_{Am} \tag{2}$$

was used, where

$$\alpha_{Am} = \frac{C_{Am}}{[Am^{3+}]} = \sum_{i=0}^{3} \frac{{}^{*}\beta_{i,Am}}{[H^+]^i} + \sum_{i=1}^{i_{max}} \left(\beta_{i,L}\, [L^{-q}]^i\right) \text{ with q=1 for monoacid and q=2 for diacid} \tag{3}$$

is a classical Ringböm Coefficient (also name as "complexation coefficient") [9] here modelled with published thermodynamic data (Table 1). For the same reason, instead of $[L]_t$, the total concentration of organic acid, we used the concentration of the actual organic ligand for the Am sorbed species:

$$[H_qL] = \frac{[L]_t}{\alpha_{H_qL}} = \frac{[L]_t}{1 + \sum_q \frac{1}{K_{q,L}[H^+]} + \frac{1}{K_{q,L}K_{q-1,L}[H^+]^2}}) \tag{4}$$

Several possible stoichiometries were tested for Am sorption, they can be generated through cationic or anionic exchanges with $\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}$ or $\left\{\overset{(i)}{\equiv}\text{Al-OH}_2^+, \text{Cl}^-\right\}$ respectively, since Am^{3+} can form anionic complexes with typically several L^{2-} ligands. There is no reason to postulate that the stoichiometry of the Am sorbed species are the same as in aqueous solution; however since Am was at trace concentration, we did not considered polynuclear species. It also appeared that in our conditions, only cationic Am species were sorbed, so, we consider here Am sorbed species of stoichiometry $\left\{\overset{(i)}{\equiv}(\text{Al-O})_{3-j-p-n\,m}\text{AmCl}_j(\text{H}_{q-n}\text{L})_m(\text{OH})_p\right\}$. Possible sorption equilibria are typically:

$$(3\text{-}j\text{-}p\text{-}n\,m) \left\{\overset{(i)}{\equiv}\text{Al-OH}\right\} + Am^{3+} + j\, Cl^- + m\, H_qL + p\, H_2O \rightleftarrows \left\{\overset{(i)}{\equiv}(\text{Al-O})_{3-j-p-n\,m}\text{AmCl}_j(\text{H}_{q-n}\text{L})_m(\text{OH})_p\right\} + (3-j)H^+$$

with q=1, 2 and n=1..(q-1) and j+p+n m<3 (5)

with associated selectivity coefficient:

$$K^{i*}_{\text{AmCl}_j(\text{H}_{q-n}\text{L})_m(\text{OH})_p} = \frac{\left[\left\{\overset{(i)}{\equiv}(\text{Al-O})_{3-j-p-n\,m}\text{AmCl}_j(\text{H}_{q-n}\text{L})_m(\text{OH})_p\right\}\right][H^+]^{3-j}}{\left[\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}\right]^{(3-j-p-n\,m)}[Am^{3+}][Cl^-]^j[H_qL]^m} \tag{6}$$

So from Eq(6) and Eq(2),

$$K_{d_{Am^{3+}}} = \sum_i K_{d,i} \tag{7}$$

where

$$\log_{10}K_{d,i} = \log_{10}K^{i*}_{\text{AmCl}_j(\text{H}_{q-n}\text{L})_m(\text{OH})_p} + (3\text{-}j\text{-}p\text{-}n{*}m)\log_{10}\left[\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}\right] + j\log_{10}[Cl^-] + m\log_{10}[H_qL] - (3-j)\log_{10}[H^+]$$

At trace concentration of Am, the surface concentration of aluminol site can be taken equal to the ionic exchange capacity of the solid :

$\left[\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}\right] \approx IEC_i$,

when Site i is saturated with H^+, where IEC_i is the ionic exchange capacity of Site i.

As constant ionic strength was obtained by adding sodium chloride, chloride concentration was constant; so, Eq(8) writes

$$\log_{10}K_{d,i} = A_i + (3\text{-}j\text{-}p\text{-}n\ m)\log_{10}\left[\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}\right] + m\ \log_{10}[H_qL] - (3\text{-}j)\log_{10}[H^+] \quad (9)$$

where

$A_i = \log_{10}K^{i^*}_{AmCl_j(H_{q-n}L)_m(OH)_p} + j\ \log_{10}[Cl^-]$

is constant.

We will use classical slope analysis based on Eq. 9 for interpreting our experimental data. When Am is mainly sorbed on site i, for constant $[H_qL]$ the slope of ($\log_{10}K_{dAm^{3+}}$) *vs* -($\log_{10}[H^+]$) is (j-3), where j is the stoichiometric coefficient of Cl in the Am sorbed species. In the case of ternary system, where fixed pH and NaCl concentration were used, the slope of ($\log_{10}K_{dAm^{3+}}$) *vs* $\log_{10}[H_qL]$ is m, the stoichiometric coefficient of L in the Am sorbed species. In these classical slope analysis, the intercept is typically ($K^{i^*}_{AmCl_j(H_{q-n}L)_m(OH)_p}$ $IEC_i^{(3-j-p-n\ m)}$), the product of the ionic exchange equilibrium constant –also called selectivity coefficient- and ionic exchange capacity for site i.

Results and interpretation

1. Binary system Am(III)/α-Al_2O_3

The logarithm of the distribution coefficient of americium (III) was found to increase with a slope equal to 1 as a function of $-\log_{10}[H^+]$ in the range corresponding to $2 \le -\log_{10}[H^+] \le 7$ (Figure 1). A plateau is observed for $-\log_{10}[H^+]$ more than 7. For $-\log_{10}[H^+] \le 8$, the plateau is the result of competitive aqueous hydrolysis of Am^{3+}, since the slope 1 is still observed up to $-\log_{10}[H^+] = 8$ for $\log K_{dAm^{3+}}$, which can be interpreted as evidence for the sorption of an Am species corresponding to the stoichiometry $\left\{\overset{(i)}{\equiv}(Al_i\text{-}O)_{1-p}AmCl_2(OH)_p\right\}$. Thess species correspond to j = 2 in Eq. 9. For this interpretation, it is assumed that the engaged sorption site was saturated with H^+: $\left\{\overset{(i)}{\equiv}\text{Al-OH}\right\}$. This is a realistic assumption since the slope started in a very acidic medium ($2 \le -\log_{10}[H^+]$). For the same reason, Am hydrolysis is unlikely: we interpreted the slope of 2 with sorbed specie $\left\{\overset{(i)}{\equiv}\text{Al-O}^-,AmCl_2^+\right\}$.

For the acidity range $8 \le -\log_{10}[H^+] \le 12$ a slope of 3 is observed for $\log K_{dAm^{3+}}$ *vs* $-\log_{10}[H^+]$, which can be interpreted as evidence for the sorption of another Am species of stoichiometry $\left\{\overset{(i)}{\equiv}AlO_{(3-p)}Am(OH)_p\right\}$ corresponding to 3-j = 3 in Eq. 9. For this interpretation it is again assumed that the corresponding sorption site was saturated with H^+. It was not possible to determine the value of p from the americium (III) trace concentration study. Stoichiometric coefficient p can certainly be determined from saturation experiments; however, this would have required too much activity of americium 241. For this reason, we can not conclude about the exact stoichiometry for the adsorbed hydroxide complex of americium (III).

It is important to notice that the half point reactions for the two first hydrolysis of americium in aqueous solution are $-\log_{10}[H^+]_{1/2,1} = \log_{10}{}^*\beta_1 = 6.8$ and $-\log_{10}[H^+]_{1/2,2} = \log_{10}({}^*\beta_2/{}^*\beta_1) = 7.9$ (Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina). These two thermodynamic constants are close to the value corresponding to the sorption of the Am hydroxide species (Figure 1): for the surface it is $-\log_{10}[H^+]_{1/2s,i} = 9.08$, a classical observation, which suggested that speciation might very well be the same on the surface and in the bulk aqueous solution, which, in turn, rather suggests the formation of outer-sphere sorbed hydroxides. The aqueous hydroxide would keep its first hydration sphere when sorbed on the surface: $\left\{\overset{(i)}{\equiv}AlO_{(3-p)}Am(OH)_p\right\}$ should better be written $\left\{\overset{(i)}{\equiv}AlO^-_{(3-p)}Am(OH)_p^{(3-p)+}\right\}$ where probably p = 1 or 2. However, we do not propose this simple interpretation.

Previous results [6] gave some evidences about the adsorption of chloride for pH less than 5, and adsorption of sodium cations for pH more than 10. In the present work, no change was observed at these pH values for the slope of $\log_{10}K_{dAm^{3+}}$ *vs.* $-\log_{10}[H^+]$. We may here assume that the surface site engaged in the Am sorption is a new site that was not observed in the previous NaCl sorption study. This new site has no acido-basic properties in our pH domain in contrast with the sorption site of Na^+ and Cl^- ions.

Righetto *et al.* obtained very similar sorption results on γ-alumina in the pH range (7-8) they used [10]. On the other hand, Moulin *et al.* [11] obtained very different sorption results on α-alumina in spite of similar experimental conditions. However, the PZNPC of their alumina was 7.5, suggesting the presence of adsorbed carbonate *i.e*. a problem in the conditioning of their solid that was indeed, studied in air conditions.

It is interesting to notice that our experimental distribution coefficient of americium (III) did not evidence any sorbed species of stoichiometry $AmCl^{2+}$. It was not necessary to consider this reaction to model our experimental data. However, chloride complexes might exist in aqueous media only as weak outer-sphere complexes –or even weak ion pairs- since no spectral change was detected for Am^{3+} on Cl^- additions [12], their effect can rather be accounted for by activity coefficients. Conversely, in their review, Guillaumont *et al.* [13] selected very weak stability constant for Am-Cl complexes.

Finally, to model the americium (III) adsorption in neutral and basic media, we needed to consider both hydroxide and complex adsorptions. The fitted parameters

$$\log_{10}\left(\sum_{p=0}^{2}\left(K^*_{Am(OH)_p}\ IEC^{3-p}\right)\right) = -19.65\pm0.12$$

$$\log_{10}\left(K^*_{AmCl_2}\ IEC\right) = 1.36\pm0.07$$

are enough to model the sorption of trace concentrations of Am(III) on alumina from NaCl aqueous solutions in the pH range 2-12. We proposed the sorption of Am species $AmCl_2^+$, and of another species of stoichiometry $\left\{\overset{(i)}{\equiv}AlO_{(3-p)}Am(OH)_p\right\}$, where stoichiometric coefficient, p, could not be determined. As a conclusion for this first study, the model is quite simple: a single sorption site and two sorbed species for modelling the sorption in a wide pH range (2 to 12).

1.1. Ternary systems (Am/surface/ligand)

1.1.1. System Am(III)/α-Al_2O_3/Acetate

The effect of acetate on Am sorption was detected beyond 0.01M at $-\log_{10}[H^+] = 4.6$ in 0.1 M NaCl aqueous solutions: Adsorption decreases, suggesting aqueous complexation, and this is indeed accounted for by independently known complexing constants (Figure 2a). At higher total acetate concentration (0.1 M), where $Am(CH_3COO)_{3(aq)}$ predominates Am(III) aqueous speciation, the distribution coefficient seems to reach a plateau.

To interpret this behaviour, we used Eq. 9 by representing the logarithm of $K_{dAm^{3+}}$, the distribution coefficient of the aquo ion Am^{3+}, as a function of the logarithm of $[CH_3COOH]$, the aqueous concentration of acetic acid (Figure 2b). For $[CH_3COOH]$ less than 2.10^{-2}M, $[CH_3COOH]$ has no effect on $K_{dAm^{3+}}$. But above this concentration, the experimental data can be interpreted with a slope of approximately 2, suggesting the adsorption of species $\left\{\overset{(i)}{\equiv}AlOAm(CH_3COO)_2\right\}$. This consideration led to the best fitting value:

$$\log_{10}\left(K^*_{AmAc2}\,IEC\right) = -7.91\pm0.33$$

The simplest interpretation was to assume that the same site as previously evidenced is involved. However, this synergic sorption was detected only in a narrow domain of experimental conditions; which did not allow sensitivity analysis. Moreover, in a previous study [6], a competition between acetate and chloride was observed, meaning that acetate and chloride can be sorbed on the same site of α-alumina, which has acid properties since chloride sorption could be interpreted as Cl^-/OH^- anionic exchange; while in the present binary system study, we evidenced that americium (III) is sorbed on a site, which have no acido-basic properties in the pH range 2-12. So, we can conclude that the adsorption site for americium is different from the previous anionic site. Indeed we did not here observed any competition between acetate and Am sorptions.

Moreover, Figure 2b does not show any evidence for the sorption of species $Am(CH_3COO)^{2+}$ in our experimental conditions, but lower NaCl concentrations are expected to decrease $AmCl_2^+$ sorption, which could possibly allow the sorption of $Am(CH_3COO)^{2+}$ In our conditions, we only determined the maximum possible value:

$\log_{10}\left(K^{*}_{AmAc}\ IEC^{2}\right) \leq -9$.

As a conclusion, for modelling these experimental data we used the parameters already determined for $AmCl_2^+$ and $Am(OH)_p^{3-p}$ adsorption in the above study in non complexing media, $\log_{10}\left(\sum_{p=0}^{2}\left(K^{*}_{Am(OH)_p}\ IEC^{3-p}\right)\right)$ and $\log_{10}\left(K^{*}_{AmCl_2}\ IEC\right)$. For this reason the modelling in Figure 2a could be improved by further fitting of parameters, which we did not do to get a maximum consistency of our data. Only the product of selectivity coefficient of acetate complexes and exchange capacity was here fitted:

$\log_{10}\left(K^{*}_{AmAc}\ IEC^{2}\right) \leq -9$

$\log_{10}\left(K^{*}_{AmAc2}\ IEC\right) = -7.91 \pm 0.33$

1.1.2. System Am(III)/α-Al_2O_3/oxalate

The effect of oxalic acid on the sorption of Am on α-alumina was studied for $-\log_{10}[H^+]$ equal to 4.2 and ionic strength to 0.1M in a similar way as the above study of acetic acid. In these conditions and using solutions of more than additions increased the sorption of Am when the concentration of oxalic acid was more than 10^{-4}M, while Am sorption decreased, when the concentration of oxalic acid was more than 10^{-3}M (Figure 3a). This decrease is consistent with the known stability constants for the Am oxalate aqueous complexes (Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina). For eliminating this effect we plotted $\log_{10}K_{dAm^{3+}}$ (Eq.2) *vs*. $\log_{10}[H_2C_2O_4]$ (Eq.4): a slope equal to 1 is observed, corresponding to m = 1 in Eq.9. This can be interpreted as the sorption of an Am cationic complex containing one oxalate ligand, namely $Am(C_2O_4)^+$ or $Am(HC_2O_4)^{2+}$ adsorption. The species, $Am(H_2C_2O_4)^{3+}$ is not realistic: Am complexation by ligand containing carboxylic groups is associated with deprotonation of the ligand complexing site. As a consequence, we can assume that the sorbed species is $\left\{\overset{(i)}{\equiv}AlOAmC_2O_4\right\}$ or $\left\{\overset{(i)}{\equiv}(AlO)_2Am(HC_2O_4)\right\}$.

Saturation studies should make the difference between these two possible species, if the stoichiometry of the sorbed complex does not vary when increasing the Am concentration. But once more, this would have required too much activity of ^{241}Am.

As for the α-Al_2O_3 / Am(III) / acetate ternary system, for modelling the experimental data in oxalate media we used the parameters previously determined for the binary system, and we only fitted the product of ionic exchange capacity and selectivity coefficient of the Am oxalate complex:

$$\log_{10}\sum_{j=1}^{2}\left(K^{i*}_{AmH_{2-j}Ox}\ IEC^{3-j}\right) = -0.82 \pm 0.09$$

1.1.3. System Am(III)/α-Al_2O_3/carbonate

The effect of carbonate on the sorption of Am on α-alumina was studied in a similar way as the above study of acetate and oxalate. Experimental conditions were chosen using the thermodynamic constants of Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina . The selected conditions are pH 8.33 and NaCl 0.1M.

The results of sorption are presented in Figure 4a. The sorption behaviour of Am in this bicarbonate media is quite similar to that in oxalate media: a low concentration of bicarbonate increased the retention of americium, while it decreased for $[CO_3^{2-}]$ more than 5.10^{-3}M. This decrease is consistent with the known stability constants for the Am carbonate aqueous complexes (Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina). For eliminating this effect we plotted $\log_{10}K_{dAm^{3+}}$ (Eq.2) *vs*. $\log_{10}[CO_3^{2-}]$ (Eq.4). We can then observe a slope equal to 1 on Figure 4b, corresponding to m = 1 in Eq.9. This can be interpreted as the sorption of an Am cationic complex containing one carbonate ligand, namely $\left\{\overset{(i)}{\equiv}\text{AlOAm}(CO_3)\right\}$ or/and $\left\{\overset{(i)}{\equiv}(\text{AlO})_2\text{Am}(HCO_3)\right\}$. Both carbonate and bicarbonate complexes are known in aqueous solutions [13], however the bicarbonate complexes are less stable, and are only formed in conditions of high carbonic gas (partial) pressure: $\left\{\overset{(i)}{\equiv}\text{AlOAm}(CO_3)\right\}$ is the most likely stoichiometry.

As for the α-Al_2O_3 / Am(III) / (acetate or oxalate) ternary systems, for modelling the experimental data in bicarbonate media we used the parameters previously determined for the binary system, and we only fitted the product of ionic exchange capacity and selectivity coefficient of the Am carbonate complex:

$$\log_{10}\sum_{j=1}^{2}\left(K^{i*}_{AmH_{2-j}CO_3}\, IEC^{3-j}\right) = -9.96 \pm 0.09$$

Conclusions

Am(III) can be sorbed on α-alumina. From 0.1 M Cl^- aqueous solutions, species $AmCl_2^+$ is sorbed in the $-\log_{10}[H^+]$ range 2 to 9. In more basic media an hydrolysed species of Am(III) is sorbed. On adding aqueous carbonic, acetic and oxalic acids synergic sorption reactions of Am(III) were first evidenced. They are the results of the sorption of Am cationic complexes with the basic forms of the organic acids as ligands. Further additions of the ligands resulted in the formation of aqueous anionic complexes of americium, which were not sorbed on the alumina, therefore decreasing the adsorption of americium. The corresponding sorption site is different from another one previously evidenced for the sorption of Na^+, Cl^- and of the ligands, since no competition between Am(III) and chloride, sodium aqueous carbonic, acetic and oxalic acids was observed. This sorption behaviour on α-alumina could be reasonably well modelled for americium (III) at trace concentration in contact with 0.1 M NaCl aqueous solutions in all the experimental conditions, by using Ion-Exchanger Theory, and a restricted set of parameters.

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Tables

Table 1. Thermodynamic data (25℃) used in this wor k for modelling the aqueous speciation of Am(III) in the presence of acetic, oxalic and carbonic aqueous organic acids.

K name	Corresponding equilibrium	$\log_{10}K°$(I=0M)	$\log_{10}K°$(I=0.1M)	Ref.
$^*K_{2,Car}$	$H_2CO_3 \rightleftarrows HCO_3^- + H^+$	$-6.34_9 \pm 0.00_5$	$-6.13_9 \pm 0.00_5$	[14]
$^*K_{1,Car}$	$HCO_3^- \rightleftarrows CO_3^{2-} + H^+$	$-10.33_7 \pm 0.00_3$	$-9.91_6 \pm 0.00_3$	[15]
$^*K_{2,Ox}$	$H_2C_2O_4 \rightleftarrows HC_2O_4^- + H^+$	$-1.40_1 \pm 0.05_2$	$-1.19_1 \pm 0.05_2$	[16]
$^*K_{1,Ox}$	$HC_2O_4^- \rightleftarrows C_2O_4^{2-} + H^+$	$-4.26_4 \pm 0.01_4$	$-3.84_3 \pm 0.01_4$	[16]
$^*K_{1,Ac}$	$CH_3COOH \rightleftarrows CH_3COO^- + H^+$	$-4.75_7 \pm 0.00_2$	$-4.54_7 \pm 0.00_2$	[17]
$^*\beta_1$	$Am^{3+} + H_2O(l) \rightleftarrows Am(OH)^{2+} + H^+$	-7.2±0.5	-7.6± 0.5	[13]
$^*\beta_2$	$Am^{3+} + 2H_2O(l) \rightleftarrows Am(OH)_2^+ + H^+$	-15.1± 0.7	-15.7± 0.7	[13]
$^*\beta_3$	$Am^{3+} + 3H_2O(l) \rightleftarrows Am(OH)_3(aq) + 3H^+$	-26.2±0.5	-26.8± 0.5	[13]
β_{1,Cl^-}	$Am^{3+} + Cl^- \rightleftarrows AmCl^{2+}$	$0.24_0 \pm 0.03_0$	$-0.39_1 \pm 0.03_0$	[13]
β_{2,Cl^-}	$Am^{3+} + 2Cl^- \rightleftarrows AmCl_2^+$	$-0.74_0 \pm 0.05_0$	$-1.79_1 \pm 0.05_0$	[13]
$\beta_{1,Car}$	$Am^{3+} + CO_3^{2-} \rightleftarrows AmCO_3^+$	8.0± 0.4	6.7± 0.4	[13]
$\beta_{2,Car}$	$Am^{3+} + 2CO_3^{2-} \rightleftarrows Am(CO_3)_2^-$	12.9± 0.6	11.2± 0.6	[13]

$\beta_{3,Car}$	$Am^{3+} + 3CO_3^{2-} \rightleftarrows$	$Am(CO_3)_3^{3-}$	15.0± 1.0	13.7± 1.0	[13]
$\beta_{1,Ac}$	$Am^{3+} + CH_3COO^- \rightleftarrows$	$Am(CH_3COO)^{2+}$	2.60±0.03	1.98± 0,03	[18]
$\beta_{2,Ac}$	$Am^{3+} + 2CH_3COO^- \rightleftarrows$	$Am(CH_3COO)_2^+$	4.39±0.03	3.34± 0.03	[18]
$\beta_{3,Ac}$	$Am^{3+} + 3CH_3COO^- \rightleftarrows$	$Am(CH_3COO)_3$	4.99±0.04	3.73±0.04	[19]
$\beta_{1,Ox}$	$Am^{3+} + C_2O_4^{2-} \rightleftarrows$	$Am(C_2O_4)^+$	6.6	5.30	[20]
$\beta_{2,Ox}$	$Am^{3+} + 2\ C_2O_4^{2-} \rightleftarrows$	$Am(C_2O_4)_2^-$	10.5	8.83	[20]
$\beta_{3,Ox}$	$Am^{3+} + 3\ C_2O_4^{2-} \rightleftarrows$	$Am(C_2O_4)_3^{3-}$	13.1	13.06	[20]
K_{s0}	$Am^{3+} + 1{,}5\ CO_3^{2-} \rightleftarrows$	$Am(CO_3)_{1.5}(cr)$	16.7± 1.1	15.1± 1.1	[21]
K_s	$Am^{3+} + CO_3^{2-} + OH^- \rightleftarrows$	$AmCO_3OH(cr)$	21.2± 1.4	19.7± 1.4	[21]
$^*K_s$	$Am^{3+} + 3H_2O(l) \rightleftarrows$	$Am(OH)_3(am) + 3H^+$	-17.0± 0.6	-17.6± 0.6	[21]

Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina

Major species	Exchange capacity (meq/g)	$Log_{10}K°$ (I=0M)	Ref
$\left\{\overset{(j)}{\equiv}AlO^-Na^+\right\} + H^+ \leftrightarrows \left\{\overset{(j)}{\equiv}AlOH\right\} + Na^+$	0.0025±0.0001	8.09± 0.03	[6]
$\left\{\overset{(k)}{\equiv}AlOH\right\} + H^+ + Cl^- \rightleftarrows \left\{\overset{(k)}{\equiv}AlOH_2^+,Cl^-\right\}$	0.0068±0.0035	8.09±0.35	[6]
$\left\{\overset{(l)}{\equiv}AlOH\right\} + H^+ + Cl^- \rightleftarrows \left\{\overset{(l)}{\equiv}AlOH_2^+,Cl^-\right\}$	0.0172±0.0023	6.81±0.21	[6]
$\left\{\overset{(k)}{\equiv}AlOH\right\} + CH_3COOH \rightleftarrows \left\{\overset{(k)}{\equiv}Al\text{-}OOCCH_3\right\} + H_2O$	0.0068±0.0035	5.71±0.55	[6]
$\left\{\overset{(l)}{\equiv}AlOH\right\} + CH_3COOH \rightleftarrows \left\{\overset{(l)}{\equiv}Al\text{-}OOCCH_3\right\} + H_2O$	0.0172±0.0023	4.07±0.16	[6]
$2\left\{\overset{(k)}{\equiv}AlOH\right\} + H_2C_2O_4 \rightleftarrows \left\{\overset{(k)}{\equiv}Al\text{-}C_2O_4\right\} + 2H_2O$	0.0068±0.0035	14.69±0.22	[6]
$2\left\{\overset{(l)}{\equiv}AlOH\right\} + H_2C_2O_4 \rightleftarrows \left\{\overset{(l)}{\equiv}Al\text{-}C_2O_4\right\} + 2H_2O$	0.0172±0.0023	12.02±0.08	[6]
$2\ \left\{\overset{(k)}{\equiv}AlOH\right\} + H_2CO_3 \rightleftarrows \left\{\overset{(k)}{\equiv}Al\text{-}CO_3\right\} + 2H_2O$	0.0068±0.0035	11.35±0.53	[6]
$2\ \left\{\overset{(l)}{\equiv}AlOH\right\} + H_2CO_3 \rightleftarrows \left\{\overset{(l)}{\equiv}Al\text{-}CO_3\right\} + 2H_2O$	0.0172±0.0023	6.19±0.12	[6]

Data measured in the present work:	$\log_{10}\left(K^{i*}_{Am_{ads}}\ IEC^{3-p}\right)$
$\left\{\overset{(i)}{\equiv}Al\text{-}OH\right\}+Am^{3+}+2Cl^- \rightleftarrows \left\{\overset{(i)}{\equiv}\ Al\text{-}OAmCl_2\right\} + H^+$	1.36±0.07
$(3\text{-}p)\left\{\overset{(i)}{\equiv}Al\text{-}OH\right\}+Am^{3+}+pH_2O \rightleftarrows \left\{\overset{(i)}{\equiv}(Al\text{-}O)_{3\text{-}p}Am(OH)_p\right\}+3H^+$	-19.65±0.12
$\left\{\overset{(i)}{\equiv}Al\text{-}OH\right\}+Am^{3+}+2CH_3COOH \rightleftarrows \left\{\overset{(i)}{\equiv}Al\text{-}OAm(CH_3COO)_2\right\}+3H^+$	-7.91±0.33
$(3\text{-}p)\left\{\overset{(i)}{\equiv}Al\text{-}OH\right\}+Am^{3+}+H_2C_2O_4 \rightleftarrows \left\{\overset{(i)}{\equiv}(Al\text{-}O)_{3\text{-}p}Am(H_{2\text{-}p}C_2O_4)\right\}+3H^+$	-0.82±0.09
$(3\text{-}p)\left\{\overset{(i)}{\equiv}Al\text{-}OH\right\}+Am^{3+}+H_2CO_3 \rightleftarrows \left\{\overset{(i)}{\equiv}(Al\text{-}O)_{3\text{-}p}Am(H_{2\text{-}p}CO_3)\right\}+3H^+$	-9.96±0.09

Figures

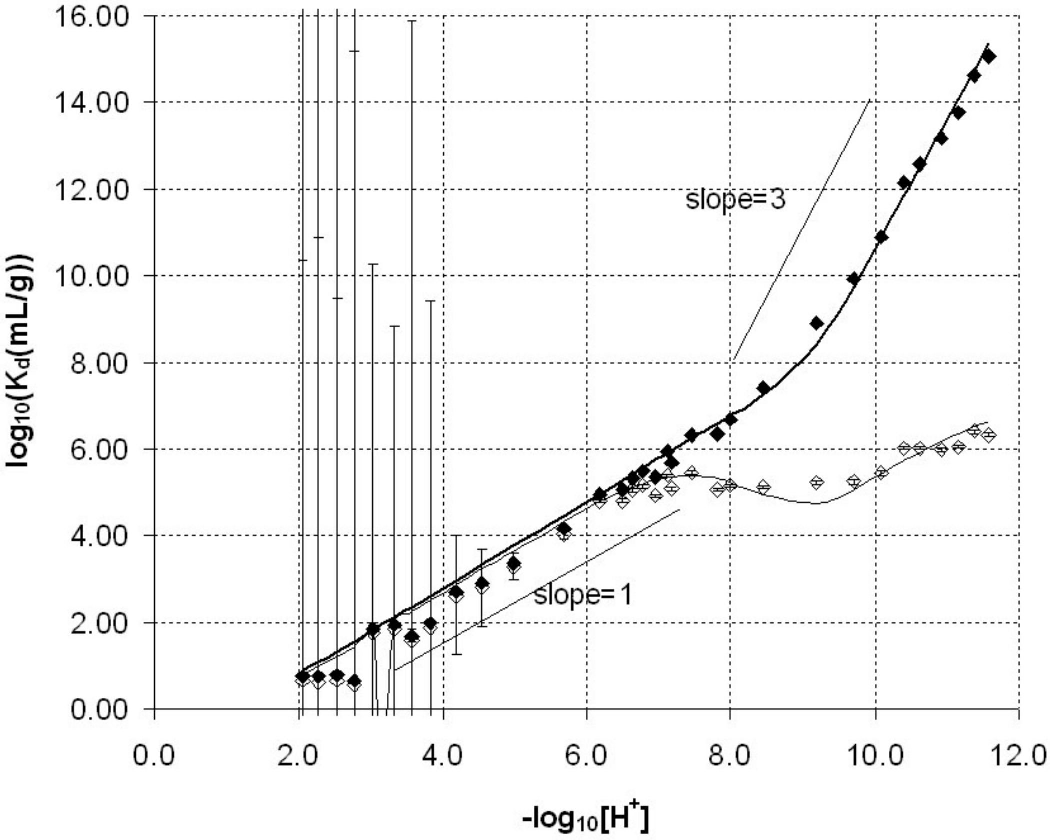


Figure 1: Distribution coefficient of Am(III) on α-Al_2O_3 (T = 22℃, [NaCl] = 0.1 M, [Al_2O_3] = 1g.L^{-1}). $K_{dAm^{3+}}$ (black symbols) was calculated with Eq(2) from $K_{dAm(III)}$ (white symbols) experimental values and calculated Ringböm coefficient α_{Am}. The solid lines were calculated with Eq.(9) and (2) using fitted parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina .

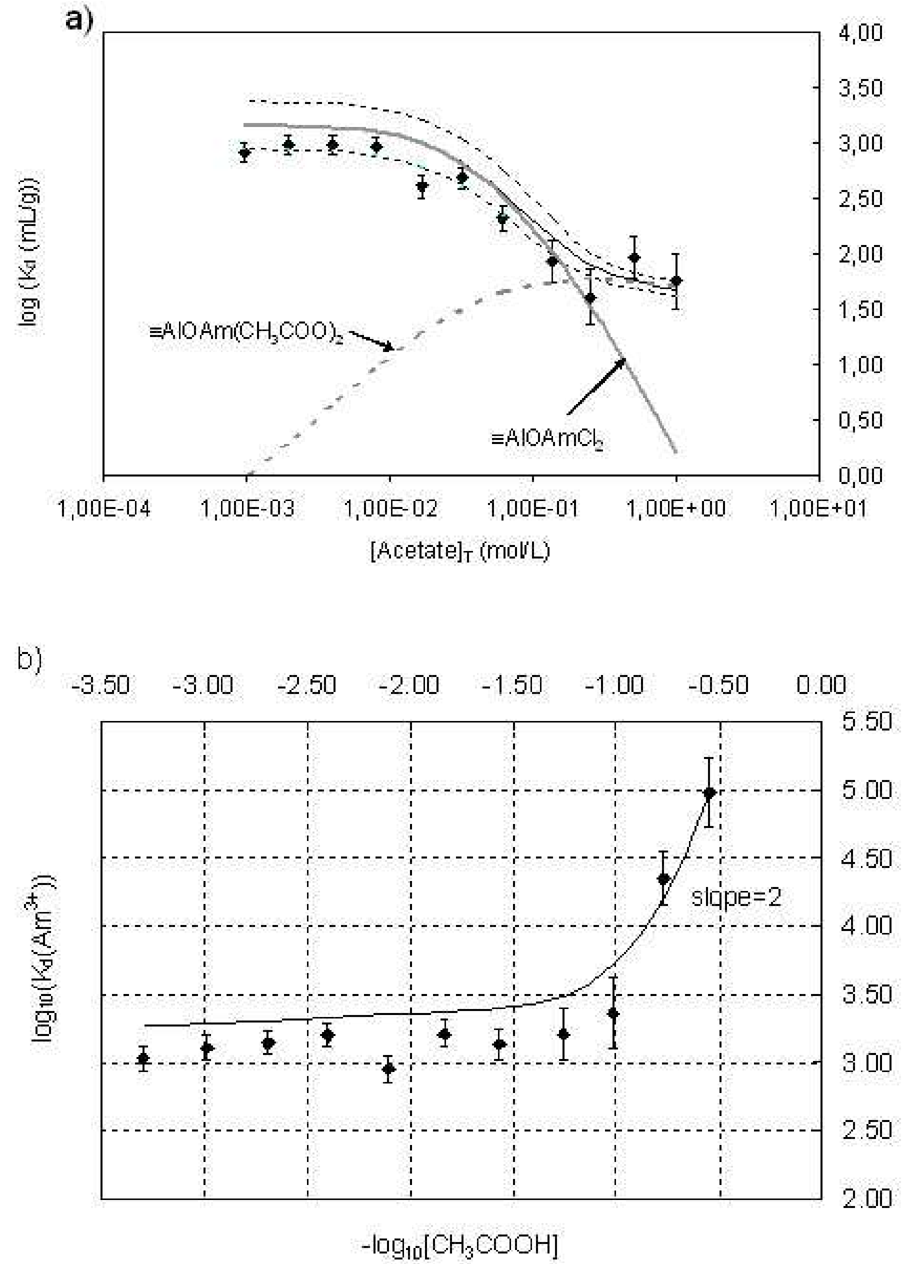
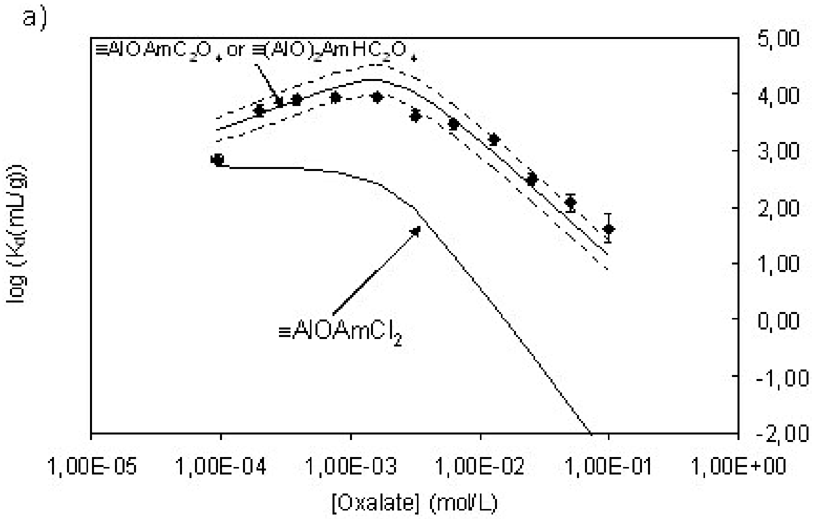


Figure 2: Effect of acetate on Am(III) sorption onto α-alumina (T=22°C; [NaCl] = 0.1 M; pH=4.6; $[Al_2O_3]$ = 5 g.L^{-1}. $K_{dAm^{3+}}$ was calculated from experimental Kd values as explained in the caption of Figure 1. The solid lines were calculated with Eq. (7) using the same parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina as in Figure 1, the only new fitted parameter is here the equilibrium constant for Ionic Exchange $\{\equiv Al\text{-}OAm(CH_3COO)_2\}$ / $\{\equiv Al\text{-}OH\}$.



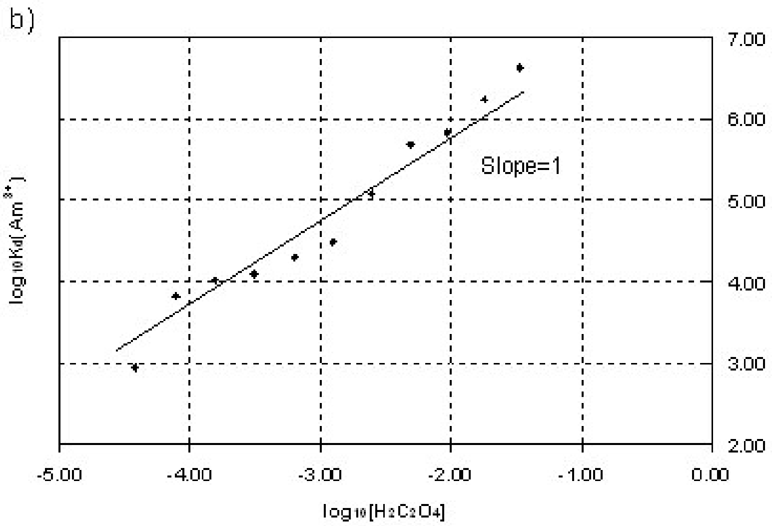


Figure 3: Distribution coefficients of Am(III) and Am^{3+} on α-alumina as a function of oxalate concentration ((T=22℃; [NaCl]=0.1M; pH=4.2; $[Al_2O_3]$=10g.L^{-1}). $K_{dAm^{3+}}$ was calculated from experimental Kd values as explained in the caption of Figure 1. The solid lines were calculated with Eq. (7) using the same parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina as in Figure 1, the only new fitted parameter is here the parameter for Ionic Exchange $\{\equiv(Al\text{-}O)_{1+r}AmH_rC_2O_4\}$ / $\{\equiv Al\text{-}OH\}$, where r = 0 or 1, the exact value of r was not determined.

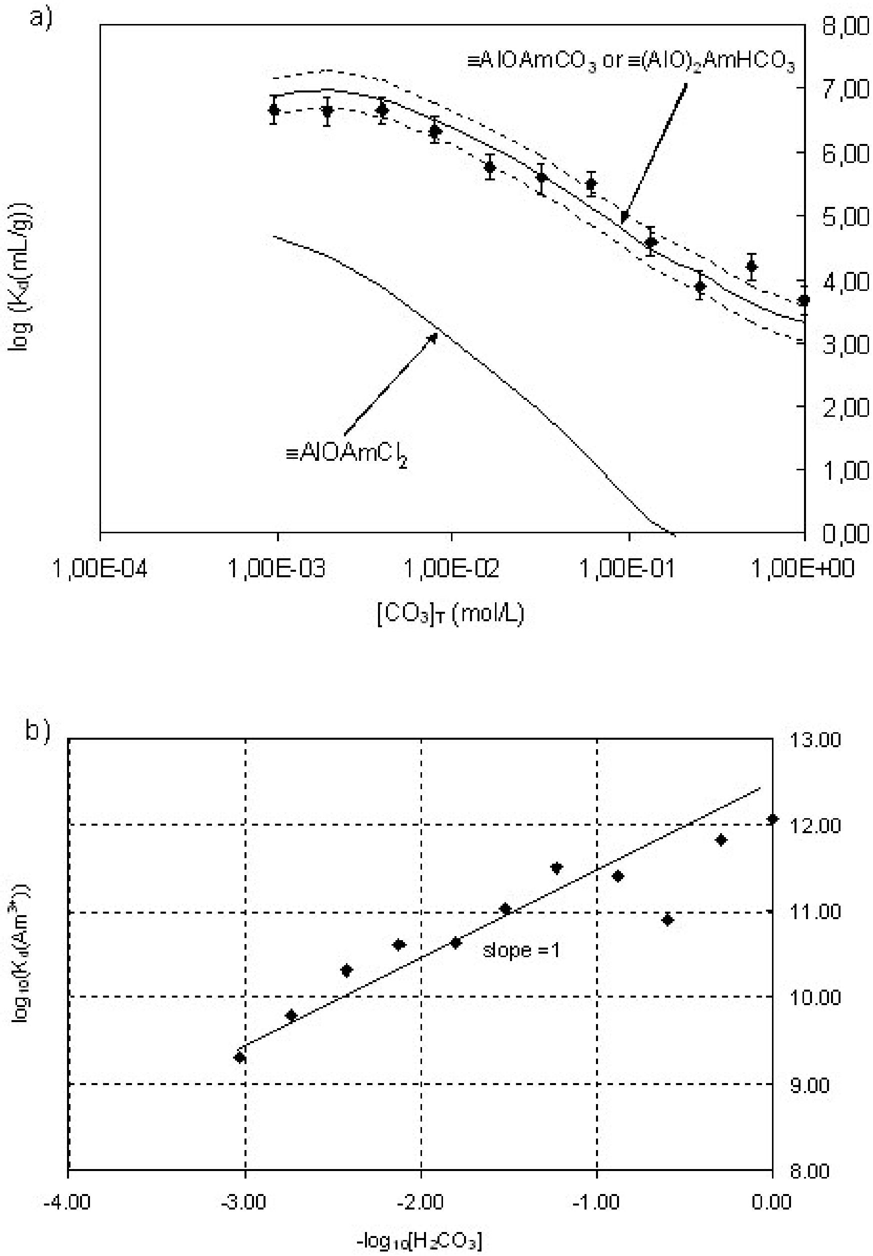


Figure 4: Distribution coefficients of Am(III) and Am^{3+} on α-alumina as a function of carbonate concentrations ((T=22°C; [NaCl]=0.1M; pH=4.2; $[Al_2O_3]$=10g.L^{-1}). $K_{dAm^{3+}}$ was calculated from experimental K_d values as explained in the caption of Figure 1. The solid lines were calculated with Eq. (7) using the same parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina as in Figure 1, the only new fitted parameter is here the parameter for Ionic Exchange {≡(Al-O)$_{1+r}$AmH$_r$CO$_3$} / {≡Al-OH}, where r = 0 or 1, the exact value of r was not determined, however r = 0 is a priori more realistic, corresponding to {≡Al-OAmCO$_3$}.

Captions

Table 3. Thermodynamic data (25°C) used in this work for modelling the aqueous speciation of Am(III) in the presence of acetic, oxalic and carbonic aqueous organic acids.

Table 4. Thermodynamic data for the sorptions of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina

Figure 5: Distribution coefficient of Am(III) on α-Al_2O_3 (T = 22°C, [NaCl] = 0.1 M, [Al_2O_3] = 1g.L-1). $K_{dAm^{3+}}$ (black symbols) was calculated with Eq(2) from $K_{dAm(III)}$ (white symbols) experimental values and calculated Ringböm coefficient α_{Am}. The solid lines were calculated with Eq.(9) and (2) using fitted parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina .

Figure 6: Effect of acetate on Am(III) sorption onto α-alumina (T=22°C; [NaCl] = 0.1 M; pH=4.6; [Al_2O_3] = 5 $g.L^{-1}$. $K_{dAm^{3+}}$ was calculated from experimental Kd values as explained in the caption of Figure 1. The solid lines were calculated with Eq. (7) using the same parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina as in Figure 1, the only new fitted parameter is here the equilibrium constant for Ionic Exchange {$\equiv$Al-OAm($CH_3COO)_2$} / {$\equiv$Al-OH}.

Figure 7: Distribution coefficients of Am(III) and Am^{3+} on α-alumina as a function of oxalate concentration ((T=22°C; [NaCl]=0.1M; pH=4.2; [Al_2O_3]=10$g.L^{-1}$). $K_{dAm^{3+}}$ was calculated from experimental Kd values as explained in the caption of Figure 1. The solid lines were calculated with Eq. (7) using the same parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina as in Figure 1, the only new fitted parameter is here the parameter for Ionic Exchange {$\equiv(Al\text{-}O)_{1+r}AmH_rC_2O_4$} / {$\equiv$Al-OH}, where r = 0 or 1, the exact value of r was not determined.

Figure 8: Distribution coefficients of Am(III) and Am^{3+} on α-alumina as a function of carbonate concentrations ((T=22°C; [NaCl]=0.1M; pH=4.2; [Al_2O_3]=10$g.L^{-1}$). $K_{dAm^{3+}}$ was calculated from experimental K_d values as explained in the caption of Figure 1. The solid lines were calculated with Eq. (7) using the same parameters from Table 2. Thermodynamic data for the sorption of aqueous carbonic, acetic and oxalic acids and americium (III) onto α-alumina as in Figure 1, the only new fitted parameter is here the parameter for Ionic Exchange {$\equiv(Al\text{-}O)_{1+r}AmH_rCO_3$} / {$\equiv$Al-OH}, where r = 0 or 1, the exact value of r was not determined, however r = 0 is a priori more realistic, corresponding to {$\equiv$Al-OAmCO_3}.