Effect of aqueous acetic, oxalic and carbonic acids on the adsorption of americium onto α-alumina

By Cyrille Alliot1, *, Lionel Bion2, Florence Mercier1, Pierre Vitorge2 and Pierre Toulhoat4

1 SUBATECH/École des Mines de Nantes, 4 rue Alfred Kastler, BP 20722, 44307 Nantes Cedex 3, France
2 CEA – DEN/DPC/SECR/LSRM, Bât. 391, Centre d’Études de Saclay, 91191 Gif-sur-Yvette Cedex, France & UMR 8587 (same address)
3 CNRS – UMR 8587 “Analyse et Environnement”, Bât. 391, Centre d’Études de Saclay, 91191 Gif-sur-Yvette Cedex, France
4 CNRS/Université Claude Bernard Lyon 1, UFR de Chimie Biochimie, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

(Received January 21, 2005; accepted in revised form March 24, 2005)

Alumina / Americium(III) / Oxalate / Acetate / Carbonate / Sorption / Synergic / Ion-exchange theory

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.

1. 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 235U, while isotopes of transuranic actinides – mainly Pu, Am and Cm – are activation products of 238U. 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 CH₃CO₂⁻, C₂O₄²⁻ and CO₃²⁻ 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]

*Author for correspondence
(E-mail: cyrille.alliot@subatech.in2p3.fr)

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 was a preliminary study allowing to compare Eu(III) and Am(III) behaviour and so to verify their analogy in sorption study onto α-alumina [7].

Even though Al₂O₃ does not occur frequently as a pure mineral in natural systems, the SCM constants are found to be similar for iron oxides and alumina concerning the sorption of Am(III) and Eu(III), indicating the very close similarity for the sorption properties of both types of minerals [4]. In contrast to iron oxides, α-Al₂O₃ is transparent for visible exciting laser light, which is convenient for using time resolved laser fluorescence spectroscopy (TRLFS), a technique that we used for studying the sorption of Eu(III), an analogue of Am(III) [7].

2. Experimental details

Alumina (α-Al₂O₃) from Interchim (pure 99.99%) was washed by NaOH 0.1 M to remove adsorbed carbonate, and equally for saturating the solid surface with Na⁺ ions [6]. 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 Al Kα (hv = 1486.6 eV) radiation. We did not detect any modification of Al 2p and O 1s peaks, which is an indication that our purification process did not modify the surface of α-alumina at interface.

The measurement of point zero net proton charge was used to control the presence of adsorbed carbonate. We obtained a PZNPC equal to 9.1 which confirmed that no carbonate was adsorbed on our alumina [5]. N2-BET surface area measurements (12 (±0.2) m²/g) were made using a Coulter

Coulter

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.
SA3100 apparatus from Beckman Coulter. This surface area is needed for comparing our partition coefficients from literature, when they are given in mL/m², since we used here mL/g.

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.

CO₂ free solutions were prepared with limited volumes of gas over the aqueous solutions in order to limit CO₂ in batches. Total carbonate concentrations were controlled and always found to be below $10^{-3}$ M. The solutions of NaCl or HCl were prepared by weighting Suprapur products from Aldrich, diluting them with Millipore water purged with 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 NaCH₃COO, Na₂C₂O₄ and NaHCO₃ 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.

3. 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 < $10^{-4}$ 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 60 000 rpm before sampling the supernatant solutions, and pH measurements. The samples were counted a time long enough to obtain an error of less than 1% 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 carboxylic 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.

4. 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 $\left[{{\text{Al} - \text{OH}}}_i}\right]$, 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 LH₂ or AcH and their ionized forms L₂⁻, L⁻ or Ac⁻. Using notations that include charge compensation, the following stoichiometries of site $i$ were taken into account: $\left[{{\text{Al} - \text{OH}}}_i}\right]$, $\left[{{\text{Al} - \text{O}}}_i\right]$, $\left[{{\text{Al} - \text{OH}}}_i\right]$, Cl⁻, $\left[{{\text{Al} - \text{OH}}}_i\right]$, CH₃COO⁻, and (or) $\left[{{\text{Al} - \text{O}}}_i\right]$, HL⁻ and $\left[{{\text{Al} - \text{OH}}}_i\right]$, L₂⁻. The later sorbed species can equivalently be written as dehydrated species $\left[{{\text{Al} - \text{Cl}}}_i}\right]$, $\left[{{\text{Al} - \text{OCCCH}}}_i\right]$, (or) $\left[{{\text{Al} - \text{HL}}}_i\right]$, $\left[{{\text{(Al)}_2L}}_i\right]$ and 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 $\left[{{\text{Al} - \text{OH}}}_i}\right]$ and $\left[{{\text{Al} - \text{O}}}_i\right]$, typically from $\left[{{\text{Al} - \text{OH}}}_i\right]$, Cl⁻, anions CH₃COO⁻, HL⁻ or 0.5 L₂⁻ can be exchanged with Cl⁻, while its sorbed species of stoichiometry $\left[{{\text{Al} - \text{Cl}}}_i}\right]$ can be obtained from species $\left[{{\text{Al} - \text{OH}}}_i}\right]$ 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 $K_d$ vs. 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

$$K_d = \frac{C_{Am}}{C_{Am}} = \left(\frac{A^+}{A^-} - 1\right) \frac{V}{m} \text{ (L kg}^{-1})$$

or equivalently (mL g⁻¹) (1)
Table 1. Thermodynamic data (25 °C) used in this work for modelling the aqeous speciation of Am(III) in the presence of acetic, oxalic and carboxylic aqueous organic acids.

<table>
<thead>
<tr>
<th>$K$ name</th>
<th>Corresponding equilibrium</th>
<th>$\log_{10} K'$ (I = 0 M)</th>
<th>$\log_{10} K'$ (I = 0.1 M)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{EIA}}$</td>
<td>H$_2$CO$_3$</td>
<td>$\rightleftharpoons$ HCO$_3^-$ + H$^+$</td>
<td>-6.34 ± 0.00</td>
<td>-6.13 ± 0.00</td>
</tr>
<tr>
<td>$K_{\text{EIA}}$</td>
<td>HCO$_3^-$</td>
<td>$\rightleftharpoons$ CO$_3^{2-}$ + H$^+$</td>
<td>-10.33 ± 0.00</td>
<td>-9.91 ± 0.00</td>
</tr>
<tr>
<td>$K_{\text{HI}}$</td>
<td>H$_2$C$_2$O$_4$</td>
<td>$\rightleftharpoons$ H$_2$C$_2$O$_4^{-}$ + H$^+$</td>
<td>-1.40 ± 0.05</td>
<td>-1.19 ± 0.05</td>
</tr>
<tr>
<td>$K_{\text{HI}}$</td>
<td>HC$_2$O$_4^-$</td>
<td>$\rightleftharpoons$ C$_2$O$_4^{2-}$ + H$^+$</td>
<td>-4.26 ± 0.01</td>
<td>-3.84 ± 0.01</td>
</tr>
<tr>
<td>$K_{\text{HI}}$</td>
<td>CH$_3$COOH</td>
<td>$\rightleftharpoons$ CH$_3$COO$^-$ + H$^+$</td>
<td>-4.75 ± 0.00</td>
<td>-4.54 ± 0.00</td>
</tr>
</tbody>
</table>

is the distribution coefficient of Am between solid and liquid phases, $C_{\text{Am}}$ (mol kg$^{-1}$) is the total concentrations of Am on the solid, $V$ is the volume (L) of solution, and $m$ is 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 $C_{\text{Am}}$, 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

\[ K_{\text{d,Am}^+} = \frac{C_{\text{Am}}}{[\text{Am}^+]} = K_d(\text{Am}) \]  

(2)

was used, where

\[ \alpha_{\text{Am}} = \frac{C_{\text{Am}}}{[\text{Am}^+]} = \sum_{q=1}^{3} \frac{\beta_{\text{Am}}}{[\text{H}^+]} + \sum_{q=2}^{3} \left( \frac{\beta_{\text{Am}}}{[\text{L}^+]^{q-1}} \right) \]

with $q = 1$ for monoacid and $q = 2$ for diacid

(3)

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

\[ [\text{H}_2\text{L}] = \frac{[\text{L}]}{\alpha_{\text{L}}}, \]

(4)

Several possible stoichiometries were tested for Am sorption, they can be generated through cationic or anionic exchanges with $[\text{Al}^-\text{OH}^-]$ or $[\text{Al}^-\text{OH}^{2-}, \text{Cl}^-]$ respectively, since $\text{Am}^+$ can form anionic complexes with typically several $\text{L}^{2-}$ 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 $[\text{Am}^-\text{OH}^-]$ were of the same order of magnitude – i.e. for small $K_d$ values – big uncertainties are associated with $C_{\text{Am}}$, and consequently with $K_d$ determinations.

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

\[ K_{\text{d,Am}^+} = \sum_{j} K_{\text{d,Am}^+}, \]

(7)

with associated selectivity coefficient:

\[ K_{\text{d,Am}^+}^{(\text{AmCl})} = \frac{[\text{AmCl}]}{[\text{Am}^-\text{OH}^-]} \]

(6)

(5)
At trace concentration of Am, the surface concentration of aluminol site can be taken equal to the ionic exchange capacity of the solid:

\[
\left[ \left[ \text{Al}^{3+} \right] \right] = \text{IEC}_i ,
\]

when site \( i \) is saturated with \( H^+ \), where \( \text{IEC}_i \) 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

\[
\log_{10} K_{d_i} = A_i + (3 - j - p - n \times m) \log_{10} \left[ \left[ \text{Al}^{3+} \right] \right] + m \log_{10} [H_2L] - (3 - j) \log_{10} [H^+] \quad (9)
\]

where

\[
A_i = \log_{10} K_{\text{AmCl}_j (\text{H}_2L)}^{i} + j \log_{10} [\text{Cl}^-]
\]

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 \([H_2L]\) the slope of \( \log_{10} K_{d_{Am^{3+}}} \) 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 \( \log_{10} K_{d_{Am^{3+}}} \) vs. \( \log_{10} [H_2L] \) is \( m \), the stoichiometric coefficient of L in the Am sorbed species. In these classical slope analysis, the intercept is typically \( (K_{\text{AmCl}_j (\text{H}_2L)}^{i} \text{IEC}_i^{(3-j-p-n \times m)}) \), the product of the ionic exchange equilibrium constant – also called selectivity coefficient – and ionic exchange capacity for site \( i \).

5. Results and interpretation

5.1 Binary system Am(III)/\( \alpha \)-Al₂O₃

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 \( 2 \leq -\log_{10} [H^+] \leq 7 \) (Fig. 1). A plateau is observed for \( -\log_{10} [H^+] \) more than 7. For \( -\log_{10} [H^+] \leq 8 \), 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 \( K_{d_{Am^{3+}}} \), which can be interpreted as evidence for the sorption of an Am species corresponding to the stoichiometry \( \left[ \left[ \text{Al}^{3+} \right] \right] \text{AmCl}_j (\text{OH})_k \). These species correspond to \( j = 2 \) in Eq. (9). For this interpretation, it is assumed that the engaged sorption site was saturated with H\(^+\): \( \left[ \left[ \text{Al}^{3+} \right] \right] \text{OH}^{-} \). This is a realistic assumption since the slope started in a very acidic medium (2 \( \leq -\log_{10} [H^+] \) 12) for the same reason, Am hydrolysis is unlikely: we interpreted the slope of 2 with sorbed species \( \left[ \left[ \text{Al}^{3+} \right] \right] \text{AmCl}_j (\text{OH})_k \). For the acidity range 8 \( \leq -\log_{10} [H^+] \leq 12 \) a slope of 3 is observed for \( \log K_{d_{Am^{3+}}} \) vs. \( -\log_{10} [H^+] \), which can be interpreted as evidence for the sorption of another Am...
species of stoichiometry $\{\equiv\text{AlO}_3\ldots\text{pAm}(\text{OH})_p\}$ corresponding to $3 - j = 3$ in Eq. (9). For this interpretation it is again assumed that the corresponding sorption site was saturated with $\text{H}^+$. 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 $-\log_{10}^\beta_{1} = 6.8$ and $-\log_{10}^\beta_{1/2} = 7.9$ (Table 1). These two thermodynamic constants are close to the value corresponding to the sorption of the Am hydroxide species (Fig. 1): for the surface it is $-\log_{10}^\beta_{1/2} = 9.08$, 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 could thus be described by the hydration sphere when sorbed on the surface: $\{\equiv\text{AlO}_3\ldots\text{pAm}(\text{OH})_p\}$ should better be written $\{\equiv\text{AlO}_3\ldots\text{pAm(OH)}_p\text{HO}_j\}$ where probably $p = 1$ or 2. However, we do not propose this simple interpretation.

Previous results [6] gave some evidences about the adsorption of chlorine for $p$ less than 3, and adsorption of sodium cations for $p$ more than 10. In the present work, no change was observed at these $p$ values for the slope of $\log_{10}^\alpha$ vs. $-\log_{10}^\beta_{1/2}$. We may thus assume here 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 acid-base properties in our $p$H domain in contrast with the sorption site of Na$^+$ and Cl$^-$ ions.

Righetto et al. obtained very similar sorption results on $\alpha$-alumina in the $p$H range (7–8) they used [10]. On the other hand, Moulin et al. [11] obtained very different sorption results on $\alpha$-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, Guillaume 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 are enough to model the sorption of trace concentrations of Am(III) on alumina from NaCl aqueous solutions in the $p$H range 2–12. We proposed the sorption of Am species AmCl$^+$, and of another species of stoichiometry $\{\equiv\text{AlO}_3\ldots\text{pAm}(\text{OH})_p\}$, 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 $p$H range (2 to 12).

5.1.1 Ternary systems (Am/surface/ligand)

5.1.1.1 System Am(III)/$\alpha$–Al$_2$O$_3$/acetate

The effect of acetate on Am sorption was detected beyond $0.01\text{ M}$ at $-\log_{10}^\beta_{1} = 4.6$ in 0.1 M NaCl aqueous solutions. Adsorption decreases, suggesting aqueous complexation, and this is indeed accounted for by independently known complexing constants (Fig. 2a). At higher total acetate concentration (0.1 M), where Am(CH$_3$COO)$_3$(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 $K^*_{\text{AmAc}}$, the distribution coefficient of the aquo ion Am$^{3+}$, as a function of the logarithm of [CH$_3$COOH], the aqueous concentration of acetic acid (Fig. 2b). For [CH$_3$COOH] less than $2 \times 10^{-2}$ M, [CH$_3$COOH] has no effect on $K^*_{\text{AmAc}}$. But above this concentration, the experimental data can be interpreted with a slope of approximately 2, suggesting the adsorption of species $\{\equiv\text{AlOAm(\text{CH}_3\text{COO})}_2\}$. This consideration led to the best fitting value:

$$\log_{10}^\beta_{(\text{K}^*_{\text{AmAc}}\text{IEC})} = -7.91 \pm 0.33$$

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 $\alpha$-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 acid-base properties in the $p$H 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, Fig. 2b does not show any evidence for the sorption of species Am(CH$_3$COO)$_3^{2+}$ in our experimental conditions, but lower NaCl concentrations are expected to decrease AmCl$^+$ sorption, which could possibly allow the sorption of Am(CH$_3$COO)$_3^{2+}$. In our conditions, we only determined the maximum possible value:

$$\log_{10}^\beta_{(\text{K}^*_{\text{AmAc}}\text{IEC})} \leq 9$$

As a conclusion, for modelling these experimental data we used the parameters already determined for AmCl$^+$ and Am(OH)$_{3-}$ adsorption in the above study in non
The effect of oxalic acid on the sorption of Am on α-alumina was studied for $-\log_{10}[\text{H}^+]$ equal to 4.2 and ionic strength to 0.1 M in a similar way as the above study of acetic acid. In these conditions and using solutions of increasing oxalate concentration, the sorption of Am increased when the concentration of oxalic acid was more than $10^{-4}$ M and less than $10^{-3}$ M, while Am sorption decreased, when the concentration of oxalic acid was more than $10^{-3}$ M (Fig. 3a). This decrease is consistent with the known stability constants for the Am oxalate aqueous complexes (Table 1). For eliminating this effect we plotted $\log_{10} K_{\text{AmC}^2/\text{IEC}}$ (Eq. (2)) vs. $\log_{10} [\text{H}_2\text{C}_2\text{O}_4]$ (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($\text{C}_2\text{O}_4$)$^{2-}$ or Am($\text{HC}_2\text{O}_4$)$^{3-}$ absorption. The species, Am($\text{C}_2\text{O}_4$)$^{2-}$ is not realistic: Am complexation by ligand containing carboxylic groups is associated with deprotonation of the ligand complexes site. As a consequence, we can assume that the sorbed species is $\text{[\text{AlOAmC}_2\text{O}_4]}$ or $\text{[\text{AlO}_2\text{Am}]}\text{Am}($$\text{HC}_2\text{O}_4$)$].

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 $\alpha$-$\text{Al}_2\text{O}_3$/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:

\[
\log_{10} \sum_{j=1}^{2} \left( K'_{AmH_{j-1}O_2} IEC^{j-1} \right) = -0.82 \pm 0.09
\]

5.1.1.3 System Am(III)/α-Al₂O₃/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 1. The selected conditions are pH 8.33 and NaCl 0.1 M.

The results of sorption are presented in Fig. 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 [CO₃²⁻] more than 5 × 10⁻⁸ M. This decrease is consistent with the known stability constants for the Am carbonate aqueous complexes (Table 1). For eliminating this effect we plotted log₁₀ \[ K_{Am^{n+}} \] (Eq. (2)) vs. log₁₀ [CO₃²⁻] (Eq. (4)). We can then observe a slope equal to 1 on Fig. 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 \( \{AlOAm(CO_3)\} \) or/and \( \{AlO_2Am(HCO_3)\} \). 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: \( \{AlOAm(CO_3)\} \) is the most likely stoichiometry.

As for the α-Al₂O₃/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:

\[
\log_{10} \sum_{j=1}^{2} \left( K'_{AmH_{j-1}CO_3} IEC^{j-1} \right) = 9.96 \pm 0.09
\]

6. Conclusions

Am(III) can be sorbed on α-alumina. From 0.1 M Cl⁻ aqueous solutions, species AmCl₂⁻ is sorbed in the − log₁₀[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.

Acknowledgment. The authors would like to thank Dr. J. Ly and Dr. P. Reillier for useful discussions.

References


This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.