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Effect of aqueous acetic, oxalic and carbonic acids on the adsorption of uranium(VI) onto α-alumina

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The prediction of the migration for radionuclides in geologic media requires a quantitative knowledge of retardation phenomena. For this purpose, the sorption of U(VI) 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 experimental evidence for the synergic sorption of uranium(VI) and the small organic ligands, namely sorption of cationic complexes onto alumina. Conversely, since its neutral and anionic complexes were not sorbed, U(VI) cation could also be desorbed as a result of the formation of neutral or 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 U(VI) cationic species onto the α-alumina was modelled under various chemical conditions.

Introduction

The sorption of radioactive species onto minerals can delay their migration in groundwaters. To assess the uptake properties of the geochemical barriers about possible geologic repositories of radioactive wastes, it is necessary to understand the chemical behaviour of radionuclides in this context, including the interactions with natural solids such as oxides or clays.

However, chemical sorption (partition of the metallic element between the aqueous and solid phases) can be modified by complexing agents: they can decrease the sorption as a result of complexation in aqueous phase[1,2] or by a competition for the sorption sites on the solid; conversely, it can increase the sorption as a result of co-sorption with radionuclides (synergic effect).[3]

In the present study, we firstly focused on the effect of ionic strength and pH on uranium(VI) sorption. We then studied the effect of various typical complexing agents: anions $CH_3CO_2^-$, $C_2O_4^{2-}$ and CO_3^{2-} of respectively acetic, oxalic and aqueous carbonic acids. Our aim is to model the effects of various parameters pH, ionic strength and concentrations of ligands on uranium(VI) sorption.

Uranium(VI) was chosen, because it can be found in toxic wastes, and uranium mobility is often associated with its +6 oxidation state in environmental waters.

Al_2O_3 was chosen as a model mineral. Indeed, it does not occur frequently as a pure mineral in natural systems; however, 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 exciting laser light, which allows studying α-Al_2O_3 by time resolved laser fluorescence spectroscopy (TRLFS).

The anions of carboxylic acids were chosen as ligands, because simple organic acids in soils may be released by decay of plant, animal and microbial tissues[5] and their anionic forms are complexing agents for hard cations, typically UO_2^{2+}. We also studied carbonate ion (CO_3^{2-}) which is the most reactive species toward U(VI) in the natural carbonate systems (CO_2(g)/HCO_3^-/CO_3^{2-}).

Experimental

Materials

Synthetic mineral, α-alumina, from Interchim® (pure 99.99%) was used. However, its surface state is not guaranteed, in particular this mineral could be carbonated. Consequently, a protocol was used to obtain a homo-ionic Na^+ and carbonate free surface: the solid was first washed with a 0.1 M NaOH carbonate free solution and rinsed with deionised water.

After this protocol, the X-ray diffraction pattern did not show any modification, but such analysis cannot detect surface modifications. For this reason, it was also analysed by X-ray photoelectron spectroscopy (XPS) to determine the crystalline form of alumina at the interface: no modification was detected. The point zero net proton charge (PZNPC) was found to be $pH_{PZNPC} = 9.1$, which confirms that no carbonate was adsorbed on α-alumina.[6] Finally, a N_2-BET surface was measured equal to 12(±0.2) $m^2\ g^{-1}$.

Solutions

Radioisotope 232U solution. Liquid scintillation was used for counting isotope 232 of Uranium, an α emitter ($T = 68.9$ years). A problem with this radioisotope is its short life-time: it has to be freshly purified for avoiding interferences with its decay product (essentially ^{228}Th). An experimental protocol was developed to separate ^{232}U from ^{228}Th. The solution from IPL (2.7 MBq/g in HCl 2 M media) was injected on chromatographic column AG1X8 that had been conditioned with a 8 M HCl aqueous solution: Uranium is fixed while Th is eluated. Uranium(VI) was eluated with a 1 mM HCl aqueous solution. The purified ^{232}U solution can be used for about three weeks before re-purifying is needed.

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Other aqueous solutions.. To avoid carbonatation from atmospheric CO_2, we worked with carbonate free aqueous solutions in closed batches, and the volume of air over the aqueous solutions was limited (less than 10% volume of solution).

The NaCl or HCl solutions were prepared by diluting weighed amounts of Suprapur products (Merck) with Millipore® water purged with argon. NaOH aqueous solutions were prepared similarly from weighed amounts of 50% NaOH from Aldrich as developed by Sipos *et al.*[7]

The solutions of ligands were prepared by weighing NaCl and $NaCH_3COO$, $Na_2C_2O_4$ and $NaHCO_3$ Suprapur products (Merck). These products were dissolved in Millipore water purged with argon.

The pH of the different batches was adjusted with the HCl or NaOH carbonate free solutions. The pH was measured with a combined glass microelectrode (Mettler Toledo). The outer reference cell was filled with a saturated NaCl/KCl solution. The combined glass microelectrode was calibrated with solutions of known $[H^+]$, and the same ionic strength as the working solutions. This procedure calibrated the glass microelectrode in $-\log_{10}[H^+]$ units, not in pH ($-\log_{10}a_{H^+}$).

Procedures and techniques

Experiments with radionuclides at trace concentration. The protocol used to study uranium(VI) sorption with trace radionuclide concentrations ($[U(VI)]_t = 3.10^{-10}$ M) on α-alumina in different binary and ternary systems is the same as described elsewhere for americium and europium.[8,9]

Sorption on the batch walls was first checked, and found not significant. The time necessary to achieve equilibrium conditions was verified and found to be less than one day. Sorption measurements were carried out as a function of pH in 10 mL polycarbonate centrifuge tubes. After spiking with ^{232}U, 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 enough times 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.

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

Studying the influence of uranium(VI) concentration. Due to the limit of detection of our spectroscopic technique, we had to work with high uranium concentrations. For this reason we checked that increasing uranium concentration did not change the sorption mechanisms determined from the trace concentration work: we studied the influence of uranium concentration on its sorption.[9] The aim was not to re-fit the model, but rather to check whether the data measured at high uranium concentrations could still be interpreted with the model and the thermodynamic constants determined from data at trace concentrations.

The solutions were always spiked with ^{232}U ($[^{232}U(VI)]_t = 3.10^{-10}$ M). To adjust its concentration, natural UO_3 was added to reach a total concentration of up to 10^{-4} M. All the parameters were fixed excepted the uranium(VI) concentration.

Treatment of data

Description of the sorption model. The surface of α-alumina is assumed to have sorption sites $\{\overset{(i)}{\equiv}\mathrm{Al{-}OH}\}$, when equilibrated with acidic aqueous solutions, in less acidic conditions these sites can exchange their protons, H^+, or hydroxyl ions, HO^-, with ions from the aqueous solution. This results in uranium sorbed species of stoichiometries $\left\{\overset{(i)}{\equiv}(\mathrm{Al{-}O})_{\nu_i,\mathrm{Al}}(\mathrm{UO_2})_{\nu_i,\mathrm{U}}\mathrm{Cl}_{\nu_i,\mathrm{Cl}}(\mathrm{H}_{q_i-n_i}\mathrm{L})_{\nu_i,\mathrm{L}}(\mathrm{OH})_{\nu_i,\mathrm{OH}}\right\}$, which we will call $^{(i)}(\mathrm{AlO})_{\nu_i,\mathrm{Al}}\mathrm{U}_{\nu_i,\mathrm{U}}$ for simplicity. Similarly $\left\{\overset{(i)}{\equiv}\mathrm{Al{-}OH}\right\}$ is now called $^{(i)}$AlOH. In these notations, superscript (i) is for site i, it will be omitted when not needed. L_q is a notation for the anion of one of the carboxylic or carbonic acid studied here; q is the charge of this anion, it is negative. Mass balance equations are

$$[^{(i)}\mathrm{Al}]_t = [^{(i)}\mathrm{AlOH}] + \nu_{i,\mathrm{Al}}[^{(i)}(\mathrm{AlO})_{\nu_{i,\mathrm{Al}}}\mathrm{U_k}] \qquad (1)$$

$$[\mathrm{U}]_t = [\mathrm{U}]_{t,aq} + [\mathrm{U}]_{t,\mathrm{Al}} \qquad (2)$$

where

$$[\mathrm{U}]_{t,\mathrm{Al}} = \sum_{i,\nu_{i,\mathrm{Al}},\nu_{i,\mathrm{U}}} \nu_{i,\mathrm{U}}[^{(i)}(\mathrm{AlO})_{\nu_{i,\mathrm{Al}}}\mathrm{U}_{\nu_{i,\mathrm{U}}}] \qquad (2a)$$

where $[U]_{t,aq}$ is the total aqueous uranium concentration, and $[^{(i)}Al]_t$ is actually the ionic exchange capacity of site i, while the total ionic exchange capacity is

$$[\mathrm{Al}]_t = \sum_i [^{(i)}\mathrm{Al}]_t \qquad (3)$$

For consistency, this model was the same as the one used for interpreting the other experimental data. We used the same modelling as we previously used for similar systems:[8,9] Thermodynamic modelling of ideal systems, also named ion exchange theory (IXT).

$$K = \frac{[\mathrm{AlO}]_{\nu_{\mathrm{Al}}}\mathrm{U}_{\nu_{\mathrm{U}}}[\mathrm{H}^+]^{\nu_{\mathrm{H}}}}{[\mathrm{AlOH}]^{\nu_{\mathrm{Al}}}[\mathrm{UO}_2^{2+}]^{\nu_{\mathrm{U}}}[\mathrm{Cl}^-]^{\nu_{\mathrm{Cl}}}[\mathrm{H_qL}]^{\nu_{\mathrm{L}}}} \qquad (4)$$

is the ionic exchange constant for equilibrium

$$\nu_{\mathrm{Al}}\,\mathrm{AlOH} + \nu_{\mathrm{U}}\,\mathrm{UO_2}^{2+} + \nu_{\mathrm{Cl}}\,\mathrm{Cl}^- + \nu_{\mathrm{L}}\,\mathrm{H_qL} + \nu_{\mathrm{OH}}\,\mathrm{H_2O} \rightleftarrows (\mathrm{AlO})_{\nu_{\mathrm{Al}}}\mathrm{U}_{\nu_{\mathrm{U}}} + \nu_{\mathrm{H}}\,\mathrm{H}^+ \qquad (5)$$

where we have omitted sub- and superscripts i in eqn (4) and (5) for simplicity. *K* is often called selectivity coefficient. AlOH and $(\mathrm{AlO})_{\nu_{\mathrm{Al}}}\mathrm{U}_{\nu_{\mathrm{U}}}$ are assumed to be neutral sorbed species: it is an assumption of IXT. For these electroneutrality conditions:

$$\nu_{\mathrm{Al}} = 2\,\nu_{\mathrm{U}} - \nu_{\mathrm{Cl}} - \mathrm{n}\,\nu_{\mathrm{L}} - \nu_{\mathrm{OH}} \qquad (6)$$

$$\nu_{\mathrm{H}} = 2\,\nu_{\mathrm{U}} - \nu_{\mathrm{Cl}} \qquad (7)$$

Based on this modelling, we determined ν_X, the stoichiometric coefficient for X in the sorption equilibrium (eqn (5)) for all species X, assuming a single stoichiometry for the sorbed uranium species. This is a correct approximation only in certain chemical conditions, where a straight line with slope ν_X is obtained, when plotting log K_d as a function of log[X]. This approach indeed gave the stoichiometries, a first step for modelling our systems.

$$K_{d_{\mathrm{U}}} = \frac{[\mathrm{U}]_{t,\mathrm{Al}}}{[\mathrm{U}]_{t,aq}} \qquad (8)$$

$$K_{d_{\mathrm{UO_2}^{2+}}} = \frac{[\mathrm{U}]_{t,\mathrm{Al}}}{[\mathrm{UO}_2^{2+}]} \qquad (9)$$

are the partition coefficients of U and of UO_2^{2+} respectively. $[U]_{t,aq}$ and $[U]_t$ were measured, $[U]_{t,Al}$ was deduced as $[U]_t-[U]_{t,aq}$ (eqn (2)). $[UO_2^{2+}]$ was the result of a speciation

Table 1 Aqueous thermodynamic data ($I = 0$; $T = 298.15$ K) used in this study. K° is the equilibrium constant at $I = 0$, 25 °C

Acidity			Log K°			Ref.
H_2CO_3	⇄	$HCO_3^- + H^+$	−6.349	±	0.005	13
HCO_3^-	⇄	$CO_3^{2-} + H^+$	−10.337	±	0.003	14
$H_2C_2O_4$	⇄	$HC_2O_4^- + H^+$	-1.40_1	±	0.052	15
$HC_2O_4^-$	⇄	$C_2O_4^{2-} + H^+$	−4.264	±	0.014	15
CH_3COOH	⇄	$CH_3COO^- + H^+$	−4.757	±	0.002	16
Complexation			Log K°			
$UO_2^{2+} + H_2O(l)$	⇄	$UO_2(OH)^+ + H^+$	−5.25	±	0.24	17
$UO_2^{2+} + 2H_2O(l)$	⇄	$UO_2(OH)_2 + 2H^+$	−12.15	±	0.07	17
$UO_2^{2+} + 3H_2O(l)$	⇄	$UO_2(OH)_3^- + 3H^+$	−20.25	±	0.42	17
$UO_2^{2+} + 4H_2O(l)$	⇄	$UO_2(OH)_4^{2-} + 4H^+$	−32.40	±	0.68	17
$2UO_2^{2+} + H_2O(l)$	⇄	$(UO_2)_2(OH)^{3+} + H^+$	−2.7	±	1.0	18
$2UO_2^{2+} + 2H_2O(l)$	⇄	$(UO_2)_2(OH)_2^{2+} + 2H^+$	−5.62	±	0.04	18
$3UO_2^{2+} + 4H_2O(l)$	⇄	$(UO_2)_3(OH)_4^{2+} + 4H^+$	−11.9	±	0.3	18
$3UO_2^{2+} + 5H_2O(l)$	⇄	$(UO_2)_3(OH)_5^+ + 5H^+$	−15.55	±	0.12	18
$3UO_2^{2+} + 7H_2O(l)$	⇄	$(UO_2)_3(OH)_7^- + 7H^+$	−32.20	±	0.80	17
$4UO_2^{2+} + 7H_2O(l)$	⇄	$(UO_2)_4(OH)_7^+ + 7H^+$	−21.9	±	1.0	18
$UO_2^{2+} + Cl^-$	⇄	UO_2Cl^+	0.17	±	0.02	18
$UO_2^{2+} + 2Cl^-$	⇄	UO_2Cl_2	−1.10	±	0.04	18
$UO_2^{2+} + CO_3^{2-}$	⇄	UO_2CO_3	9.94	±	0.03	17
$UO_2^{2+} + 2CO_3^{2-}$	⇄	$UO_2(CO_3)_2^{2-}$	16.61	±	0.09	17
$UO_2^{2+} + 3CO_3^{2-}$	⇄	$UO_2(CO_3)_3^{4-}$	21.84	±	0.04	17
$UO_2^{2+} + 6CO_3^{2-}$	⇄	$(UO_2)_3(CO_3)_6^{6-}$	54	±	1	18
$UO_2^{2+} + CH_3COO^-$	⇄	$UO_2CH_3COO^+$	2.86	±	0.18	9
$UO_2^{2+} + 2CH_3COO^-$	⇄	$UO_2(CH_3COO)_2$	5.57	±	0.2	9
$UO_2^{2+} + 3CH_3COO$	⇄	$UO_2(CH_3COO)_3^-$	7.25	±	0.2	9
$UO_2^{2+} + C_2O_4^{2-}$	⇄	$UO_2C_2O_4$	6.23	±	0.1	9
$UO_2^{2+} + 2C_2O_4^{2-}$	⇄	⇄ $UO_2(C_2O_4)_2^{2-}$	10.42	±	0.1	9
Solubility product			Log K_{S0}			
$UO_2^{2+} + 2H_2O(l)$	⇄	$UO_2(OH)_2 \cdot H_2O + 2H^+$	5.000	±	0.006	18

calculation by using published equilibrium constants (Table 1) from measured $[U]_{t,aq}$ and other aqueous chemical conditions as typically pH and total L concentration. ν_H was calculated from ν_U and ν_{Cl} (eqn (7)).

Radionuclide at trace concentrations. The stoichiometric coefficients ν_{Cl} and ν_L were determined from $K_{d_{UO_2^{2+}}}$ measurements at trace concentrations of Uranium. In these conditions: $\nu_U = 1$, $[AlOH] = [Al]_t$. Substituting these in eqns (4), (7) and (9), and rearranging,

$$\log_{10}K_{d_{UO_2^{2+}}} = \log_{10}K + \nu_{Al}\log_{10}[Al]_t + \nu_{Cl}\log_{10}[Cl^-] + \nu_L\log_{10}[H_qL] - (2 - \nu_{Cl})\log_{10}[H^+] \quad (10)$$

where $[H_qL]$ is obtained by a speciation calculation from the known $[L]_t$ value, other chemical conditions and published equilibrium constant (Table 1). At constant $[H_qL]$ as typically for binary system ($[H_qL] = 0$ M), and for fixed ionic strength and $[Cl^-]$, the slope of ($\log_{10}K_{d_{UO_2^{2+}}}$) *vs.* $-(\log_{10}[H^+])$ is $(2 - \nu_{Cl})$. For ternary systems we fixed pH and NaCl Concentration, when measuring $\log_{10}K_{d_{UO_2^{2+}}}$ *vs.* $\log_{10}[H_qL]$, the slope is ν_L. In these classical slope analysis, ($\log_{10}K + \nu_{Al}\log_{10}[Al]_t$) was obtained from the intercept. Unfortunately, since $[Al]_t$ could not be deduced from saturation experiments as a result of uranium precipitation, only $\log_{10}(K^\circ[Al]_t^{\nu_{Al}})$ was obtained, not $\log_{10}K$. In this way, using classical slope analysis for interpreting $K_{d,U}$ measurements at trace concentrations of U, all the stoichiometric coefficients can be determined except ν_{OH}, since it cancelled in eqn (10). It should be deduced from the shape of saturation curves, when almost saturation conditions are achieved, which was not the case in the present work for solubility reasons.

Influence of the uranium concentration. The shape of the saturation curve allows to verify that the stoichiometry of the sorbed species did not change when increasing the total concentration of U, *i.e.* it is needed to check whether ν_U is still one. But the shape of the saturation curve can equally be used to verify if saturation of the Al site was reached. Indeed, if the saturation is reached, we can observe an inflexion for high uranium concentration which allows to determine ν_{Al}, which in turns gives ν_{OH} (eqn (6))

Stoichiometric coefficient of uranium in its sorbed species. Up to now, we assumed $\nu_U = 1$ for calculating the theoretical value of $\log_{10}K_{d_{UO_2^{2+}}}$ (eqn (10)). Not using this assumption allows checking the value of ν_U from experimental observations. Assuming the only uranium sorbed species is $(AlO)_{\nu_{Al}}U_{\nu_U} = [U]_{t,Al}$, and rearranging eqn (4)

$$\log_{10}[U]_{t,Al} = f([Cl^-],[H_qL],[H^+]) + \nu_{Al}\log_{10}[AlOH] + \nu_U\log_{10}[UO_2^{2+}] \quad (11)$$

where

$$f([Cl^-],[H_qL],[H^+]) = \log_{10}K + \nu_{Cl}\log_{10}[Cl^-] + \nu_L\log_{10}[H_qL]^{\nu_L} - \nu_H\log_{10}[H^+] \quad (12)$$

was constant during a set of measurements. When the total uranium concentration increased, but α-alumina was still far from saturation, the above approximation $[AlOH] = [Al]_t$ was still valid. Consequently, the slope of ($\log_{10}[U]_{t,Al}$ *vs.* $\log_{10}[UO_2^{2+}]$) was ν_U since $f([Cl^-],[H_qL],[H^+]) + \nu_{Al}\log_{10}[AlOH] = f([Cl^-],[H_qL],[H^+]) + \nu_{Al}\log_{10}[Al]_t$ was constant in eqn (11).

Stoichiometric coefficient of hydroxide in the uranium sorbed species. We will now discuss the shape of the saturation curve, we will see that it depends on the ν_{Al} value and consequently the ν_{OH} value. By deriving eqn (2) and (ln K) from eqn (4) for saturation conditions we determined

$$s = \frac{d(\ln [U]_{t,Al})}{d(\ln [UO_2^{2+}])} = \frac{\nu_U}{1 + \nu_{Al}^2 \frac{[U]_{t,Al}}{[AlOH]}} \qquad (13)$$

the slope of the saturation curve (see Appendix). In the half point reaction conditions for the saturation of Al sites by U and H

$$\frac{[Al]_t}{2} = [AlOH]_{1/2} = \nu_{Al}\,[U]_{t,Al,1/2} \qquad (14)$$

and

$$s_{1/2} = \left(\frac{d(\ln[U(VI)]_{ads})}{d(\ln[UO_2^{2+}])}\right)_{1/2} = \frac{\nu_U}{1 + \nu_{Al}} \qquad (15)$$

is the slope of the saturation curve at the half point reaction (see Appendix). It was graphically estimated; since $\nu_U = 1$ was also determined from the saturation study as explained above, eqn (15) gives the ν_{Al} value, which in turn can give ($\nu_{Cl} - n\,\nu_L - \nu_{OH}$) (eqn (7)), and this finally would give the ν_{OH} coefficient, since ν_{Cl} and ν_L were obtained from sorption studies at trace concentrations of U as a function of [Cl$^-$] or [H$_q$L] respectively (eqn (10)). Conversely the slope can be estimated graphically and used to estimate the ratio $\frac{[U]_{t,Al}}{[AlOH]}$ (eqn (13)), which gives an idea of how much site Al is saturated.

Results and interpretation

Binary system U(VI)/α-Al$_2$O$_3$

Trace radionuclide concentration. The logarithm of the distribution coefficient of uranium(VI) was found to linearly increase with a slope equal to 1 as a function of $-\log_{10}[H^+]$ in the range corresponding to $2 \leq -\log_{10}[H^+] \leq 3.5$ (Fig. 1). Since the major uranium(VI) species is UO_2^{2+} in these pH conditions, the slope of the logarithm of the distribution coefficient of UO_2^{2+} is equally equal to 1. This slope was interpreted as evidence for the sorption of U species with stoichiometry $\left\{\overset{(i)}{\equiv}(Al{-}O)_{1-\nu_{OH}}UO_2Cl(OH)_{\nu_{OH}}\right\}$ (see eqn (10)). Indeed, since the concentration of uranium was very low, we assume that no polynuclear species are sorbed onto alumina. So, these species correspond to $(2 - \nu_{Cl}) = 1$ in eqn (10), hence $\nu_{Cl} = 1$. For this interpretation, we also assume that the sorption site was saturated with H$^+$: $\left\{\overset{(i)}{\equiv}Al{-}OH\right\}$. This is a realistic assumption since the slope started in a very acidic medium ($2 \leq -\log_{10}[H^+]$). For the same reason, U(VI) hydrolysis is unlikely—*i.e.* $\nu_{OH} = 1$: finally we propose to interpret the slope of 1 with sorbed species $\left\{\overset{(i)}{\equiv}Al{-}\ O^-, UO_2Cl^+\right\}$. This species is consistent with the opinions of Criscenti *et al.*[10] who proposed that divalent metals can be sorbed on oxide or hydroxide surfaces together with anion of the aqueous electrolyte, when M^{2+}—here UO_2^{2+}—forms a strong enough aqueous complex with this anion. However, no experimental results in the literature seemed to evidence clearly the impact of chloride on uranium(VI) sorption.

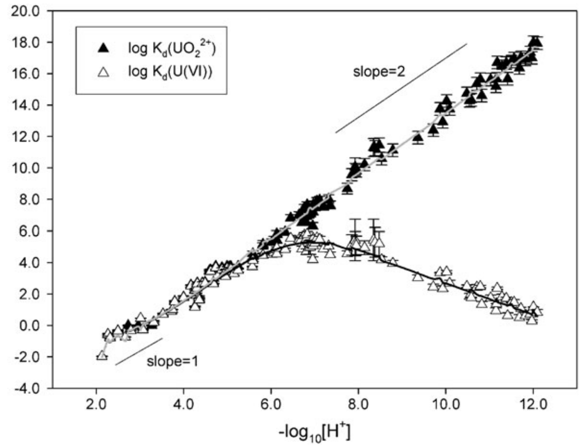

Fig. 1 Distribution coefficient of U(VI) on α-Al$_2$O$_3$ (T = 22 °C; [NaCl] and [Cl$^-$] variable; [Al$_2$O$_3$] variable, [U(VI)] = 3.10^{-10} M). $Kd_{UO_2^{2+}}$ (black symbols) was calculated with eqn (2) from $Kd_{U(VI)}$ (white symbols) experimental values and calculated Ringböm coefficient $\alpha_{UO_2^{2+}}$. The solid lines were calculated using fitted parameters from Table 2.

In the acidity range $3.5 \leq -\log_{10}[H^+] \leq 12$ a slope of 2 is observed for $\log K_{d_{UO_2^{2+}}}$ *vs.* $-\log_{10}[H^+]$, which can be interpreted as evidence for the sorption of another U species of stoichiometry $\left\{\overset{(i)}{\equiv}AlO_{(2-\nu_{OH})}UO_2(OH)_{\nu_{OH}}\right\}$ corresponding to $2 - \nu_{Cl} = 2$ in eqn (10). 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 ν_{OH} from the uranium(VI) trace concentration study. If the stoichiometric coefficients of the sorbed species are positive, the only possibility is $\nu_{OH} = 1$ corresponding to $\left\{\overset{(i)}{\equiv}AlOUO_2OH\right\}$, while $\nu_{OH} = 2$ rather correspond to eventually surface precipitation and higher values of ν_{OH} are not realistic.

The half point reactions for the first hydrolysis of uranium (VI) in aqueous solution is $-\log_{10}[H^+]_{1/2,1} = -\log_{10}{}^*\beta_1 = 5.25$ (Table 1); while $-\log_{10}[H^+]_{1/2s,i} = 3.5$ for the sorption of the uranium hydroxide species (Table 1). When the values of such half point reactions are close—in aqueous solution and at the surface— speciations are virtually 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: $\left\{\overset{(i)}{\equiv}AlOUO_2OH\right\}$ should typically better be written as ion pair $\left\{\overset{(i)}{\equiv}AlO^-, HOUO_2^+\right\}$. However, this simple interpretation needs confirmations, and anyhow a difference of 1.75 log$_{10}$ unit in the values of the half point reactions was found here.

Previous results[11] showed evidence of the adsorption of chloride at 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 $\log_{10}K_{d_{UO_2^{2+}}}$ *vs.* $-\log_{10}[H^+]$. For this reason we may here assume that U(VI) is sorbed on a new sorption 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. Jakobsson *et al.*[12] obtained very similar sorption results onto alumina in the pH range (4–12) they used.

Finally, to model the uranium(VI) adsorption in neutral and basic media, we needed to consider both hydroxide and complex adsorptions. The fitted parameters $\log_{10}\left(\sum_{p=0}^{1}(K^*_{UO_2(OH)_{\nu OH}}[Al]_t^{2-\nu}OH)\right) = -6.30 \pm 0.05$, where certainly $\nu_{OH} = 1$

$$\log_{10}(K^*{}_{UO_2Cl}IEC) = -1.95 \pm 0.10$$

are enough to model the sorption of trace concentrations of U(VI) on alumina from NaCl aqueous solutions in the pH range 2–12. We propose the sorption of U species UO$_2$Cl$^+$, and of another species of stoichiometry $\left\{\overset{(i)}{\equiv}AlO_{(2-\nu_{OH})}UO_2(OH)_{\nu_{OH}}\right\}$, where the stoichiometric coeffi-

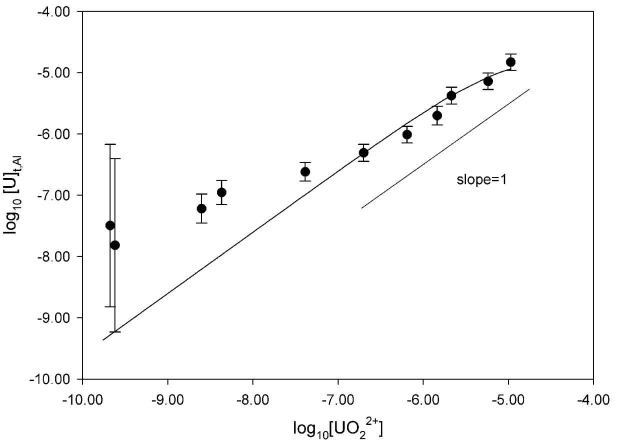

Fig. 2 Adsorbed uranium(VI) on α-Al_2O_3 ($T = 22$ °C; $[Al_2O_3] = 12.5$ g L^{-1}; pH $= 5.0 \pm 0.2$; [NaCl] $= 0.1$ M; [U(VI)] $= 3.10^{-10}$ M) as a function of $[UO_2^{2+}]$. The solid lines were calculated using the same parameters from Table 2.

cient, ν_{OH}, is likely to be equal to 1, which could not be confirmed. 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).

Influence of the uranium concentration. The logarithm of adsorbed U(VI) as a function of $\log_{10}[UO_2^{2+}]$ is presented in Fig. 2. We can observe a slope equal to about one for $-7 < \log_{10}[UO_2^{2+}] < -4.5$, while for lower values of $[UO_2^{2+}]$ uncertainties are too important for drawing clear conclusions. Consequently, no polynuclear species are adsorbed onto α-alumina even though aqueous polynuclear species could represent up to 40% of total aqueous concentration of uranium(VI).

Moreover, the behaviour of uranium(VI) could not be studied for higher concentrations than 4.10^{-5} M for pH equal to 5 for avoiding the precipitation of typically Schoepite. It is difficult to determine whether the partition coefficient of uranium is reflecting its sorption or precipitation. We did not find chemical conditions avoiding precipitation, and saturating the alumina, for measuring its exchange capacity. However, we estimated a minimum value for this exchange capacity by modelling experimental data of saturation curve: $[Al]_t > 0.020$ mmol g^{-1}.

Ternary systems U(VI)/α-Al_2O_3/complexing agent

System U(VI)/α-Al_2O_3/acetate. The effect of acetate on U(VI) sorption was detected beyond 10^{-3} M 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; nevertheless, the corresponding calculated sorption is always significantly less than the measurements (Fig. 3a). This positive effect of acetate sorption on the global sorption—*i.e.* synergic sorption—evidences that a new species is sorbed.

To interpret this behaviour, we used eqn (10) by representing the logarithm of $K_{d_{UO_2^{2+}}}$, the distribution coefficient of the aquo ion UO_2^{2+}, as a function of the logarithm of $[CH_3COOH]$, the aqueous concentration of acetic acid (Fig. 3b). The experimental data can be interpreted with a slope of approximately 0.9 ± 0.2, suggesting the adsorption of species $\left\{\overset{(i)}{\equiv} AlOUO_2(CH_3COO)\right\}$. The best fitting value for the corresponding parameter is: $\log_{10}(K^*_{UO_2Ac}[Al]_t) = -3.11 \pm 0.05$.

The simplest interpretation was to assume that in those complexing conditions uranium was sorbed on the same site as previously evidenced for uranium sorption in non-complexing conditions. Moreover, in a previous study,[11] 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 uranium(VI) is sorbed on a site, which has no acido-basic properties in the pH range 2–12. So, we can conclude that the adsorption site for uranium is different from the previous anionic site. Indeed we did not observe any competition here between acetate and U sorptions.

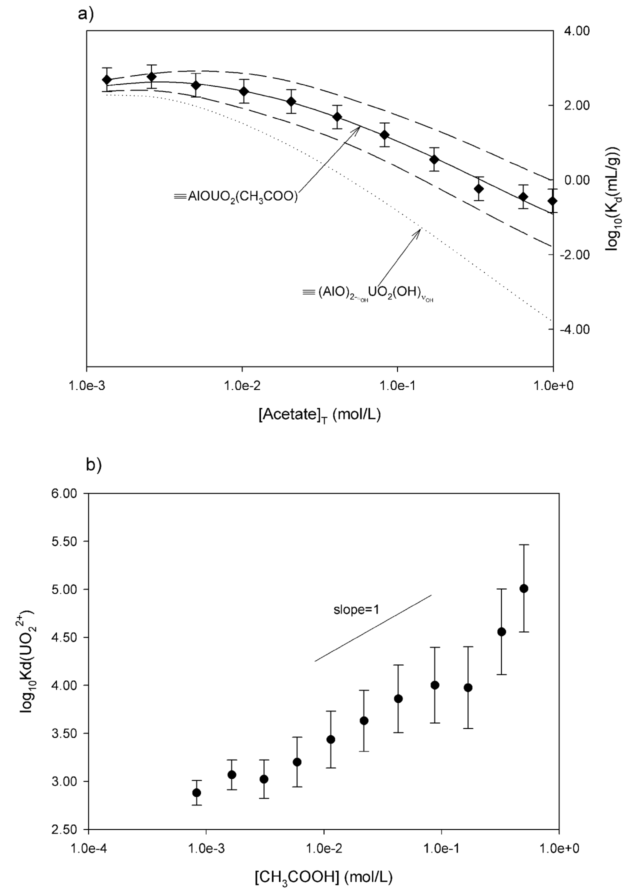

Fig. 3 Effect of acetate on U(VI) sorption onto α-alumina ($T = 22$ °C; [NaCl] $= 0.1$ M; pH $= 4.6$; $[Al_2O_3] = 1$ g L^{-1}; [U(VI)] $= 3.10^{-10}$ M). $K_d(UO_2^{2+})$ was calculated from experimental K_d values and Ringböm coefficient. The curve corresponding to species $\equiv AlO_{2-\nu_{OH}}UO_2(OH)_{\nu OH}$ (dotted line) is significantly below the experimental points; this is the reason for considering that another species is sorbed, namely $\equiv AlOUO_2(CH_3COO)$.

As a conclusion, for modelling these experimental data we used the parameters already determined for UO_2Cl^+ and $UO_2(OH)_p^{2-p}$ adsorption in the above study in non complexing media, $\log_{10}\left(\sum_{p=0}^{1}(K^*_{UO_2(OH)_{\nu OH}}[Al]_t^{2-\nu}OH)\right)$ and $\log_{10}(K^*_{UO_2Cl}[Al]_t)$. Only the product of selectivity coefficient of acetate complex and exchange capacity was here fitted: $\log_{10}(K^*_{UO_2Ac}[Al]_t) = -3.11 \pm 0.05$.

System U(VI)/α-Al_2O_3/oxalate. The effect of oxalic acid on the sorption of U(VI) onto α-alumina was studied for $-\log_{10}[H^+]$ equal to 4.2 and ionic strength to 0.1 M in a similar way as in the above study of acetic acid. In these conditions and using solutions of increasing oxalate concentration, the sorption of U(VI) decreased with the total aqueous concentration of oxalic acid (Fig. 4). This decrease is consistent with the known stability constants for the U(VI) oxalate aqueous complexes (Table 1). This can be interpreted as the

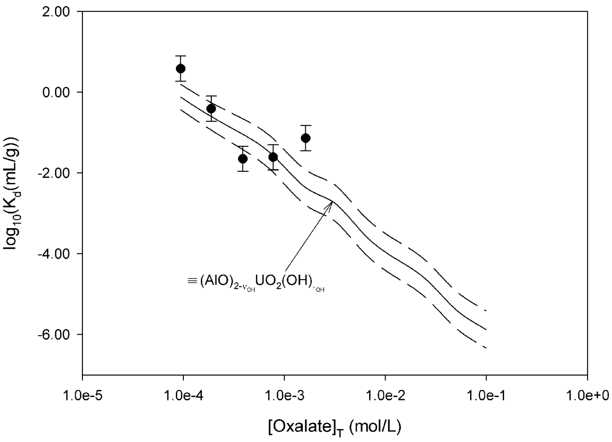

Fig. 4 Effect of oxalate on U(VI) sorption onto α-alumina ($T = 22$ °C; [NaCl] = 0.1 M; pH = 4.2; $[Al_2O_3] = 100$ g L^{-1}). The fit curves are simply obtained using the sorption data for UO_2Cl^+ and $UO_2(OH)_{\nu_{OH}}$ and the data for solution complexes of the ligands.

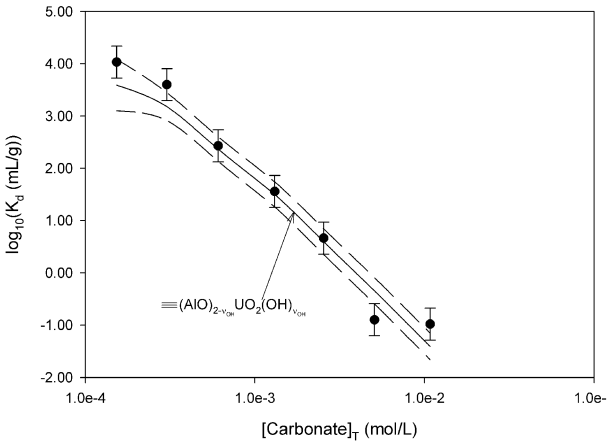

Fig. 5 Effect of carbonate on U(VI) sorption onto α-alumina ($T = 22$ °C; [NaCl] = 0.1 M; pH = 8.33; $[Al_2O_3] = 1$ g L^{-1}, [U(VI)] = 3.10^{-10} M). The fit curves are simply obtained using the sorption data for UO_2Cl^+ and $UO_2(OH)_{\nu_{OH}}$ and the data for solution complexes of the ligands.

competition between aqueous uranium oxalate complex and adsorbed uranium hydroxide complexes.

The studied domain of oxalate concentration is restricted due to the weak values of the logarithm of the partition coefficient. To obtain experimental data, for total aqueous concentration of oxalate higher than 2.10^{-3} M, we must work with high solid concentrations (superior to 100 g L^{-1}). These concentrations are difficult to use experimentally.

For the α-Al_2O_3/U(VI)/oxalate ternary system, for modelling the experimental data in oxalate media we used the parameters previously determined for the binary system, and the constants of aqueous oxalate complexation.

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

Major species	Exchange capacity (meq g^{-1})	$\log_{10} K^\circ$ ($I = 0$ M)	Ref.
$\left\{\overset{(j)}{\equiv}\text{AlO}^-\text{Na}^+\right\} + H^+ \rightleftarrows \left\{\overset{(j)}{\equiv}\text{AlOH}\right\} + Na^+$	0.0025 ± 0.0001	8.09 ± 0.03	11
$\left\{\overset{(k)}{\equiv}\text{AlOH}\right\} + H^+ + Cl^- \rightleftarrows \left\{\overset{(k)}{\equiv}\text{AlOH}_2^+, Cl^-\right\}$	0.0068 ± 0.0035	8.09 ± 0.35	11
$\left\{\overset{(l)}{\equiv}\text{AlOH}\right\} + H^+ + Cl^- \rightleftarrows \left\{\overset{(l)}{\equiv}\text{AlOH}_2^+, Cl^-\right\}$	0.0172 ± 0.0023	6.81 ± 0.21	11
$\left\{\overset{(k)}{\equiv}\text{AlOH}\right\} + CH_3COOH \rightleftarrows \left\{\overset{(k)}{\equiv}\text{Al–OOCCH}_3\right\} + H_2O$	0.0068 ± 0.0035	5.71 ± 0.55	11
$\left\{\overset{(l)}{\equiv}\text{AlOH}\right\} + CH_3COOH \rightleftarrows \left\{\overset{(l)}{\equiv}\text{Al–OOCCH}_3\right\} + H_2O$	0.0172 ± 0.0023	4.07 ± 0.16	11
$2\left\{\overset{(k)}{\equiv}\text{AlOH}\right\} + H_2C_2O_4 \rightleftarrows \left\{\overset{(k)}{\equiv}\text{Al–C}_2\text{O}_4\right\} + 2H_2O$	0.0068 ± 0.0035	14.69 ± 0.22	11
$2\left\{\overset{(l)}{\equiv}\text{AlOH}\right\} + H_2C_2O_4 \rightleftarrows \left\{\overset{(l)}{\equiv}\text{Al–C}_2\text{O}_4\right\} + 2H_2O$	0.0172 ± 0.0023	12.02 ± 0.08	11
$2\left\{\overset{(k)}{\equiv}\text{AlOH}\right\} + H_2CO_3 \rightleftarrows \left\{\overset{(k)}{\equiv}\text{Al–CO}_3\right\} + 2H_2O$	0.0068 ± 0.0035	11.35 ± 0.53	11
$2\left\{\overset{(l)}{\equiv}\text{AlOH}\right\} + H_2CO_3 \rightleftarrows \left\{\overset{(l)}{\equiv}\text{Al–CO}_3\right\} + 2H_2O$	0.0172 ± 0.0023	6.19 ± 0.12	11

Data measured in the present work:	$\log_{10}(K^{i*}_{U(VI)ads\ [Al]t}{}^{2-\nu_{OH}})$
$\left\{\overset{(i)}{\equiv}\text{Al–OH}\right\} + UO_2^{2+} + Cl^- \rightleftarrows \left\{\overset{(i)}{\equiv}\text{Al–OUO}_2\text{Cl}\right\} + H^+$	−1.95 ± 0.10
$(2-p)\left\{\overset{(i)}{\equiv}\text{Al–OH}\right\} + UO_2^{2+} + pH_2O \rightleftarrows \left\{\overset{(i)}{\equiv}(\text{Al–O})_{2-p}\text{UO}_2(\text{OH})p\right\} + 2H^+$	−6.30 ± 0.05
$\left\{\overset{(i)}{\equiv}\text{Al–OH}\right\} + UO_2^{2+} + CH_3COOH \rightleftarrows \left\{\overset{(i)}{\equiv}\text{Al–OUO}_2(\text{CH}_3\text{COOH})\right\} + 2H^+$	−3.11 ± 0.05

System U(VI)/α-Al_2O_3/carbonate. The effect of carbonate on the sorption of U(VI) onto 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. 5. The sorption behaviour of U(VI) in this bicarbonate media is quite similar to that in oxalate media: the uptake of uranium decreased with bicarbonate concentration. This decrease is consistent with the known stability constants for the U(VI) carbonate aqueous complexes (Table 1). So, this can be equally interpreted as the competition between aqueous carbonate complexes and adsorbed hydroxide species.

As for the α-Al_2O_3/U(VI)/oxalate ternary systems, for modelling the experimental data in bicarbonate media we used the parameters previously determined for the binary system, and only aqueous database for carbonate/uranium (VI) complexes.

Conclusions

U(VI) can be adsorbed onto α-alumina. From 0.1 M Cl^- aqueous solutions, species UO_2Cl^+ is sorbed in the $-\log_{10}[H^+]$ range 2 to 3.5. In less acid media hydrolysed species of U(VI) are adsorbed. On adding aqueous acetic acid, a synergic sorption reaction of U(VI) was first evidenced. They are the results of the sorption of uranium cationic complexes with the basic forms of the acetic acid. Further additions of the acetate ligands resulted in the formation of aqueous anionic complexes of uranium, which were not sorbed on the alumina, therefore decreasing the adsorption of uranium. Such decreases were the only effects observed on the uranium sorptions for the carbonate and oxalate ligands: on adding aqueous carbonic and oxalic acids, no synergic sorption reaction was observed. Only a competition between aqueous complexes and adsorbed hydroxide complex was evidenced.

The uranium(VI) sorption site is different from the one previously evidenced for the sorption of Na^+, Cl^- and of the ligands[11] but probably the same as the one previously evidenced for Am(III),[8] since, as already found for Am(III) no competition between U(VI) and chloride, sodium aqueous carbonic, acetic and oxalic acids was observed. This sorption behaviour on α-alumina could be reasonably well modelled for uranium(VI) at trace concentration in contact with 0.1 M NaCl aqueous solutions in all the experimental conditions, by using ion-exchange theory, and quite a restricted set of parameters.

Appendix

$$[\mathrm{Al}]_\mathrm{t} = [\mathrm{AlOH}] + \nu_\mathrm{Al}\,[\mathrm{U}]_\mathrm{t,Al} \qquad \text{(A1)}$$

Deriving eqn (1)

$$0 = \mathrm{d}[\mathrm{AlOH}] + \nu_\mathrm{Al}\,\mathrm{d}[\mathrm{U}]_\mathrm{t,Al} \qquad \text{(A2)}$$

Using $\mathrm{d}(\ln X) = \frac{\mathrm{d}X}{X}$ for X = [AlOH] or $\mathrm{d}[\mathrm{U}]_\mathrm{t,A}$ in eqn (A2)

$$\mathrm{dln}[\mathrm{AlOH}] = -\nu_\mathrm{Al}\frac{[\mathrm{U}]_\mathrm{t,Al}}{[\mathrm{AlOH}]}\mathrm{dln}(\ln[\mathrm{U}]_\mathrm{t,Al}) \qquad \text{(A3)}$$

At constant $[Cl^-]$, $[H_qL]$ and $[H^+]$

$$\ln K' = \ln[\mathrm{U}]_\mathrm{t,Al} - \nu_\mathrm{Al}\ln[\mathrm{AlOH}] - \nu_\mathrm{U}\ln[\mathrm{UO_2}^{2+}] \qquad \text{(A4)}$$

is constant (eqn (4)). Deriving eqn (A4) at constant $[Cl^-]$, $[H_qL]$ and $[H^+]$

$$0 = \mathrm{d}(\ln[\mathrm{U}]_\mathrm{t,Al}) - \nu_\mathrm{Al}\mathrm{d}([\mathrm{AlOH}]) - \nu_\mathrm{U}\,\mathrm{d}(\ln[\mathrm{UO_2}^{2+}]) \qquad \text{(A5)}$$

Substituting eqn (A3) in eqn (A5)

$$\frac{\mathrm{d}(\ln[\mathrm{U}]_\mathrm{t,Al})}{\mathrm{d}(\ln[\mathrm{UO}_2^{2+}])} = \frac{\nu_\mathrm{U}}{1 + \nu_\mathrm{Al}^2\frac{[\mathrm{U}]_\mathrm{t,Al}}{[\mathrm{AlOH}]}} \qquad (13)$$

Substituting eqn (14) in eqn (13) in the half point reaction conditions, we obtain the slope at the half point reaction

$$s_{1/2} = \left(\frac{\mathrm{d}(\ln[\mathrm{U(VI)}]_\mathrm{ads})}{\mathrm{d}(\ln[\mathrm{UO}_2^{2+}])}\right)_{1/2} = \frac{\nu_\mathrm{U}}{1 + \nu_\mathrm{Al}} \qquad (15)$$

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