Effect of aqueous acetic, oxalic and carbonic acids on the adsorption of Uranium(VI) 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 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 evidences for the synergic sorption of Uranium(VI) and the small organic ligands, namely sorption of cationic complexes onto the alumina. As, its neutral and anionic complexes were not sorbed, U(VI) cation can 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 in various chemical conditions.

Keywords

Introduction

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

However, chemical retention (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. 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 [4] 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 ($CO_2(g)/HCO_3^-/CO_3^{2-}$).

Materials and solutions

1. Materials

Synthetic mineral, α-alumina, from interchim® (pure 99.99%) was used. However, its surface state is not guaranteed, particularly 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 0.1M 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) for knowing the crystalline form of alumina at interface: no modification was either 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 [5]. Finally, a N2-BET surface was measured equal to $12(\pm0.2)m^2/g$.

2. Solutions

2.1. Radioisotope ^{232}U 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 (2.7MBq/g in HCl 2M 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 1mM HCl aqueous solution. The purified ^{232}U solution can be used for about three weeks before re-purifying is needed.

2.2.   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 (inferior to 10% volume of solution).

The NaCl or HCl solutions were prepared by diluting weighted amounts of Suprapur products (Merck) with Millipore® water purged with Argon. NaOH aqueous solutions were prepared similarly from weighted amounts of 50% NaOH from Aldrich as developed by Sipos et al. [6].

The solutions of ligands were prepared by weighting 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 and measured with a combine glass microelectrode (Mettler Toledo). The outer reference cell was filled with saturated NaC/KCl. The combined glass microelectrode was calibrated with solutions of known [H$^+$] and same ionic strength as the working solutions, which means that it was calibrated in $-\log_{10}[H^+]$ units, not in pH ($-\log_{10}a_{H^+}$).

Procedures and techniques

1.   Experiments with radionuclides at trace concentration

The protocol used to study Uranium(VI) sorption with trace radionuclide concentrations on α-alumina in different binary and ternary systems is the same as described elsewhere for Americium and Europium [7, 8].

Sorption on the batch walls was firstly checked, and found not significant. The time necessary to achieve equilibrium conditions was verified and found to be inferior to one day. Sorption measurements were carried out as a function of pH in 10mL polycarbonate centrifuge tubes. After spiking with ^{232}U, and shaking for at least 2 days, the samples were centrifuged for 2 hours at 60000 rpm before sampling of the supernatant solutions, and pH measurements. The samples were counted enough time for obtaining 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 at fixed other chemical conditions. Sorption isotherms were determined as a function of ligand concentrations.

2. *Study of saturation by Uranium (VI)*

Due to the limit of detection of our spectroscopic technique, we had to work with high Uranium concentrations. For this reason we checked the influence of Uranium concentration on its retention. 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.

We first study the influence of Uranium (VI) concentration on its sorption. This type of saturation study allows to determine the number of sorption sites and the corresponding exchange capacities. The solutions were always spiked with ^{232}U. 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

1. *Description of the sorption model*

The surface of α-alumina is assumed to have sorption sites $\left\{ \overset{(i)}{\equiv}\text{Al-OH} \right\}$, 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. The stoichiometries of uranium sorbed species are $\left\{ \overset{(i)}{\equiv}(\text{Al-O})_{v_{i,Al}}(UO_2)_{v_{i,U}}Cl_{v_{i,Cl}}(H_{q_i,-n_i,}L)_{v_{i,L}}(OH)_{v_{i,OH}} \right\}$, which we will note $^{(i)}(\text{AlO})_{v_{i,Al}}U_{v_{i,U}}$ for simplicity. Similarly $\left\{ \overset{(i)}{\equiv}\text{Al-OH} \right\}$ is now noted $^{(i)}$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

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

$$[U]_t = [U]_{t,aq} + [U]_{t,Al} \tag{2}$$

where

$$[U]_{t,Al} = \sum_{i,v_{i,Al}} k \left[{}^{(i)}(AlO)_{v_{Al}} U_{v_{i,U}} \right] \tag{2a}$$

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

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

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 [7, 8]: Thermodynamic modelling of ideal systems, also named the Ion Exchange Theory (IXT).

$$K = \frac{[(AlO)_{v_{Al}} U_{v_U}] \, [H^+]^{v_H}}{[AlOH]^{v_{Al}} \, [UO_2^{2+}]^{v_U} \, [Cl^-]^{v_{Cl}} \, [H_qL]^{v_L}} \tag{4}$$

is the ionic exchange constant for Equilibrium

$$v_{Al} \, AlOH + v_U \, UO_2^{2+} + v_{Cl} \, Cl^- + v_L \, H_qL + v_{OH} \, H_2O \rightleftarrows (AlO)_{v_{Al}} U_{v_U} + v_H \, H^+ \tag{5}$$

where we have omitted sub- and super-scripts i in Eq. 4 and 5 for simplicity. K is often called selectivity coefficient. AlOH and $(AlO)_{v_{Al}} U_{v_U}$ are assumed to be neutral sorbed species: it is an assumption of the IXT. For these electroneutrality conditions:

$$v_{Al} = 2 \, v_U - v_{Cl} - n \, v_L - v_{OH} \tag{6}$$

$$v_H = 2 \, v_U - v_{Cl} \tag{7}$$

Based on this modelling, we determined v_X, the stoichiometric coefficient for X in the sorption equilibrium (Eq 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 v_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.

$$K_{d_U} = \frac{[U]_{t,Al}}{[U]_{t,aq}} \tag{8}$$

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

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 $[U]_t$ - $[U]_{t,aq}$ (Eq. 2). $[UO_2^{2+}]$ was the result of a speciation calculation by using published equilibrium constants (Table 1) from $[U]_{t,aq}$ and other aqueous chemical conditions as typically pH and total L concentration. ν_H was calculated from ν_U and ν_{Cl} (Eq. 7).

2. *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 Eq. 4, 7 and 9, and rearranging,

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

where $[H_qL]$ is obtained by a speciation calculation from the known $[L]_t$ value, other chemical conditions and published equilibrium constant (Tab.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, where $[Al]_t$ was estimated from saturation experiments, which allowed to obtain $\log_{10}K$. 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 excepted ν_{OH}, since it cancelled in Eq. 10. However, it was deduced from the shape of saturation curves.

3. *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 is equally used to verify if saturation of 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} (Eq. 6)

3.1. Stoichiometric coefficient of uranium in its sorbed species

Up to now, we assumed $\nu_U = 1$ for calculating the theoretical value of $\log_{10}K_{d_{UO_2}^{2+}}$ (Eq. 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 Eq. 4

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

where

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

was constant during the saturation experiment. 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 Eq. 11.

3.2. Stoichiometric coefficient of hydroxide in the uranium sorbed species

We will now see that ν_{Al} and consequently ν_{OH} can also be obtained from the shape of the saturation curve. Indeed, by deriving Eq 2 and (ln K) from Eq 4 for saturation conditions we determined

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

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

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

and

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

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, Eq.15 gives the ν_{Al} value, which in turn can give $(\nu_{Cl}\text{-n }\nu_L\text{-}\nu_{OH})$ (Eq.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 $[H_qL]$ respectively (Eq.10).

Results and interpretation

1. Binary system U(VI)/α-Al$_2$O$_3$

1.1. 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 $2 \leq -\log_{10}[H^+] \leq 3.5$ (Figure 1). Since the major Uranium(VI) 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 can be interpreted as evidence for the sorption of U species with stoichiometry $\left\{ \overset{(i)}{\equiv}(Al_i\text{-}O)_{1\text{-}p}UO_2Cl(OH)_{\nu_{OH}} \right\}$. Indeed, since the concentration of Uranium was very low, we assume that no polynuclear are sorbed onto alumina. So, these species correspond to $(2\text{-}\nu_{Cl})=1$ in Eq.(10), hence $\nu_{Cl}=1$. For this interpretation, we also assume that the sorption site was saturated with H^+: $\left\{ \overset{(i)}{\equiv}Al\text{-}OH \right\}$. 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. $\nu_{OH} = 1$: we interpreted the slope of 1 with the sorbed specie $\left\{ \overset{(i)}{\equiv}Al\text{-}O^-,UO_2Cl^+ \right\}$.

In the acidity range $3.5 \leq -\log_{10}[H^+] \leq 12$ a slope of 2 is observed for $\log K_{dUO_2^{2+}}$ vs $-\log_{10}[H^+]$, which can be interpreted as evidence for the sorption of another U species of stoichiometry $\left\{ \overset{(i)}{\equiv}AlO_{(2\text{-}p)}UO_2(OH)_p \right\}$ corresponding to $2\text{-}\nu_{Cl} = 2$ in Eq. 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 p from the uranium (VI) trace concentration study. Stoichiometric coefficient p can probably be determined from saturation experiments (see below).

Note that 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). This thermodynamic constant is close to the value corresponding to the sorption of the uranium hydroxide species (**Erreur ! Source du renvoi introuvable.**): for the surface it is $-\log_{10}[H^+]_{1/2s,i} = 3.5$, 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: $\left\{\equiv^{(i)}AlO_{(2-p)}UO_2(OH)_p\right\}$ should better be written $\left\{\equiv^{(i)}AlO^-UO_2(OH)^+\right\}$. However, this simple interpretation needs confirmations.

Previous results [9] showed evidences 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 $\log_{10}K_{dUO_2}{}^{2+}$ *vs.* $-\log_{10}[H^+]$. We may here assume that the surface site engaged in the U(VI) 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. Jakobsson *et al.* [10] 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

$$\log_{10}\left(\sum_{p=0}^{1}\left(K^*_{UO_2(OH)_p}\,[Al]_t^{2-p}\right)\right) = -6.30\pm0.05$$

$$\log_{10}\left(K^*_{UO_2Cl}\,IEC\right) = -1.95\pm0.10$$

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_2Cl^+, and of another species of stoichiometry $\left\{\equiv^{(i)}AlO_{(2-p)}UO_2(OH)_p\right\}$, 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).

1.2. Influence of the Uranium concentration

The shape of saturation curve allows us to verify if polynuclear species are sorbed onto alumina and to determine the ν_{OH} stoichiometric coefficient if saturation conditions are reached. The logarithm of adsorbed U(VI) as a function of $[UO_2{}^{2+}]$ is presented in figure 2. We can observe a slope around equal to one for $10^{-10}M<[U(VI)]t<4.10^{-5}M$. Consequently, no polynuclear species are adsorbed onto α-alumina even though aqueous polynuclear species represent more than 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 because of potential schoepite or $UO_2(OH)_2$ precipitation. It's difficult to determine if partition coefficient is the consequence of sorption or precipitation. So, if we want to use higher concentration, the study must be reached in more acidic medium, where adsorption is inferior and but uncertainties become also very important. Consequently, the necessary conditions to saturate the exchange capacity of alumina were not reached: we can not determine this exchange capacity and so the selectivity coefficient of all thermodynamic adsorption reactions and the ν_{OH} coefficient. We can only give a minimum value for this exchange capacity by modelling experimental data of saturation curve:

$[Al]_t > 0.020$ mmol/g

2. Ternary systems U(VI)/α-Al$_2$O$_3$/complexing agent

2.1. System U(VI)/α-Al$_2$O$_3$/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 (Figure 3a).

To interpret this behaviour, we used Eq. 10 by representing the logarithm of $K_{dUO_2^{2+}}$, 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 (Figure 3b). The experimental data can be interpreted with a slope of approximately 1, suggesting the adsorption of species $\left\{ \overset{(i)}{\equiv}AlOUO_2(CH_3COO) \right\}$. This consideration led to the best fitting value:

$\log_{10}\left(K^*_{UO_2Ac} [Al]_t \right) = -3.11 \pm 0.05$

The simplest interpretation was to assume that the same site as previously evidenced is involved. Moreover, in a previous study [9], 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 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 U sorptions.

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, $\log_{10}\left(\sum_{p=0}^{1}\left(K^*_{UO_2(OH)_p}[Al]_t^{2-p}\right)\right)$ and $\log_{10}\left(K^*_{UO_2Cl}[Al]_t\right)$. Only the product of selectivity coefficient of acetate complex and exchange capacity was here fitted:

$$\log_{10}\left(K^*_{UO_2Ac}[Al]_t\right) = -3.11 \pm 0.05$$

2.2. System U(VI)/α-Al₂O₃/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 0.1M in a similar way as 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 (Figure 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 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 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 100g/L). These concentrations are difficult to use experimentally.

For the α-Al₂O₃ / Am(III) / 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.

2.3. System U(VI)/α-Al₂O₃/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 0.1M.

The results of sorption are presented in Figure 5. The sorption behaviour of U(VI) in this bicarbonate media is quite similar to that in oxalate media: the retention 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$_2$O$_3$ / 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$_2$Cl$^+$ 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 organic acid as ligands. Further additions of the ligands resulted in the formation of aqueous anionic complexes of uranium, which were not sorbed on the alumina, therefore decreasing the adsorption of uranium. On adding aqueous carbonic and oxalic acids, no synergic sorption reaction was observed. Only a competition behaviour between aqueous complexes and adsorbed hydroxide complex was evidenced.

The uranium (VI) sorption site is different from another one previously evidenced for the sorption of Na$^+$, Cl$^-$ and of the ligands but probably the same as for Am(III) previously evidenced, since 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-Exchanger Theory, and a restricted set of parameters.

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Appendix

$$[Al]_t = [AlOH] + \nu_{Al}\,[U]_{t,Al} \tag{A1}$$

Deriving Eq.(1)

$$0 = d[AlOH] + \nu_{Al}\,d[U]_{t,Al} \tag{A2}$$

Using $d(\ln X) = \dfrac{dX}{X}$ for $X = [AlOH]$ or $d[U]_{t,A}$ in Eq.(A2)

$$d\ln[AlOH] = -\nu_{Al}\,\frac{[U]_{t,Al}}{[AlOH]}\,d\ln\big(\ln[U]_{t,Al}\big) \tag{A3}$$

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

$$\ln K' = \ln[U]_{t,Al} - \nu_{Al}\,\ln[AlOH] - \nu_U\,\ln[UO_2^{2+}] \tag{A4}$$

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

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

Substituting Eq.(A3) in Eq.(A5)

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

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

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

Tables

Acidity	Log K°	Ref
$H_2CO_3 \rightleftarrows HCO_3^- + H^+$	-6.349 ± 0.005	
$HCO_3^- \rightleftarrows CO_3^{2-} + H^+$	-10.337 ± 0.003	
$H_2C_2O_4 \rightleftarrows HC_2O_4^- + H^+$	$-1.40_1 \pm 0.05_2$	
$HC_2O_4^- \rightleftarrows C_2O_4^{2-} + H^+$	-4.264 ± 0.014	
$CH_3COOH \rightleftarrows CH_3COO^- + H^+$	-4.757 ± 0.002	

Complexation	Log K°	
$UO_2^{2+} + H_2O(l) \rightleftarrows UO_2(OH)^+ + H^+$	-5.25	± 0.24
$UO_2^{2+} + 2H_2O(l) \rightleftarrows UO_2(OH)_2 + 2H^+$	-12	
$UO_2^{2+} + 3H_2O(l) \rightleftarrows UO_2(OH)_3^- + 3H^+$	-19.2	± 0.4
$UO_2^{2+} + 4H_2O(l) \rightleftarrows UO_2(OH)_4^{2-} + 4H^+$	-33	± 2
$2UO_2^{2+} + H_2O(l) \rightleftarrows (UO_2)_2(OH)^{3+} + H^+$	$-2._7$	$\pm 1._0$
$2UO_2^{2+} + 2H_2O(l) \rightleftarrows (UO_2)_2(OH)_2^{2+} + 2H^+$	-5.62	± 0.04
$3UO_2^{2+} + 4H_2O(l) \rightleftarrows (UO_2)_3(OH)_4^{2+} + 4H^+$	-11.9	± 0.3
$3UO_2^{2+} + 5H_2O(l) \rightleftarrows (UO_2)_3(OH)_5^+ + 5H^+$	-15.55	± 0.12
$3UO_2^{2+} + 7H_2O(l) \rightleftarrows (UO_2)_3(OH)_7^- + 7H^+$	-31	± 2
$4UO_2^{2+} + 7H_2O(l) \rightleftarrows (UO_2)_4(OH)_7^+ + 7H^+$	-21.9	± 1.0
$UO_2^{2+} + Cl^- \rightleftarrows UO_2Cl^+$	0.17	± 0.02
$UO_2^{2+} + 2Cl^- \rightleftarrows UO_2Cl_2$	-1.10	± 0.04
$UO_2^{2+} + CO_3^{2-} \rightleftarrows UO_2CO_3$	9.68	± 0.04
$UO_2^{2+} + 2CO_3^{2-} \rightleftarrows UO_2(CO_3)_2^{2-}$	16.94	± 0.12
$UO_2^{2+} + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{4-}$	21.60	± 0.05
$UO_2^{2+} + 6CO_3^{2-} \rightleftarrows (UO_2)_3(CO_3)_6^{6-}$	54	± 1
$UO_2^{2+} + CH_3COO^- \rightleftarrows UO_2CH_3COO^+$	2.86	± 0.18
$UO_2^{2+} + 2CH_3COO^- \rightleftarrows UO_2(CH3COO)_2$	5.5_7	± 0.2
$UO_2^{2+} + 3CH_3COO^- \rightleftarrows UO_2(CH_3COO)_3^-$	7.2_5	± 0.2
$UO_2^{2+} + C_2O_4^{2-} \rightleftarrows UO_2C_2O_4$	6.2_3	± 0.1

$UO_2^{2+} + 2C_2O_4^{2-} \rightleftarrows UO_2(C_2O_4)_2^{2-}$	10.4_2	$\pm\ 0.1$

Solubility products	Log K_{S0}
$UO_2^{2+} + 2H_2O(l) \rightleftarrows UO_2(OH)_2.H_2O + 2H^+$	5.000 ± 0.006

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

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	[9]
$\left\{ \overset{(k)}{\equiv}AlOH \right\} + H^+ + Cl^- \rightleftarrows \left\{ \overset{(k)}{\equiv}AlOH_2^+,Cl^- \right\}$	0.0068±0.0035	8.09±0.35	[9]
$\left\{ \overset{(l)}{\equiv}AlOH \right\} + H^+ + Cl^- \rightleftarrows \left\{ \overset{(l)}{\equiv}AlOH_2^+,Cl^- \right\}$	0.0172±0.0023	6.81±0.21	[9]
$\left\{ \overset{(k)}{\equiv}AlOH \right\} + CH_3COOH \rightleftarrows \left\{ \overset{(k)}{\equiv}Al-OOCCH_3 \right\} + H_2O$	0.0068±0.0035	5.71±0.55	[9]
$\left\{ \overset{(l)}{\equiv}AlOH \right\} + CH_3COOH \rightleftarrows \left\{ \overset{(l)}{\equiv}Al-OOCCH_3 \right\} + H_2O$	0.0172±0.0023	4.07±0.16	[9]
$2\left\{ \overset{(k)}{\equiv}AlOH \right\} + H_2C_2O_4 \rightleftarrows \left\{ \overset{(k)}{\equiv}Al-C_2O_4 \right\} + 2H_2O$	0.0068±0.0035	14.69±0.22	[9]
$2\left\{ \overset{(l)}{\equiv}AlOH \right\} + H_2C_2O_4 \rightleftarrows \left\{ \overset{(l)}{\equiv}Al-C_2O_4 \right\} + 2H_2O$	0.0172±0.0023	12.02±0.08	[9]
$2\left\{ \overset{(k)}{\equiv}AlOH \right\} + H_2CO_3 \rightleftarrows \left\{ \overset{(k)}{\equiv}Al-CO_3 \right\} + 2H_2O$	0.0068±0.0035	11.35±0.53	[9]
$2\left\{ \overset{(l)}{\equiv}AlOH \right\} + H_2CO_3 \rightleftarrows \left\{ \overset{(l)}{\equiv}Al-CO_3 \right\} + 2H_2O$	0.0172±0.0023	6.19±0.12	[9]

Data measured in the present work:	$\log_{10}\left(K^{i*}_{U(VI)_{ads}} [Al]_t^{2-p} \right)$
$\left\{ \overset{(i)}{\equiv}Al-OH \right\}+UO_2^{2+}+Cl^- \rightleftarrows \left\{ \overset{(i)}{\equiv}Al-OUO_2Cl \right\} + H^+$	-1.95±0.10
$(2-p)\left\{ \overset{(i)}{\equiv}Al-OH \right\}+UO_2^{2+}+pH_2O \rightleftarrows \left\{ \overset{(i)}{\equiv}(Al-O)_{2-p}UO_2(OH)_p \right\}+2H^+$	-6.30±0.05
$\left\{ \overset{(i)}{\equiv}Al-OH \right\}+UO_2^{2+}+CH_3COOH \rightleftarrows \left\{ \overset{(i)}{\equiv}Al-OUO_2(CH_3COO) \right\}+2H^+$	-3.11±0.05

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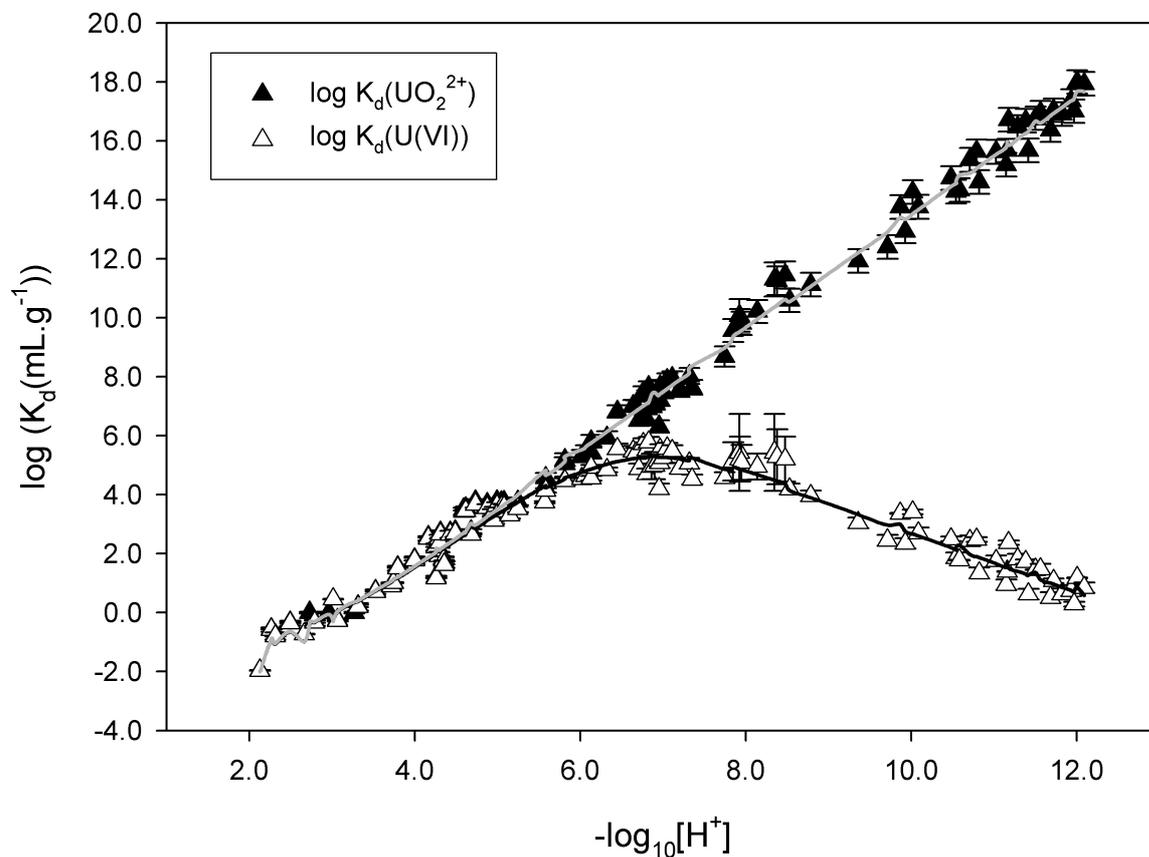
Figures

Figure 1: Distribution coefficient of U(VI) on α-Al$_2$O$_3$ (T=22°C; [NaCl] variable; [Al$_2$O$_3$] variable). K$_{dUO_2^{2+}}$ (black symbols) was calculated with Eq(2) from K$_{dU(VI)}$ (white symbols) experimental values and calculated Ringböm coefficient $\alpha_{UO_2^{2+}}$. The solid lines were calculated using fitted parameters from Table 2.
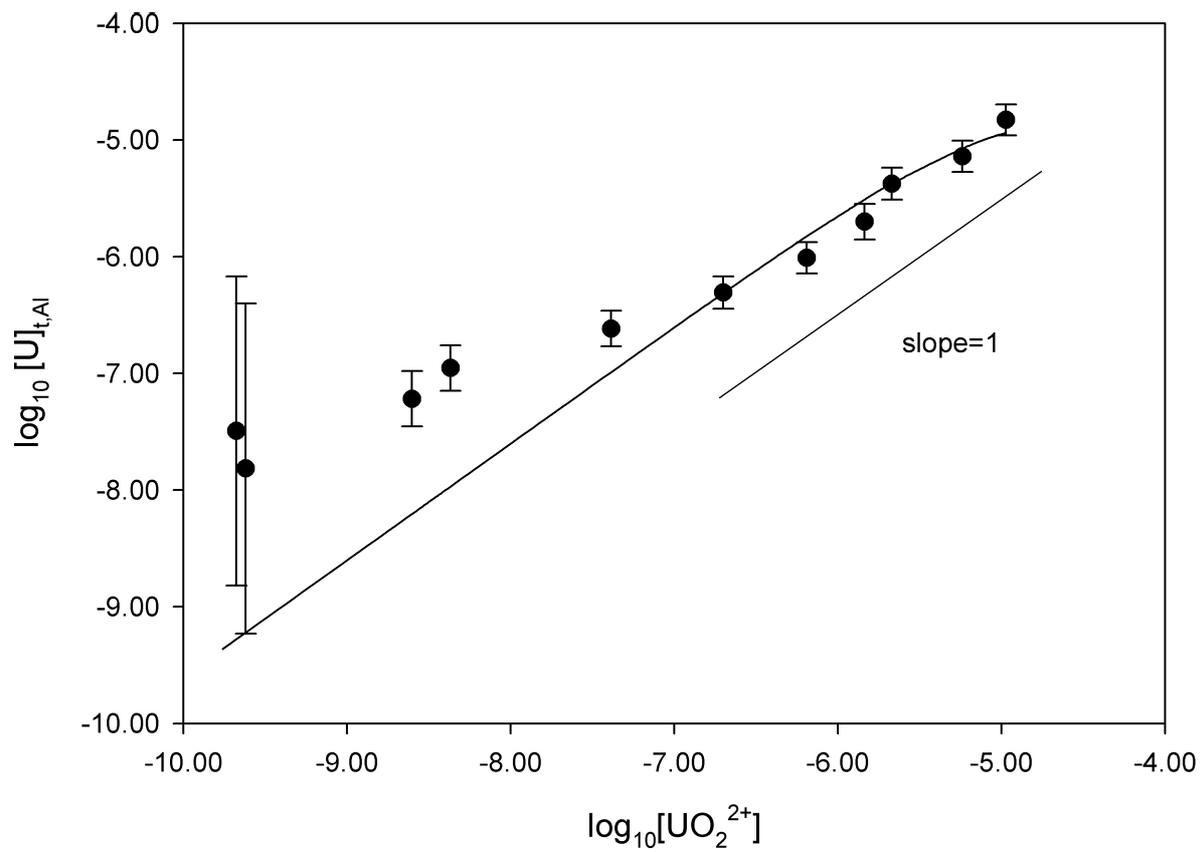
Figure 2: adsorbed Uranium (VI) on α-Al$_2$O$_3$ (T=22°C; [Al$_2$O$_3$]=12.5g/L; pH=5.0±0.2) as a function of [UO$_2^{2+}$]. The solid lines were calculated using the same parameters from Table 2

a)

b)
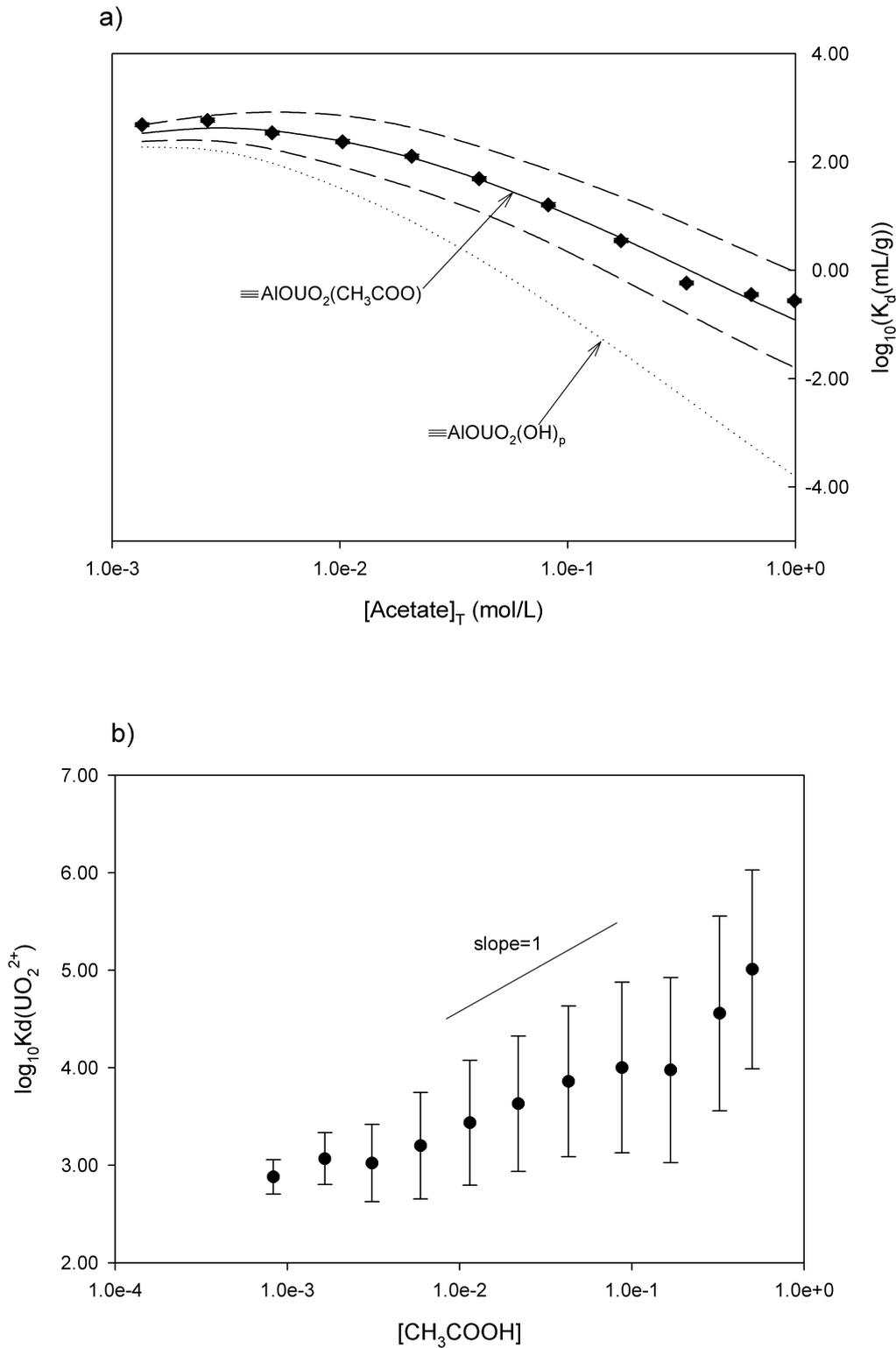
Figure 3: effect of acetate on U(VI) sorption onto α-alumina (T=22°C; [NaCl]=0.1M; pH=4.6; [Al$_2$O$_3$]=1g/L). Kd (UO$_2^{2+}$) was calculated from experimental Kd values and Ringböm coefficient.
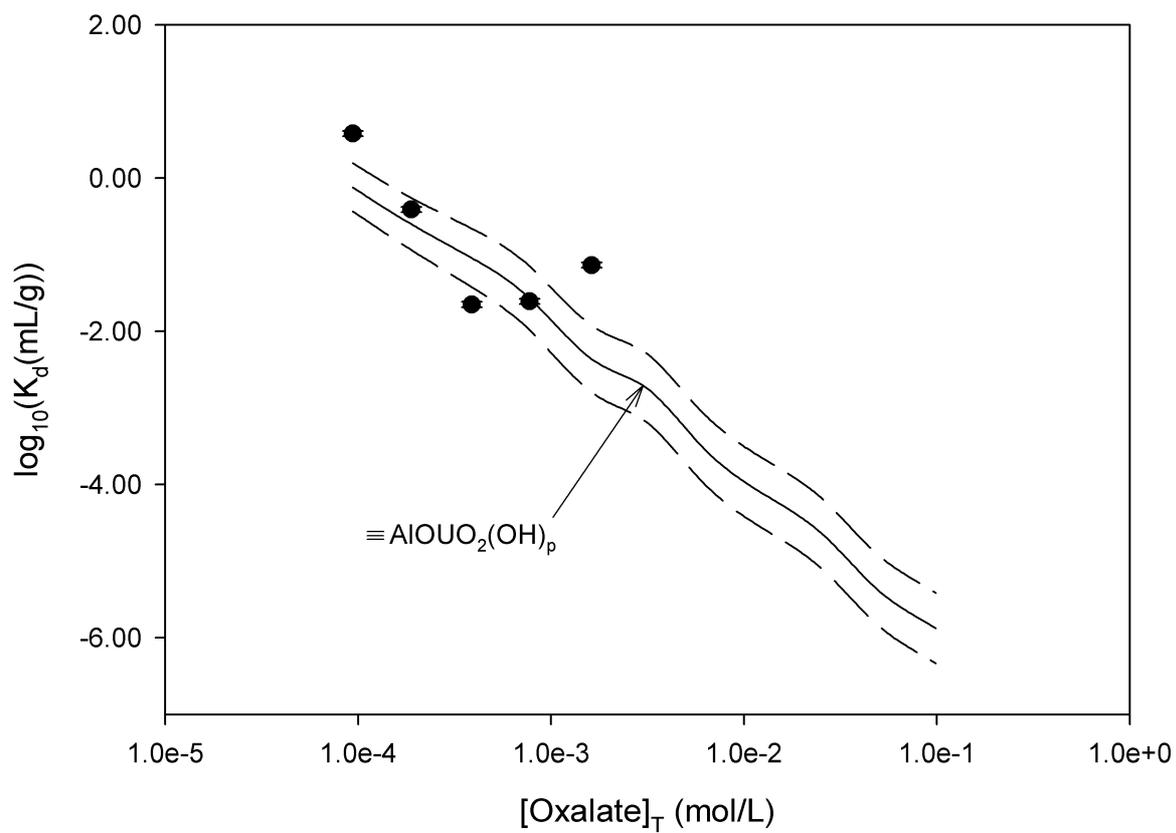
Figure 4: effect of oxalate on U(VI) sorption onto α-alumina (T=22°C; [NaCl]=0.1M; pH=4.2; [Al₂O₃]=100g/L).
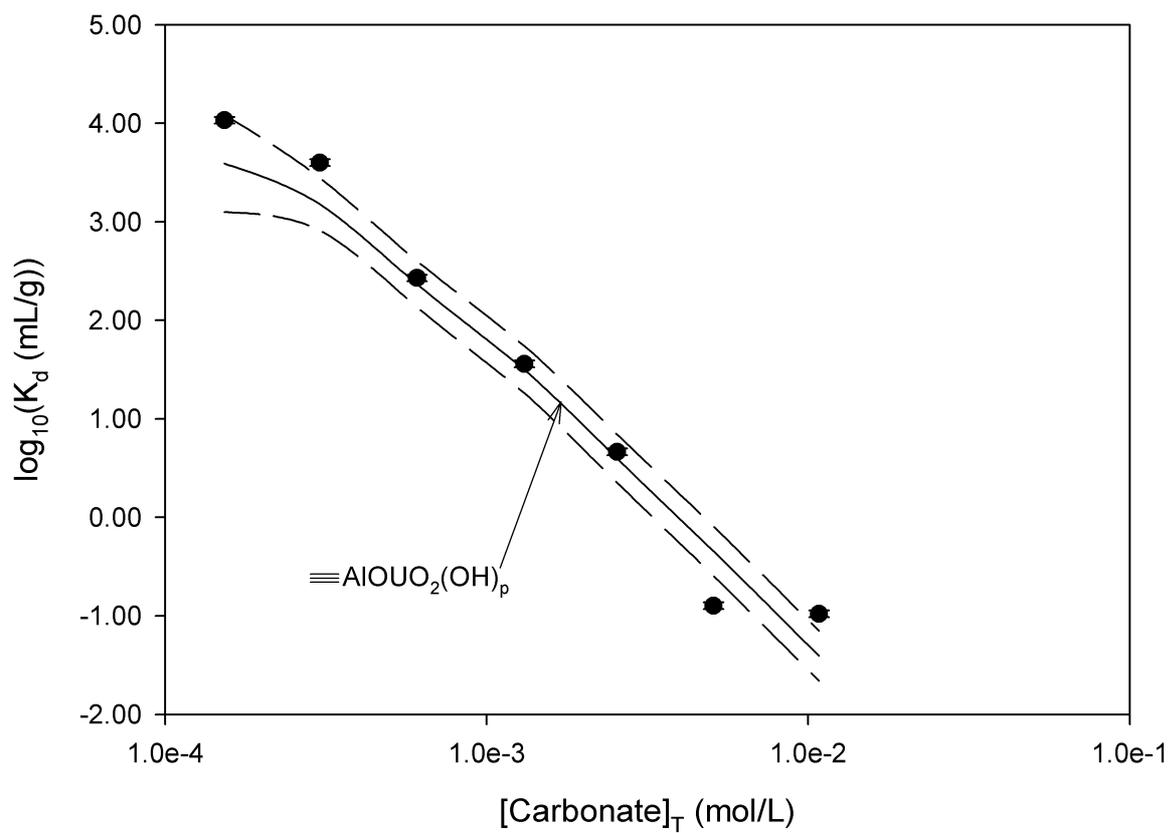
Figure 5: effect of oxalate on U(VI) sorption onto α-alumina (T=22°C; [NaCl]=0.1M; pH=8.33; [Al₂O₃]=1g/L).