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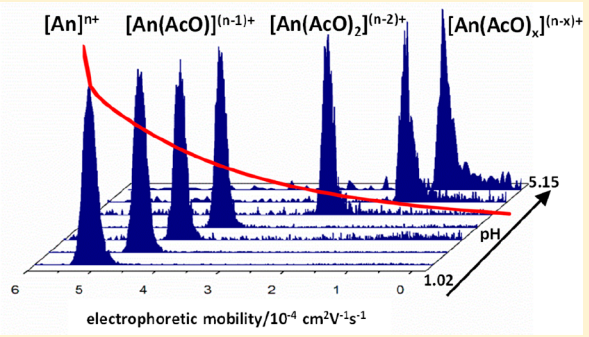
Determination of the Stability Constants of the Acetate Complexes of the Actinides Am(III), Th(IV), Np(V), and U(VI) Using Capillary Electrophoresis-Inductively Coupled Plasma Mass Spectrometry

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Supporting Information

ABSTRACT: Capillary electrophoresis-inductively coupled plasma mass spectrometry (CE-ICP-MS) was used to determine the stability constants of the actinides Am(III), Th(IV), Np(V), and U(VI) at an ionic strength of I = 0.3 M. The obtained stability constants were extrapolated to zero ionic strength by means of the Davies equation. For both U(VI) and Am(III), three consecutive acetate complexes with $\log(\beta_1^0)$ = 3.01 ± 0.12, $\log(\beta_2^0)$ = 5.27 ± 0.07, $\log(\beta_3^0)$ = 6.82 ± 0.09, and $\log(\beta_1^0)$ = 3.70 ± 0.09, $\log(\beta_2^0)$ = 5.35 ± 0.08, $\log(\beta_3^0)$ = 6.45 ± 0.09, respectively, could be identified. For Np(V), there was just one acetate complex, with $\log(\beta_1^0)$ = 1.56 ± 0.03. In the case of Th(IV), five different complex species could be determined: $\log(\beta_1^0)$ = 4.73 ± 0.16, $\log(\beta_2^0)$ = 8.92 ± 0.09, $\log(\beta_3^0)$ = 12.16 ± 0.11, $\log(\beta_4^0)$ = 12.96 ± 0.87, and $\log(\beta_5^0)$ = 14.39 ± 0.16. The actinides were selected with regard to their most stable oxidation state in aqueous solution so that four different oxidation states from +III to +VI could be investigated. A great benefit of CE-ICP-MS is the opportunity to measure at significantly lower concentrations compared to the available literature, allowing the study of actinide complexation in environmentally relevant concentration ranges. Furthermore, it is possible to analyze all four actinides simultaneously in one and the same sample.



1. INTRODUCTION

Geological clay formations are considered as host rocks for future high-level nuclear waste repositories. In deep geological repositories, the most toxic and long-lived radionuclides contained in spent nuclear fuels must be isolated as effectively as possible from human beings and the environment for up to one million years.[1] In case of a possible leakage of radionuclides from the repository, their chemical and geochemical behavior and their interaction with the surrounding biosphere must be evaluated.[2] Some actinides, namely, uranium (^{238}U, $t_{1/2}$ = 4.47 × 10^9 a), neptunium (^{237}Np, $t_{1/2}$ = 2.14 × 10^6 a), plutonium (^{239}Pu, $t_{1/2}$ = 2.41 × 10^4 a), and americium (^{241}Am, $t_{1/2}$ = 432.2 a) are the main contributors to the long-term radiotoxicity of spent nuclear fuels in a radioactive waste repository.[3] Therefore, a detailed knowledge of the aqueous speciation and thermodynamic data of these actinides is of great importance for the safety assessment of a possible nuclear waste repository since they provide the basis for modeling sorption and transportation of radionuclides. Besides a deep understanding of the redox-chemistry and hydrolysis of actinides in environmental systems, their complexation behavior with natural organic and inorganic ligands plays a key role in predicting their long-term migration in the near- and far-field of the repository.[4,5]

Many studies have shown that in pore waters of different clay formations, such as Opalinus clay (OPA) and Callovo-Oxfordian clay (COX), the content of low molecular weight organic compounds plays an important role making up large fractions of the total dissolved organic matter (DOM) (i.e., 36% in OPA, 88% in COX). The greatest proportion of the DOM is acetate, with the highest concentrations of 203 μM (OPA)[6] and 1865 μM (COX).[7] The acetate can act as a ligand for the actinides and thus affects their speciation, solubility, mobility, and toxicity in the aquatic environment. Besides this, acetate, being a small carboxylic acid, can be used as a model for more complex DOMs such as humic or fulvic acids. These substances are bigger organic molecules holding several carboxylic groups, which can also influence the geochemical behavior of radionuclides in the environment.[8] Consequently, obtaining reliable thermodynamic data about the stability of these complexes at environmentally relevant concentrations (<10^{-9} M) supports the safety assessment of a possible nuclear waste repository.

In the available literature the interactions of actinides with acetate ligands have been investigated using different methods such as extraction techniques, potentiometric and calorimetric approaches, X-ray absorption spectroscopy (XAS), and infrared absorption (IR), Raman scattering, and ultraviolet−visible (UV−vis) absorption spectroscopy.

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The U(VI)−acetate system is the one most intensively studied. The first works were carried out by Ahrland et al.[9,10] who determined stability constants of three U(VI)−acetate complexes in sodium perchlorate solution using a potentiometric method. Subsequent studies by different groups on both stability constants and structural aspects are summarized in the literature.[11−14] Most recently the stability constant for the 1:1 acetate/U(VI) complex was determined by Meinrath et al.[15] by means of UV−vis spectroscopy. The majority of the works mentioned identified three successive complexes (1:1, 1:2, and 1:3) with a bidentate binding of the acetate ligand.

Less data are given in the literature for the NpO_2^+−acetate system. Many works mention stability constants for just one or two different neptunyl complexes with acetate (see references given by Takao et al.[16] and the publication of Rao et al.[17]). Takao et al.[16] however showed the three-step complexation of Np(V) by acetate in aqueous solution by means of UV−vis-near-IR (NIR) and X-ray absorption fine structure (XAFS) spectroscopy and determined three successive values for log(β).

Since Th^{4+} is the ion with the highest charge investigated, it should be expected to be able to bind the highest number of acetate ligands. However, most of the available literature only gives data for thorium/acetate ratios up to 1:1,[18,19] 1:2,[20,21] or 1:3.[22] Only Portanova et al.[23] and Rao et al.[24] identified five successive complexes.

The Am^{3+}−acetate system was investigated in the 1960s and early 1970s by Choppin et al.[25] (1:1 complex only) and by Grenthe et al.[26] and Moskvin et al.[27−29] (three successive complexes). The results are rather inconclusive since the values differ in part by about one logarithmic unit. Later works[30−32] just mention the 1:1 complex. More recently, the Am complexation with acetate was investigated by means of extended X-ray absorption fine structure (EXAFS) spectroscopy, identifying bidentate acetate binding for all the three possible complexes.[33]

Because of the difficulty of comparing different values for the stability constants determined under different experimental conditions (e.g., ionic strength, temperature, ligand concentration, or pH), we will just refer to the values given in the ANDRA Thermodynamic Database[34] and the NIST Standard Reference Database.[35] In both databases, the thermodynamic stability constants log(β^0) for zero ionic strength are given. The particular values are listed and compared to the values determined in our work in Section 3.6.

What all these mentioned publications (and analytical techniques, respectively) have in common is a detection limit considerably higher than the concentration range required for environmental investigations.

In this work, a coupling between capillary electrophoresis (CE) and inductively coupled plasma mass spectrometry (ICP-MS) was used for the determination of the complex binding constants of Am^{3+}, Th^{4+}, NpO_2^+, and UO_2^{2+} with acetate ligands, representing a set of possible oxidation states for the actinides. Since these are the most stable oxidation states for each respective element, any impact of redox processes on our results can be ruled out. The benefit of the coupling between CE and ICP-MS is the possibility to investigate the complexation reactions at environmentally relevant concentrations due to the combination of the high separation capability of CE with the high sensitivity and the opportunity for multielement analysis of ICP-MS.[36−39] Furthermore, the affinity CE method has proved to be an appropriate analytical tool for the determination of complex binding interactions at low concentrations.[40−42] Besides a wide utilization in the field of biochemistry,[43−46] its application to metal complexation[47,48] and more especially to actinide systems[49,50] is also described extensively in the literature. Moreover, the coupling of CE to ICP-MS for this purpose has been reviewed.[51,52]

Complex binding constants have been determined for actinides with CE-ICP-MS for various ligands by Aupiais et al.[53] such as sulfate and chloride,[54] carbonate,[55] nitrate,[56] oxalate,[57−60] and diethylenetriaminepentaacetic acid.[61,62] Furthermore, affinity CE has been used for the investigation of the interaction of Np(V)[63] and U(VI)[13] with acetate, but no coupling with ICP-MS was performed. Therefore, for the actinide−acetate system there are no studies described using a coupling between CE and ICP-MS, and, as mentioned above, all the available literature for this system provides data for actinide concentrations orders of magnitude higher than those used in this work.

2. EXPERIMENTAL SECTION

2.1. Determination of Complex Binding Constants by Capillary Electrophoresis. The capability to separate different species in CE is based on the fact that the different ions vary in their radius r and their charge q and by that in their electrophoretic mobilities μ_i. The electrophoretic mobility is determined experimentally by relating the retention time of the analyte t_i to the retention time of the electroosmotic flow (EOF) t_{EOF} at a given capillary length l and applied high voltage U (eq 1):

$$\mu_i = \frac{l^2}{U}\left(\frac{1}{t_i} - \frac{1}{t_{EOF}}\right) \tag{1}$$

In determining the complex binding constant of a given central ion with a certain type of ligand, the electrophoretic mobility of the central ion decreases with an increase in the number of ligands. This is because the ligand has a shielding effect on the positive charge of the metal ion, which is thus less influenced by the applied voltage. In the case of acetate there are labile complexes formed, meaning that the exchange of ligands and the adjustment of the chemical equilibrium is fast on the time scale of an electrophoretic experiment (more details can be found in the literature[44,50,64]). Hence, only one peak is present in every electropherogram. The so-called effective electrophoretic mobility μ_{eff} of this peak is dependent on the relative ratios of the different complex species in the sample solution. It can be expressed as the sum of the electrophoretic mobility of each individual species μ_i weighted by its mole fraction x_i (eq 2):

$$\mu_{eff} = \sum_{i=0}^{N} x_i \mu_i \tag{2}$$

The investigated complex equilibria are given in general in eq 3 for the neptunyl ($n = 1$) and uranyl ($n = 2$) acetate complexes and in eq 4 for the americium ($n = 3$) and thorium ($n = 4$) complexes.

$$AnO_2^{n+} + i\,AcO^- \rightleftarrows AnO_2(AcO)_i^{(n-i)+} \tag{3}$$

$$An^{n+} + i\,AcO^- \rightleftarrows An(AcO)_i^{(n-i)+} \tag{4}$$

An stands for the respective actinide and AcO^- represents the acetate ligand. On the basis of this, the successive complex binding constants β_i are defined in eqs 5 and 6. The square brackets indicate molar concentrations.

$$\beta_i = \frac{[AnO_2(AcO)_i^{(n-i)+}]}{[AnO_2^{n+}][AcO^-]^i} \tag{5}$$

$$\beta_i = \frac{[An(AcO)_i^{(n-i)+}]}{[An^{n+}][AcO^-]^i} \tag{6}$$

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The change of the effective electrophoretic mobility μ_{eff} of the actinide ions with respect to their degree of complexation was investigated as a function of the concentration of free acetate in the sample solution. The free acetate concentration $[AcO^-]$ can be calculated and adjusted through the pH value of the solution by means of the initial concentration c_0 and the acidity constant of the acetic acid as given in eqs 7 and 8. The ionic strength was kept constant at I = 0.3 M unless stated otherwise.

$$K_a = \frac{[H^+][AcO^-]}{[AcOH]} = \frac{[H^+][AcO^-]}{c_0 - [AcO^-]} \quad (7)$$

$$[AcO^-] = \frac{c_0 \cdot K_a}{K_a + [H^+]} = \frac{c_0 \cdot 10^{-pK_a}}{10^{-pK_a} + 10^{-pH}} \quad (8)$$

For the determination of the free acetate concentration $[AcO^-]$, the pK_a value of acetic acid (pK_s = 4.756 ± 0.003[65] at zero ionic strength) was corrected to an ionic strength of I = 0.3 M with activity coefficients calculated with the Davies equation (see eq 13). In the following evaluations the corrected value of pK_a = 4.50 was thus used. This values satisfyingly fits with experimental results for I = 0.3 M presented in the literature, e.g., pK_a = 4.59 ± 0.01 by Tedesco et al.[66] and pK_a = 4.42 by Hynes et al.[67] with an average of pK_a = 4.505.

Now, the mole fractions x_i in eq 2 can be expressed as a function of the complex binding constant β_i and the free acetate concentration $[AcO^-]$ as shown in eq 9:

$$x_0 = \frac{1}{1 + \sum_{i=1}^{N} \beta_i [AcO^-]^i} \text{ and } x_i = \frac{\beta_i [AcO^-]^i}{1 + \sum_{i=1}^{N} \beta_i [AcO^-]^i} \quad (9)$$

In this equation i = 1, 2, ..., N represents the complexed species with the respective number of ligands. Finally, combining eq 2 with eq 9 results in eq 10, which allows the determination of the complex binding constants β_i from the measured electrophoretic mobility μ_{eff} as a function of the free acetate concentration $[AcO^-]$. μ_0 is the electrophoretic mobility of the noncomplexed actinide.

$$\mu_{eff} = \frac{\mu_0 + \sum_{i=1}^{N} \mu_i \beta_i [AcO^-]^i}{1 + \sum_{i=1}^{N} \beta_i [AcO^-]^i} \quad (10)$$

At this point, a further benefit of the CE-ICP-MS method for the determination of stability constants becomes obvious. Because of the capability of analyzing very low actinide concentrations, a large ligand to metal ratio arises which drastically simplifies the data evaluation since the consumption of acetate ligand for the formation of the complex species can be neglected.

In order to extrapolate the stability constants to zero ionic strength, the results were corrected by the correspondent activity coefficients γ_i (see eq 11 for uranyl and neptunyl and eq 12 for thorium and americium).

$$\beta_i^0 = \beta_i \frac{\gamma_{AnO_2(AcO)_i^{(n-i)+}}}{\gamma_{AnO_2^{n+}} \cdot \gamma_{AcO^-}^i} \quad (11)$$

$$\beta_i^0 = \beta_i \frac{\gamma_{An(AcO)_i^{(n-i)+}}}{\gamma_{An^{n+}} \cdot \gamma_{AcO^-}^i} \quad (12)$$

For calculating the activity coefficients at 25 °C and at a given ionic strength I, the Davies equation was used, as given in eq 13.

$$\log(\gamma_i) = -0.509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (13)$$

In the ionic strength range employed in this work, this theory is described to be a suitable approximation. A comparison of some $\log(\beta_i^0)$ values of higher charged actinide-acetate species derived from the Davies equation with results obtained from the specific ion interaction (SIT) theory further proved the suitability of this extrapolation since the values were identical within the limits of error (see Table S10 in SI).

2.2. CE-ICP-MS System. For performing the electrophoresis experiments, an Agilent 7100 CE system was hyphenated to an Agilent 7500 ce ICP-MS (both Agilent Technologies, Santa Clara, California, USA). An effective coupling was realized using a MiraMist CE nebulizer (Burgener Research, Mississauga, Canada) in connection with a Scott-type spray chamber (AHS Analysentechnik, Tübingen, Germany). As a makeup electrolyte, a 1.25% HNO_3 solution with 10% ethanol and 5 ppb ^{89}Y, ^{103}Rh, ^{140}Ce, and ^{209}Bi (internal standards) was inserted via a syringe pump (PicoPlus, Harvard Apparatus, Holliston, Massachusetts, USA). The flow rate was adjusted experimentally to 5 μL min^{-1} as the optimal value.

The electrophoretic runs were performed in fused silica capillaries (Polymicro Technologies, Phoenix, Arizona, USA) with an inner diameter of 50 μm and a length of 76 cm. The high voltage was set to 10 kV. The capillary was filled with the background electrolyte of the respective experiment. The samples were prepared in conical microinserts of borosilicate glass (Carl Roth AG, Arlesheim, Switzerland), which were placed in polyethylene vials sealed with polyethylene olefin snap caps (both Agilent Technologies, Santa Clara, California, USA). The introduction into the capillary was by hydrodynamic injection (100 mbar for 8 s). Before every use the capillary was preconditioned by flushing with Milli-Q water, 0.1 M NaOH solution, 0.1 M HCl, and the background electrolyte. In order to change the complete background electrolyte between all measurements, the capillary was flushed for 15 min with the respective solution needed for the next experiment. Temperature was controlled at 25 °C by the air cooling device of the Agilent apparatus. Temperature rise in this system due to Joule heating was calculated to be on average 0.5 °C and to not exceed 1 °C.[68]

Detection was carried out with the ICP-MS using a time-resolved analysis detection mode with a dwell time of 100 ms and a plasma power of 1550 W. To find the optimal parameters for the lens system and the argon flow rates before each day of measurement, tuning to the masses of the internal standards was executed. Carrier gas and makeup gas flow rates were adjusted to 0.86−1.15 L min^{-1} and 0.28−0.77 L min^{-1}, respectively. Data processing was conducted with MassHunter Workstation software (G7200B, Agilent Technologies, Santa Clara, California, USA).

2.3. Reagents. All chemicals employed were of pro-analysis quality or better. The dilutions were performed with Milli-Q water (18.2 MΩ, Synergy Millipore water system, Millipore GmbH, Schwalbach, Germany), and all solutions were filtered through 0.2 μm syringe filters (Nalgene, Rochester, New York, USA) to prevent a clogging of the capillary.

Sodium hydroxide, 2-bromopropane, and rhodium ICP-MS standard solution were from Merck (Darmstadt, Germany). Acetic acid and perchloric acid were supplied by Riedel-de Haën (Seelze, Germany), hydrochloric acid by Fisher Scientific (Loughborough, UK), and sodium perchlorate by Sigma-Aldrich (St. Louis, Missouri, USA). The ICP-MS elemental standard solution for bismuth, cerium, and yttrium were ordered from High-Purity Standards (Charleston, South Carolina, USA). As plasma gas, 4.6 Ar was used (Westfalen AG, Münster, Germany).

In-house stock solutions of known concentrations of $^{237}Np(V)$ and U(VI) (dep.) in 1 M perchloric acid were used. A stock solution of $^{241}Am(III)$ was prepared by evaporating an in-house Am(III) solution in nitric acid five times until near dryness and dissolving the residue in 1 M perchloric acid. The concentrations of Np(V) and Am(III) were checked by γ-ray spectrometry using the γ-lines at 86.5 keV for ^{237}Np and 59.5 keV for ^{241}Am with a high-purity Ge-detector (GMX-13280-S, EG & G ORTEC, USA) and the Canberra InSpector 2000 DSP Portable Spectroscopic Workstation (model IN2K, Canberra Industries Inc., USA), and Genie 2000 Gamma software (V. 3.0, Canberra Industries Inc., USA). The γ-ray spectrometer was calibrated with a multiple γ-ray emitting solution (serial number: 1850−27, Eckert & Ziegler Isotope Products, Braunschweig, Germany). The $^{232}Th(IV)$ stock solution was obtained by diluting the ICP-MS standard solution (Accu Trace, Accu Standard, New Haven, Connecticut, USA) of known concentration in 1 M perchloric acid.

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2.4. Sample Preparation. Each sample was prepared starting from a 0.3 M acetic acid solution. By adding certain amounts of 11.6 M perchloric acid or 10 M sodium hydroxide solution, the different desired pH values were set. Experiments were conducted in a pH range starting from pH 1, where the actinides should be completely uncomplexed, to a maximum pH value at which hydroxide formation did not significantly influence the actinide−acetate system (pH 4.8 for Th(IV), pH 5.8 for U(VI), pH 6.0 for Np(V), and pH 5.7 for Am(III)). All samples were brought to an equal ionic strength of I = 0.3 M by adding appropriate amounts of sodium perchlorate. The detailed sample compositions are summarized in the Supporting Information, Tables S1−S9. Volumes of 200 μL of each of these solutions were added to a CE glass vial as the background electrolyte of the respective sample and were used for flushing the capillary before every experiment.

For every measuring series, solutions containing only one particular actinide were prepared. To 10 mL of the background electrolyte solutions, a few μL of the respective actinide stock solution was added to obtain the following actinide sample concentrations: c(Th) = (1.00 ± 0.09) × 10^{-6} M, c(U) = (1.42 ± 0.13) × 10^{-7} M, c(Np) = (5.00 ± 0.45) × 10^{-8} M, and c(Am) = (5.27 ± 0.47) × 10^{-8} M. The volume of added actinide solution was kept as small as possible so as to not significantly alter the ionic strength of the solution. Again, 200 μL of the actinide sample solution was transferred to a CE glass vial, together with 1 μL of 2-bromopropane as the EOF marker (detected via ICP-MS on the bromine mass 79). As can be seen from the data given above, the ligand concentration by far exceeds the concentration of the actinide ion, which is known to be a crucial point in accurately determining stability constants by measuring effective electrophoretic mobilities.[69]

The pH value of the solution was controlled before and after the addition of the actinide stock solution, and no significant difference was observed. For the pH measurements, an inoLab/Cond pH 720 pH meter (WTW GmbH, Weilheim, Germany) equipped with a blue line 16 pH electrode (SI Analytics, Mainz, Germany) and temperature sensor (TFK 150, WTW GmbH, Weilheim, Germany) was used. Calibration was realized with certified commercial buffers (pH 4.01 and 6.87, SI Analytics, Mainz, Germany).

2.5. Data Treatment. By plotting the free acetate concentration [AcO^-] against the effective electrophoretic mobility μ_{eff} and fitting these experimental data with the function given in eq 10, values for the electrophoretic mobility of the individual species μ_i and the complex binding constants β_i were obtained. The individual equations for the different actinide−acetate systems employed are given in the Supporting Information (eqs S1−S4). The fit was performed with Origin 7 software (OriginLab Corporation, Northampton, Massachusetts, USA) by a least-squares curve fitting method using the Levenberg−Marquardt algorithm. In order to obtain reliable values, constraints were formulated. The choice of these constraints was based on physical and chemical requirements. In general, four requirements were presumed, as follows:

(1) The electrophoretic mobility of a neutral complex is zero.
(2) Complexes with a positive charge have an electrophoretic mobility greater than zero; for negative complexes the electrophoretic mobility is less than zero.
(3) The values for the electrophoretic mobilities decrease with increasing number of associated ligands.
(4) The values for the complex binding constants β_i are greater than zero and increase with increasing ligand number. (This constraint is based on the available literature data.)

3. RESULTS AND DISCUSSION

All electropherograms are shown in the Supporting Information, Figures S1 and S2 (Am(III) series), S3 and S4 (Th(IV) series), S5−S7 (Np(V) series) and S8 and S9 (U(VI) series).

3.1. U(VI)−acetate System. In the case of the U(VI)−acetate system, three successive acetate complexes were determined. The respective function used for the fit is thus given in eq 10 for i = 0, 1, 2, 3. The experimental data and the related results for the fit are shown in Figure 1.

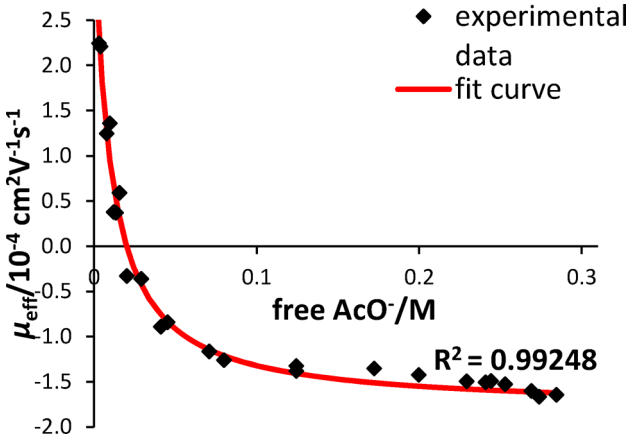


Figure 1. Measured effective electrophoretic mobilities μ_{eff} of the U(VI)−acetate series as a function of the free acetate concentration [AcO^-] at I = 0.3 M with the related fit curve.

Since both positively and negatively charged complexes are formed depending on the free acetate concentration, it is reasonable that the values for the effective electrophoretic mobilities also change from positive at the beginning to negative for higher free acetate concentrations. As one can further see, the experimental data could be fitted satisfactorily with a coefficient of determination R^2 of 99.2%. The determined values for the complex binding constants at I = 0.3 M are given in Table 1. All electrophoretic mobilities of the individual species μ_i are summarized in Table 2 and discussed in Section 3.5. The results for extrapolation the complex binding constants to zero ionic strength and the comparison with literature data can be found in Section 3.6 (the same is true for the following actinide−acetate systems).

Table 1. Complex Binding Constants β_i for the Three Successive U(VI)−Acetate Complexes (I = 0.3 M)[a]

i	β_i/M^{-i}	$\Delta(\beta_i)/M^{-i}$	$\log(\beta_i)$	$\Delta(\log(\beta_i))$
1	2.99×10^2	8.49×10^1	2.48	0.12
2	2.94×10^4	4.97×10^3	4.47	0.07
3	1.03×10^6	2.05×10^5	6.01	0.09

[a]The standard errors $\Delta(\beta_i)$ result from the fitting procedure.

3.2. Np(V)−acetate System. For the Np(V)−acetate system, only the 1:1 complex could be identified, and the respective complex binding constant was determined (Table 3). Since in some parts of the literature[16,34] the formation of three successive Np−acetate complexes has been described, we also tried to fit our experimental data with a function representing three binding constants. But with the constraints mentioned in Section 2.5, no solution could be obtained. The same result occurred, when considering the formation of 1:1 and 1:2 Np(V)-acetate complexes.

The experimental data and the respective fit can be seen in Figure 2. In contrast to the U(VI) data, no negative values for the electrophoretic mobilities were measured, even for high concentrations of free acetate. This is also an indication for just a 1:1 complex being formed because if the negatively charged 1:2 and 1:3 Np−acetate species were present to a significant

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Table 2. Electrophoretic Mobility of the Individual Species μ_i[a]

		$\mu_i/10^{-4}$ cm^2 V^{-1} s^{-1}
U(VI)	UO_2^{2+}	3.4
	$[UO_2(AcO)]^+$	1.9
	$[UO_2(AcO)_2]_{aq}$	0.0[b]
	$[UO_2(AcO)_3]^-$	−1.8
Np(V)	NpO_2^+	2.4
	$[NpO_2(AcO)]_{aq}$	0.0[b]
Th(IV)	Th^{4+}	5.0
	$[Th(AcO)]^{3+}$	3.4
	$[Th(AcO)_2]^{2+}$	1.9
	$[Th(AcO)_3]^+$	0.3
	$[Th(AcO)_4]_{aq}$	0.0[b]
	$[Th(AcO)_5]^-$	−0.5
Am(III)	Am^{3+}	5.1
	$[Am(AcO)]^{2+}$	3.8
	$[Am(AcO)_2]^+$	1.7
	$[Am(AcO)_3]_{aq}$	0.0[b]

[a]The uncertainties are estimated to be $\Delta\mu_i = 0.1 \times 10^{-4}$ cm^2 V^{-1} s^{-1} in all cases. [b]Held constant during the fits.

Table 3. Complex Binding Constant β_1 for the Np(V)−Acetate Complex (I = 0.3 M)[a]

β_1/M^{-1}	$\Delta(\beta_1)/M^{-1}$	$\log(\beta_1)$	$\Delta(\log(\beta_1))$
19.4	1.4	1.29	0.03

[a]The standard error $\Delta(\beta_1)$ results from the fitting procedure.

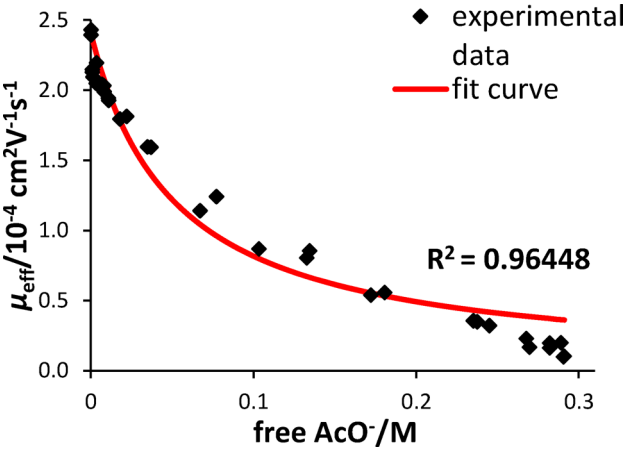


Figure 2. Measured effective electrophoretic mobilities μ_{eff} of the Np(V)−acetate series as a function of the free acetate concentration [AcO$^-$] at I = 0.3 M with the related fit curve.

extent the overall electrophoretic mobility would become negative. The results for μ_i and β_i are given in Tables 2, 3, and 6.

3.3. Th(IV)−Acetate System. The complexation of Th(IV) with acetate leads to the most elaborate system. Because of the high charge of +4 of the thorium ion, it is able to bind the highest number of ligands of all the actinides investigated in this work. The experimental data and the related results for the fit for five successive complexes are shown in Figure 3.

In contrast to the other systems, in this case the results of the two data series are quite inconsistent. Consequently, the first data series was not used for the data evaluation, and the

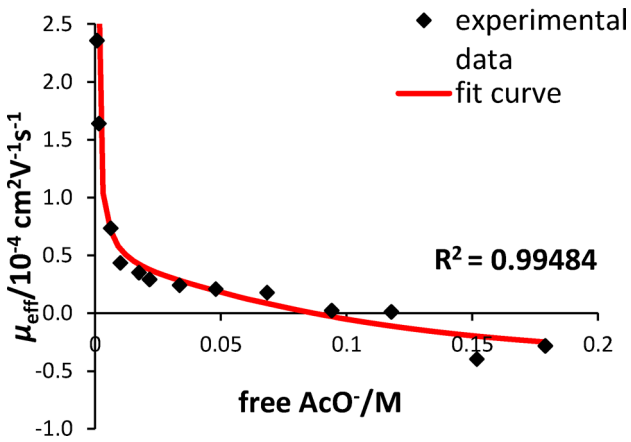


Figure 3. Measured effective electrophoretic mobilities μ_{eff} of the Th(IV)−acetate series as a function of the free acetate concentration [AcO$^-$] at I = 0.3 M with the related fit curve.

second measurement series was considered to be more reliable. As in the U(VI) example, both positive and negative effective electrophoretic mobilities were measured, substantiating the formation of a 1:5 thorium−acetate complex that is negatively charged. Since in this case the fit function (eq 10) contained 11 parameters, it was the most difficult system to process with the Origin software, and the errors are somewhat higher than in the other systems (for $\log(\beta_4)$ even higher than the absolute value itself). The results presented in Table 4 are the best

Table 4. Complex binding constants β_i for the five successive Th(IV)−acetate complexes (I = 0.3 M)[a]

i	β_i/M^{-i}	$\Delta(\beta_i)/M^{-i}$	$\log(\beta_i)$	$\Delta(\log(\beta_i))$
1	4.53×10^3	1.63×10^3	3.66	0.16
2	1.09×10^7	6.30×10^7	7.04	0.09
3	5.58×10^9	7.62×10^{10}	9.75	0.11
4	1.89×10^{10}	7.92×10^{11}	10.28	0.87
5	5.09×10^{11}	1.51×10^{13}	11.71	0.16

[a]The standard errors $\Delta(\beta_i)$ result from the fitting procedure.

values that could be calculated using all constraints mentioned above. In spite of these difficulties, the values for the complex binding constants are in good agreement with the literature, as discussed in Section 3.6.

3.4. Am(III)−Acetate System. As can be seen in Figure 4, for the Am(III)−acetate system no negative effective electrophoretic mobilities could be measured over the whole pH range. This indicates, as in the case of Np(V), that no negatively charged americium−acetate complexes are formed under these conditions. Consequently, three was set as the highest ligand number for the fit shown in Figure 4, which led to satisfactory results. The complex binding constants β_i at I = 0.3 M are given in Table 5.

3.5. Electrophoretic Mobilities of the Individual Species μ_i. In addition to the complex binding constants, the electrophoretic mobilities of the individual species μ_i have also been determined by means of the fit function given in eq 10. For the fitting procedure, the constraints given in Section 2.5 were used. As one can see from the results given in Table 2, a set of individual electrophoretic mobilities complying with these conditions could be obtained.

The order in the individual electrophoretic mobilities of the noncomplexed species corresponds to the charge of the

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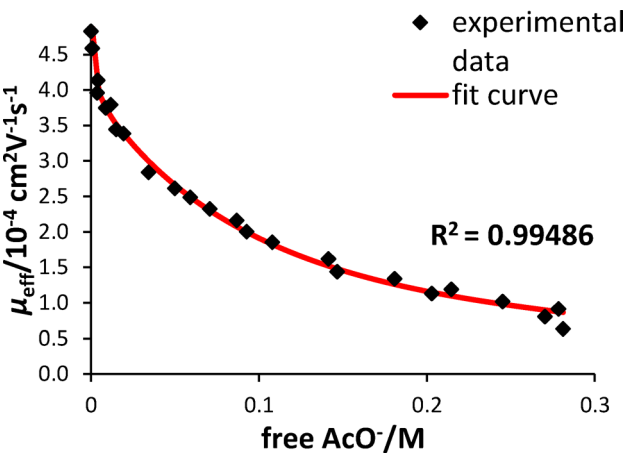


Figure 4. Measured effective electrophoretic mobilities μ_{eff} of the Am(III)−acetate series as a function of the free acetate concentration [AcO^-] at I = 0.3 M with the related fit curve.

Table 5. Complex Binding Constants β_i for the Three Successive Am(III)−Acetate Complexes (I = 0.3 M)[a]

i	β_i/M^{-i}	$\Delta(\beta_i)/M^{-i}$	$\log(\beta_i)$	$\Delta(\log(\beta_i))$
1	7.80×10^2	1.57×10^2	2.89	0.09
2	1.01×10^4	1.90×10^3	4.00	0.08
3	6.82×10^4	1.36×10^4	4.83	0.09

[a]The standard errors $\Delta(\beta_i)$ result from the fitting procedure.

respective actinide ion. Thorium and americium, with the highest charges of +4 and +3, respectively, have the highest mobility; the least charged neptunyl ion is the slowest. Species with the same charge have comparable electrophoretic mobilities.

3.6. Extrapolation to Zero Ionic Strength. The complex binding constants β_i determined by CE-ICP-MS were extrapolated to thermodynamic stability constants β_i^0 at zero ionic strength by eqs 11 and 12, respectively, by means of the Davies equation given in eq 13.

The results are summarized in Table 6. For comparison with the literature, data available from the ANDRA database[34] as well as from the NIST database[35] are also given.

The binding constants of the different actinide−acetate systems obtained in this work are, in general, in good agreement with the literature data mentioned above; they all follow the same trends. Small deviations of our values from the literature data may be explained by the orders of magnitude differences in the concentrations of the actinides. As mentioned earlier, we investigated systems at environmentally relevant concentrations ($\sim 10^{-7}$ M), while the literature data are given for mostly millimolar concentrations. According to our experimental results, Np(V) forms just one complex under the given experimental conditions; this is in accordance with the findings of Pokrovsky and Choppin[70] and Rao et al.[17] but disagrees with the results of Takao et al.,[16] who quote values for three successive complexes. Since the CE-ICP-MS method enables reliable statements about the charge of a complex species, and no negative effective electrophoretic mobilities referring to a negatively charged Np(V)−acetate species were detected, it is reasonable that only the 1:1 complex is formed.

For the oxidation states III, IV, and VI of the investigated actinides, the successive acetate complexes exhibit increasing $\log(\beta_i^0)$ values, indicating an increase in the stability of the

Table 6. Thermodynamic Stability Constants β_i^0 for the Different Actinide−Acetate Systems and Comparison with the Literature

	$\log(\beta_i^0)$		
	this work	ANDRA database[34]	NIST database[35]
U(VI)	3.01 ± 0.12	3.02 ± 0.2	3.11
	5.27 ± 0.07	5.20 ± 0.3	5.04
	6.82 ± 0.09	7.03 ± 0.4	7.06
Np(V)	1.56 ± 0.03	1.32 ± 1.0	1.35
		3.42 ± 0.01	
		3.57 ± 0.01	
Th(IV)	4.73 ± 0.16	5.24 ± 0.15	4.69
	8.92 ± 0.09	9.44 ± 0.15	8.18
	12.16 ± 0.11	12.56 ± 0.50	10.85
	12.96 ± 0.87	14.38 ± 0.50	12.44
	14.39 ± 0.16	15.37 ± 1.00	13.04
Am(III)	3.70 ± 0.09	2.94 ± 0.5	2.8
	5.35 ± 0.08	5.07 ± 0.5	4.62
	6.45 ± 0.09	6.54 ± 0.5	5.51

complexes. By comparing the different actinide series, one can directly read off the tendency of the strength of the acetate complexes. Th(IV) forms by far the strongest complexes, while Np(V) tends to build the weakest complexes. The binding constants of U(VI) and Am(III) are rather similar and lie in between the two others. This sequence follows the usual order of increasing strength of actinide complexes $AnO_2^+ < An^{3+} \approx AnO_2^{2+} < An^{4+}$, which mirrors the effective charge of the actinide.[71]

4. SUMMARY AND CONCLUSIONS

The application of CE coupled to ICP-MS has proven to be a very suitable and appropriate analytical tool for the determination of the binding constants of complexes of different actinides with acetate. In particular, operation at very low concentrations is a benefit that allowed the investigation of systems in the environmentally relevant range. The results determined by this method for U(VI), Np(V), Th(IV), and Am(III) are given in Table 6. They are in good agreement with the available literature given for higher concentrations of the respective actinide. We were able to determine three successive complexes and the respective complex binding constants for U(VI) and Am(III), five for Th(IV), and only one for Np(V). Concerning the last, there is disagreement in the literature about the number of complexes. With this work we were able to show that no negative Np(V) acetate complex is formed, and thus just a 1:1 complex is to be expected. Our values may be used as a database for the long-term safety analysis of a future nuclear waste repository since they provide more accurate information about the actual conditions in such a system.

In order to improve further the databases for these concerns, the CE-ICP-MS system may be used in future works for the investigation of other actinides with acetate (e.g., plutonium), for the determination of binding constants with different ligands (such as citrate) and for different temperature ranges.

■ ASSOCIATED CONTENT

Supporting Information

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Electropherograms of all measurement series, detailed composition of all samples, equations used to fit the experimental data, comparison of different extrapolations to zero ionic strength (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

AcOH, acetic acid; An, actinide; aq, dissolved in aqueous solution; CE-ICP-MS, capillary electrophoresis-inductively coupled plasma mass spectrometry; COX, Callovo-Oxfordian clay; DOM, dissolved organic matter; EOF, electroosmotic flow; (E)XAFS, (extended) X-ray absorption fine structure; OPA, Opalinus clay; UV−vis-near-IR, ultraviolet visible near-infrared; XAS, X-ray absorption spectroscopy.

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