Fluoride complexation of rutherfordium (Rf, element 104)

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Summary. The fluoride complexation of the group-4 elements Zr, Hf and Rf, and of the pseudo-homolog Th, has been investigated in mixed HNO₃/HF solutions by studying K_d values on both cation exchange resins (CIX) and anion exchange resins (AIX) using the automated rapid chemistry apparatus ARCA. On the CIX, the four elements are strongly retained as cations below 10⁻³ M HF. For Zr and Hf, the decrease of the K_d values due to the formation of fluoride complexes occurs between 10⁻³ M HF and 10⁻² M HF. For Rf and Th, this decrease is observed at one order of magnitude higher HF concentrations. On the AIX, for Zr and Hf, a rise of the K_d values due to the formation of anionic fluoride complexes is observed between 10⁻³ M HF and 10⁻² M HF, i.e. in the same range of HF concentrations where the decrease of the K_d values on the CIX is observed, yielding a consistent picture. For Rf and Th, on the AIX, no rise of the K_d values is observed even if the HF concentration is increased up to 1 M. By varying the concentration of the counter ion NO₃⁻ which is competing for the binding sites on the AIX resin, it could be shown, nevertheless, that Rf does form anionic fluoride complexes. Apparently, there is a more specific competition of NO₃⁻ with respect to [RfF_x]^{(x-4)-} than with [ZrF_y]^{(y-4)-} and [HfF_z]^{(z-4)-}.

Introduction

The first aqueous chemistry study of seaborgium (Sg, element 106) [1, 2] was performed recently with the Automated Rapid Chemistry Apparatus ARCA II. ²⁶⁵Sg ($T_{1/2} = 7.4^{+3.3}_{-2.7}$ s [3]) was eluted from a cation exchange resin (CIX, Aminex A6) in 0.1 M HNO₃/5 · 10⁻⁴ M HF which is typical for a group-6 element. Due to the half-minute time span needed to prepare samples and to start counting [2], ²⁶⁵Sg itself was not detected, but correlated mother-daughter decays of its descendant, 78-s ²⁶¹Rf. Therefore, it was important that a HF concentration was selected that was insuff-

ficient to elute group-4 elements [2]. This had been demonstrated for Zr and Hf and was assumed for Rf.

Due to the HSAB (Hard Soft Acid Base) concept [4], hexavalent Sg shows a higher affinity to F⁻ ions than any 4+ ion. In this concept, ions are characterized by their hardness. Small, multiply charged ions are hard; big, singly charged ions are soft. Strong interactions between anions and cations occur either if both of them are hard (maximum of the ionic interaction) or if both of them are soft (maximum of the electronic overlap interaction). Sg⁶⁺ is both smaller and higher charged than Rf⁴⁺ and, therefore, it is the harder cation and will interact stronger with the hard fluoride anion. Thus, the tendency to form anionic fluoride complexes should increase from Rf to Sg. So even if the Rf fluoride complexing behaviour is different from that of Zr and Hf and is more similar to that of the pseudo-homolog Th, it should stick to the CIX column even at higher HF concentrations than 5 · 10⁻⁴ M.

In any case, it was of interest to verify experimentally that ²⁶¹Rf, under the condition of the seaborgium experiments, is not eluted from the CIX column and can only appear in the seaborgium sample as a result of the α decay of ²⁶⁵Sg.

This verification of the Rf behaviour was the starting point for a detailed study of the Rf behaviour on both CIX and AIX. These data were related to data for the group 4 homologs Zr and Hf as well as to the actinide pseudo-homolog Th.

Several experiments have been performed concerning the fluoride complexation of Rf by other groups within the last years. Szegłowski *et al.* [5] showed that Rf forms anionic fluoride complexes in 0.2 M HF that were retained on an anion exchange column. The extraction of fluoride complexes of the group 4 elements, Ti, Zr, Hf and Rf, into TiOA was reported by Kacher *et al.* [6]. This work presents some evidence for the extraction of Rf into TiOA from 0.5 M HF. By selecting conditions such that the retention time is on the order of the nuclear half life, Pfrepper *et al.* [7] showed that, within the error bars, the K_d value for Rf on an AIX in mixed HNO₃/0.27 M HF solutions is identical

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with that of Hf and that the structure of the anionic complexes is $[\text{MF}_6]^{2-}$ both for Hf and Rf. The aqueous chemistry of Rf is reviewed in Ref. [8].

2. Definitions of K_d values

The distribution of a chemical compound between two phases is defined by the distribution coefficient K_d . The most simple definition in a static system is derived directly from the concentrations of the concerning species in both phases:

$$K_d = \frac{c'}{c''} \quad (1)$$

where the indices mark the different phases. With this definition, the K_d value is dimensionless.

The observables in all experiments of this paper were radioactive decays. Therefore, it is suitable to describe the distribution coefficient as a ratio of specific activities instead of concentrations. The applied systems were always heterogenic containing a liquid (aqueous) and a solid (exchange resin) phase. Then, the K_d is calculated as follows:

$$K_d = \frac{A_s}{A_l} = \frac{A_{s0} V_l}{A_{l0} m_s} \quad (2)$$

with A_s specific activity in the solid phase [Bq/g], A_l specific activity in the liquid phase [Bq/ml], A_{s0} activity in the solid phase [Bq], A_{l0} activity in the liquid phase [Bq], m_s mass of the resin [g], V_l volume of the solution [ml].

Thus, because the specific activity is either Bq/g or Bq/ml, the dimension of the K_d values is ml/g.

These definitions are based on the assumption that equilibrium is reached.

In a dynamic chromatography system, the K_d is described as

$$K_d = (t_r - t_0) \frac{V}{m_s} \quad (3)$$

with t_r retention time [s], t_0 dead time of the chromatography system due to the free column volume [s], V flow rate of the liquid phase [ml/s], m_s mass of the solid phase [g].

The dimension of the K_d value is again ml/g. A prerequisite for a meaningful K_d value is that equilibrium is reached for the applied flow rates. Equilibrium is verified if static and dynamic partition experiments yield the same results.

3. Experimental

3.1 Tracer production

3.1.1 Production of ^{95}Zr

^{95}Zr was produced at the TRIGA reactor at Mainz in thermal-neutron induced fission of ^{235}U . A ^{235}U target covered with an Al backing was irradiated. The Al backing was removed and dissolved in concentrated HCl. ^{95}Zr was chemically separated from the fission products on an AIX column (Dowex 1x8, 200–400 mesh). The fission products were fed onto the column in 12 M HCl, and Zr was eluted with 2 M HCl.

Alternatively, a solution of $^{95}\text{Zr}/^{95}\text{Nb}$ in 0.5 M oxalic acid was purchased from CIS Diagnostik GmbH, Dreieich. To obtain an oxalic-acid free solution it was evaporated to dryness several times in the presence of $\text{H}_2\text{O}_2/\text{HCl}$ in a teflon crucible and taken up in 12 M HCl.

3.1.2 Production of ^{175}Hf

^{175}Hf was produced at the Philips Cyclotron at Karlsruhe in the reaction $^{175}\text{Lu}(p,n)^{175}\text{Hf}$. 500 mg Lu oxide were pressed in between two 1.1 mm graphite disks. This target was irradiated for one hour with a 10 μA 20 MeV proton beam, resulting in 16 MeV protons entering the target. These conditions were chosen such that the protons were fully stopped in the target material. Thus the energy of the protons covered a large portion of the excitation function for the (p,n) reaction. The excitation function was calculated with the HIVAP code [9]. After irradiation, the target material was dissolved in concentrated HCl. Lu was removed on an AIX column (Dowex 1x8, 200–400 mesh) from which the ^{175}Hf was subsequently eluted with 4 M HCl.

3.1.3 Production of ^{233}Th

^{233}Th was produced by neutron irradiation of ^{232}Th at the TRIGA reactor Mainz. The Th results are the only data described within this work that were obtained with non carrier-free isotopes. The irradiation times were chosen such that the carrier amount in the used solutions was about a factor of 100 lower than the loading capacity of the exchanger material.

3.2 Batch experiments

All tracer solutions for batch experiments were stored in 12 M HCl in polypropylene flasks. Batches of 100 to 200 mg of ion-exchange resin and 2 to 4 ml acid solution were shaken for about 20 minutes. After centrifuging, half of the aqueous phase was measured by γ -spectroscopy. The activity of an equal amount of the genuine tracer solution was also measured. The activity of the solid phase was calculated as the difference of both activities and the K_d values were calculated using Eq. (2).

Hence, geometric effects as they would result in the direct measurement of the exchanger resin, could be avoided. No wall-adsorption effects were observed.

3.3 On-line experiments

3.3.1 Rf production and transport

^{261}Rf was produced directly in the reaction $^{248}\text{Cm}(^{18}\text{O},5n)^{261}\text{Rf}$ at the Philips Cyclotron of the Paul Scherrer Institute (PSI) Villigen, Switzerland.

The 730 $\mu\text{g}/\text{cm}^2$ ^{248}Cm target¹ was prepared by electrodeposition of $\text{Cm}(\text{NO}_3)_3$ on Be. After the plating process, the nitrate was converted into the oxide by heating. It was

¹ 871 $\mu\text{g}/\text{cm}^2$ ^{248}Cm oxide plus 96 $\mu\text{g}/\text{cm}^2$ Gd oxide of a mean mass $m_{\text{Gd}} = 155$ amu.

bombarded with average $^{18}\text{O}^{5+}$ beam intensities of $3 \cdot 10^{12} \text{ s}^{-1}$.

The 128.6 (133)² MeV ion beam passed through a 10 (12.5) μm Havar window, 4 mm N_2 cooling gas and the 12.7 μm Be backing entering the target material with a projectile energy of 100.3 (100.2) MeV, and leaving the target material with 98.7 (98.6) MeV. This corresponds to the maximum of the excitation function [9]. A production cross section of approximately 5 nb is observed in the $^{248}\text{Cm}(^{18}\text{O},5\text{n})$ reaction close to the maximum of the excitation function [10]. This results in a production rate of about 2 atoms/min under the given conditions.

The target contained 10% Gd^3 to produce simultaneously short-lived Hf isotopes that were used to monitor on-line the behaviour of Hf and to perform yield checks by γ -spectroscopy. Reaction products recoiling out of the target were stopped in He gas containing KCl aerosols generated by sublimation from solid KCl at 640 °C [8]. The aerosols together with the recoil products were transported through a steel capillary (2 mm inner diameter, length 50 m) to the automated chemistry apparatus ARCA II [11]. At a flow rate of about 2.5 l/min He, this leads to a transport yield of about 50%.

In ARCA, the He is pumped away while the KCl clusters are collected by impaction on the top slider of ARCA II [12].

3.3.2 On-line production of short-lived Hf isotopes

The short lived Hf isotopes $^{166,167,168,\dots}\text{Hf}$ were produced with the ^{18}O beam at the Philips Cyclotron at PSI in the xn-reactions using the Gd content of the Cm target or at the GSI UNILAC in the xn-reactions of ^{12}C with an enriched ^{158}Dy target. The targets were irradiated with a 100 MeV ^{18}O beam, populating mostly the 5n channel, or with a 95 MeV ^{12}C beam, respectively, populating the 4n and 5n channel (energies are corrected for the energy loss in the entrance window, cooling gas and target backing). The recoil products were collected as the Rf recoils described above.

3.4 Automated HPLC with Rf and Hf produced on-line

3.4.1 Rf experiments with the CIX

Rf and Hf were transported by a $\text{He}(\text{KCl})$ gas jet and collected for 90 s by impaction on the slider in ARCA II [11]. The deposit was dissolved in 200 μl 0.1 M HNO_3 /x M HF (x varied) and fed onto the $1.6 \times 8 \text{ mm}$ cation-exchange column⁴ at a flow rate of 1 ml/min. The column had been conditioned with 500 μl of the feeding solution. The effluent was evaporated to dryness as sample 1. In order to elute remaining Rf and Hf from the column, a second fraction of 200 μl 0.1 M HNO_3 /0.1 M HF was collected to strip all

group 4 elements from the column. This fraction was prepared as sample 2.

3.4.2 Rf experiments with the AIX

Rf and Hf were transported, collected and loaded onto the anion-exchange column⁵ as in the experiments with the CIX. Again, the effluent was evaporated to dryness as sample 1. In order to elute remaining Rf and Hf from the column, a second fraction of 200 μl 5 M HNO_3 /0.01 M HF was used. This fraction was prepared as sample 2.

3.4.3 Detection of Rf

78-s ^{261}Rf was detected by α -spectroscopy using sixteen 450 mm–2 passivated implanted planar silicon (PIPS) detectors. At a given cycle time of 90 s and the possibility to measure 8 pairs of samples, the counting time for each sample was 12 min. List mode data were stored for each α decay, including energy, detector number and time after start of the measurement. The α -energy resolution was about 30 keV for α -particles between 5 and 10 MeV.

The detection efficiency for an α particle was 30% thus being 9% for $\alpha\alpha$ correlations detecting both the decay of ^{261}Rf and its daughter ^{257}No . These efficiencies lead to an expected ratio of 4.67:1 between α singles and $\alpha\alpha$ correlations⁶.

In the Rf experiments, every 8th pair of samples was additionally monitored by γ -spectroscopy to determine the distribution of Hf and its chemical yield.

The K_d values were calculated using Eq. (2) such that the activity of sample 1 was attributed to the aqueous phase, the activity of sample 2 was attributed to the solid phase. The amount of exchange resin (6.6 mg) was determined from the average weight of 20 used columns. The number of α counts in fraction 2 was corrected for the decay occurring between the elution of fraction 1 and 2. The effluent volume was corrected for the dead volume of ARCA (35 μl).

In the AIX chemistry, the cations are expected to run through the column. Therefore, the ^{261}Rf daughter ^{257}No formed during the collection time before the chemical separation (“primordial No”) has to be taken into account. (The distribution of No formed after the chemical separation is characteristic of the behaviour of its mother nuclide Rf).

As can be calculated from the equations of radioactive decay and growth, the contribution of the “primordial No” activity to the measured α -singles is 4.6%. The distribution of these No events between the two fractions was assumed to be modeled by the behaviour of the actinide Fm represented by the 6.9 to 7.2 MeV group in the α -particle spectra⁷.

² The values given in parenthesis refer to the conditions when a thicker Havar window was chosen.

³ Isotopic composition 26.2% ^{152}Gd , 9.8% ^{154}Gd , 22.3% ^{155}Gd , 16.5% ^{156}Gd , 8.3% ^{157}Gd , 10.2% ^{158}Gd , 6.7% ^{160}Gd .

⁴ BioRad Aminex A6 in the H^+ form, an exchange resin of the AG50WX8 type, produced especially for HPLC with a particle size of $17.5 \pm 2 \mu\text{m}$.

⁵ Riedel-de Haën in the chloride form, an ion-exchange resin similar to the BioRad AG1X8 type, produced especially for HPLC with a particle size of $26 \pm 6 \mu\text{m}$.

⁶ 100 Rf decays cause 60 measured events, i.e. 9 correlations, 21 decays missing the daughter decay and 21 events missing the mother decay, assuming a time window open infinitely long.

⁷ It should be noticed that the effective correction for the “primordial” No becomes almost negligible if the K_d values are relatively low.

Fig. 1. Sorption of Zr, Hf and Th (in batch experiments) on the CIX resin (Aminex A6) in 0.1 M HNO_3 at various HF concentrations. The lines are tanh functions fitted to the data points.

Fig. 2. Sorption of Hf (produced on-line) on the CIX resin (Aminex A6) in 0.1 M HNO_3 at various HF concentrations. The lines are tanh functions fitted to the off-line data points (shown in Fig. 1).

4. Results

4.1 Tracer experiments

4.1.1 Behaviour of Zr, Hf and Th on the CIX

The results of the batch tracer experiments on the CIX are given in Fig. 1. In 0.1 M HNO_3 , all elements stick to the cation-exchange resin at HF concentrations $< 10^{-3}$ M, indicating that, at low HF concentrations, cationic species are formed and are held back very strongly on the resin with $\log(K_d)$ values > 3 . In a concentration range between 10^{-3} M $< [\text{HF}] < 10^{-2}$ M, the K_d values of the group 4 elements decrease. At these concentrations, neutral or anionic fluoride complexes may be formed. The behaviour of Zr and Hf is very similar (Hf sticking to the resin even at slightly higher HF concentrations). This is in agreement with the known general similarities of these elements. The elution of Th from the column is observed at about 1 order of magnitude higher HF concentrations.

The data taken for Hf on-line (short lived isotopes measured with ARCA) are in full agreement with the off-line (batch) data (Fig. 2), indicating that at the flow rate

Fig. 3. Sorption of Zr, Hf and Th (in batch experiments) on the AIX resin (Riedel-de Haën) in 0.1 M HNO_3 at various HF concentrations. The lines are tanh functions fitted to the data points.

Fig. 4. Sorption of Hf (produced on-line) on the AIX resin (Riedel-de Haën) in 0.1 M HNO_3 at various HF concentrations. The lines are tanh functions fitted to the off-line data points (shown in Fig. 3).

of 1 ml/min equilibrium is reached in the column experiments.

4.1.2 Behaviour of Zr, Hf and Th on the AIX

The results of the tracer experiments on the AIX are given in Fig. 3. As is expected, at low HF concentrations, all elements are running through the column. In a concentration range of about 10^{-3} M $< [\text{HF}] < 10^{-2}$ M, the K_d values of Zr and Hf rise simultaneously, i.e. in the same range as they decrease on the CIX. This shows clearly, that the disappearance of the cationic species at low HF concentrations is followed immediately by the formation of anionic complexes.

For Th, no anionic species are known. This results in the neutral ThF_4 being the final compound. Hence Th is eluted from the AIX at all HF concentrations. The scattering of the Th data in the high HF concentration range might be attributed to the usage of non-carrier free Th. The data taken for Hf on-line (measured with ARCA) are consistent with the off-line (batch) data (Fig. 4), indicating that at the flow rate of 1 ml/min equilibrium is reached in the column experiments.

Fig. 5. Sorption of Zr, Hf, Th, and Rf on the CIX resin (Aminex A6) in 0.1 M HNO_3 at various HF concentrations. The data points of Hf and Rf are taken from the on-line experiments. The lines are *tanh* functions fitted to the off-line data points. The different error bars are described in the text.

4.2 Rutherfordium experiments

In more than 3000 experiments 92 single events and 18 correlations were detected in the E_α window between 8.1 and 8.5 MeV that could be attributed to the decay of ^{261}Rf and/or the decay of its daughter ^{259}No . From the 61 single events in the AIX chemistry, 3 are considered to be decays of “primordial” No. This results in an overall single/correlation ratio of 4.9:1. Thus within the statistical error, this number is in full agreement with the expected ratio of 4.67:1 determined by the detector geometry (see above).

4.2.1 Behaviour of Rf on the CIX

The results of the on-line experiments with the CIX are given in Fig. 5. It was shown experimentally that ^{261}Rf is not eluted from the CIX column under the conditions of the previously performed Sg experiment and can only appear in the Sg sample as a result of the decay of ^{265}Sg . The measured K_d (Rf) was >148 at $5 \cdot 10^{-4}$ M HF. Further, the distribution coefficient of ^{261}Rf on a cation exchange resin at a higher HF concentration (0.1 M HNO_3 /0.01 M HF) was studied. At this concentration, despite Zr and Hf being eluted, Rf is still retained on the column (Fig. 5). The K_d (Rf) is >312 at 10^{-2} M HF.

These K_d values are lower limits, because no Rf events were detected in fraction 1. In order to define these lower limits, a Monte Carlo simulation was performed to calculate which number of events would be in agreement with a measured number of 0 at a significance level of 90 %. There is no reason why the K_d at higher HF concentrations should be higher than at $5 \cdot 10^{-4}$ M HF, so it could be concluded that the K_d at any concentration <0.01 M HF should be >312 . The $\log(K_d \text{ (Rf)})$ in the strip fraction (0.1 M HF) was fixed at 0 assuming that the behaviour of Rf is the same as that of Zr and Hf at this concentration. The number of measured events is in agreement with the number of expected events calculated from the known cross section.

The different behaviour of Rf as compared to that of Zr and Hf was felt to deserve further investigation. Therefore, the K_d values of Rf at HF concentrations of 0.03 M and

Fig. 6. Sorption of Zr, Hf, Th, and Rf on the AIX resin (Riedel-de Haën) in 0.1 M HNO_3 at various HF concentrations. The data points of Hf and Rf are taken from the on-line experiments. The lines are *tanh* functions fitted to the off-line data points.

Fig. 7. Evidence for the existence of negatively charged Rf Fluoride complexes in 0.05 M HF. Hf and Rf data points are taken from on-line experiments.

0.05 M (both in 0.1 M HNO_3) were determined in order to establish at which concentration the K_d decreases indicating that neutral or anionic complexes of Rf are being formed (Fig. 5). On the CIX, the decrease of the K_d values for Rf occurs between 0.01 M and 0.1 M HF, i.e. at one order of magnitude higher HF concentrations than for Zr and Hf. Under the given conditions, Rf seems to resemble rather its pseudo-homolog Th than its group members Zr and Hf.

4.2.2 Behaviour of Rf on the AIX

The results of the on-line experiments with the AIX are given in Fig. 6. It was expected that Rf would form anionic complexes at high HF concentrations resulting in high K_d values, while Th, which does not form anionic fluoride complexes, should have low K_d values. To our surprise, the data show that Rf behaves differently from Zr and Hf and that it seems to resemble Th also on the AIX. Even for 1 M HF which is about 2 orders of magnitude higher than the concentration from whereon maximum K_d values are observed for Zr and Hf, there is no indication of a rise of the K_d value for Rf.

Table 1. Concentrations of different species in HNO₃/HF media calculated from pK_s (HF) = 2.85.

[HNO ₃]	[HF] ₀	[F ⁻]	[H ⁺]	[HF]
0.1	0.03	0.00021	0.1002	0.0298
0.1	0.05	0.00035	0.1003	0.0497
0.1	0.1	0.0007	0.1007	0.0993
0.1	0.3	0.0021	0.1021	0.30
0.1	0.5	0.0034	0.1034	0.50
0.1	1.0	0.0067	0.1067	0.99
0.01	0.03	0.0016	0.0116	0.0284
0.01	0.05	0.0026	0.0126	0.0474
0.01	0.1	0.0048	0.0148	0.0952
0.01	0.3	0.012	0.0216	0.29
0.01	0.5	0.017	0.0269	0.48
0.01	1.0	0.027	0.0372	0.97

Table 2. Ionic radii of Zr, Hf, Rf and Th.

Ion	Zr ⁴⁺	Hf ⁴⁺	Rf ⁴⁺	Th ⁴⁺
Ionic radius, (Å)	0.72 ^a	0.71 ^a	0.79 ^b	1.08 ^b

a: [14]; b: [15].

As it would be in contradiction to the results of Refs. [5–7] that there are no anionic fluoride complexes formed for Rf at any HF concentration, the concentration of HNO₃ with NO₃⁻ serving as a counter ion competing for the binding sites on the anion-exchange resin was varied from 0.1 to 0.01 at a constant HF concentration of 0.05 M in an additional experiment. By plotting $\log(K_d)$ vs. $\log(c(\text{NO}_3^-))$ one expects to obtain a linear relation with a slope corresponding to the charge of the complex [13].

As is shown in Fig. 7, in this experiment, qualitative evidence for negatively charged complexes of Hf and Rf was observed as in both cases, the K_d value rises with decreasing NO₃⁻ concentration. Due to the large uncertainties, the ionic charge state cannot be determined unambiguously from the present data. One might argue that the analysis of $\log(K_d)$ vs. $\log(c(\text{NO}_3^-))$ must be done at a constant free fluoride concentration rather than at constant HF concentration. According to Table 1, the same F⁻ concentration as in 0.01 M HNO₃/0.05 M HF is present in 0.1 M HNO₃ if the HF concentration is chosen between 0.3 M and 0.5 M HF. As the K_d values for Rf in 0.1 M HNO₃ are all the same for HF concentrations between 0.01 M and 1 M within the uncertainties, a figure literally indistinguishable from Fig. 7 would result if a constant F⁻ concentration were chosen as the condition. Fig. 7 gives the hint that it is the action of the counter ion NO₃⁻ which is responsible for the different behavior of Rf as compared to Zr and Hf.

5. Discussion

We have observed properties of Rf in 0.1 M HNO₃ in the presence of variable HF concentrations that deviate significantly from those of its homologs Zr and Hf and resemble those of Th.

On the CIX columns, the K_d values for Zr and Hf decrease between 10⁻³ and 10⁻² M HF due to the formation

of fluoride complexes. For Rf and Th, this decrease occurs at one order of magnitude higher HF concentrations. A qualitative interpretation from the HSAB point of view is possible by using the ionic radii contained in Table 2. The radii of Zr⁴⁺ and Hf⁴⁺ are very similar due to the lanthanide contraction resulting in a similar complexation behaviour. As the hardness as electron acceptors correlates with the size of the ions it will decrease in the order Zr⁴⁺ ≈ Hf⁴⁺ > Rf⁴⁺ > Th⁴⁺. The fluoride anion is a hard anion and interacts stronger with small (hard) cations. From this, one would expect a weaker fluoride complexation of Rf as compared to Zr and Hf as experimentally observed. However, the apparent coincidence of the Rf K_d values with those of Th is unexpected.

On the AIX columns, the absence of a rise of the K_d values of Rf is even more surprising, and a theoretical explanation is not at hand at this time. Very informative was the variation of the concentration of the counter ion NO₃⁻ which gave the hint that, at the F⁻ concentration of about 3 · 10⁻³ M, Rf does form anionic fluoride complexes, however, the competition of the counter ion NO₃⁻ for the binding sites on the anion-exchange resin seems to be more effective with respect to the Rf complex than with respect to the Zr and Hf complexes.

To shed more light on the remaining open questions, additional experiments are necessary in which i) the NO₃⁻ concentration is varied systematically at a given fluoride concentration and ii) the fluoride concentration is varied systematically at a significantly lower NO₃⁻ concentration (e.g. 0.01 M HNO₃) than in the present work.

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