Chromatographic Study of Rutherfordium (Element 104) in the System HCl/Tributylphosphate (TBP)

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Summary

Liquid-liquid extractions of ^{95}Zr and ^{175}Hf from various concentrations of HCl were conducted using tributylphosphate (TBP) in toluene (benzene), and undiluted TBP. Quantitative extraction of both Zr and Hf into TBP in toluene (benzene) was observed from ≥ 8 M HCl and into undiluted TBP from ≥ 10 M HCl. Extraction from 8 M HCl into undiluted TBP was 80% for Zr and 20% for Hf. Based on these results, a chromatographic separation of Hf from Zr with the Automated Rapid Chemistry Apparatus ARCA II was performed on 1.6×8 mm columns containing undiluted TBP on an inert support. This separation was also studied on-line with short-lived ^{169}Hf produced in the Gd(^{18}O,xn) reaction and with 78-s ^{261}Rf produced in the ^{248}Cm(^{18}O,5n) reaction at the Philips Cyclotron of the Paul Scherrer Institute. From the distribution of α-decays of ^{261}Rf between the Hf- and Zr-fraction, the K_d-value for Rf in 8 M HCl was determined, and the following extraction trend was established: Zr > Rf > Hf. This is at variance with earlier results where Rf seemingly did not extract as well as Hf which was tentatively attributed to increased hydrolysis of Rf.

1. Introduction

Tributylphosphate (TBP) is one of the most important organic extractants. It is widely used to separate U and Pu from spent nuclear fuel [1, 2] and to separate various actinides and lanthanides from reprocessing wastes [3]. The phosphoryl oxygen coordinates with the metal ion forming an adduct:

$$M^{z+} + z\,A^- + x\,TBP \rightarrow MA_z \cdot x\,TBP_{org} \qquad (1)$$
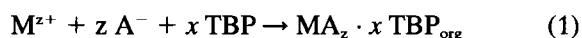
where M^{z+} is the metal ion and A^- is the deprotonated form of the acid. TBP always extracts the metal in the form of a neutral species. The distribution coefficient, K_d, is defined as the ratio of the concentration of the metal in the organic phase to the metal concentration in the aqueous phase at equilibrium. Because of aggregation of the TBP, K_d values for undiluted TBP are found to be relatively lower than for TBP diluted by an organic solvent which was recognized in the development of the PUREX process [4].

Early experiments on the aqueous chemistry of element 104, rutherfordium, Rf, showed that its chemical properties are analogous to those of the group 4 elements Zr and Hf [5, 6] and that a new transition element series filling the $6d$ shell starts with Rf. Silva *et al.* [5] demonstrated this by eluting Rf from cation-exchange columns with 0.1 M α-hydroxyisobutyrate at pH = 4.0 within the first few column volumes while trace quantities of the 3^+ actinide ions did not elute in over 100 column volumes. Hulet *et al.* [6] used the known chloride complexing of the group 4 elements to extract Rf anionic chlorides from 12 M HCl into columns loaded with trioctylmethylammonium chloride, i.e. under conditions where the actinides are not appreciably extracted. Zr, Hf, and Rf were subsequently eluted in 6 M HCl, in which anionic chloride complexation of the group-4 elements is less favored.

More recently, Czerwinski *et al.* [7] corroborated the anionic chloride complexation of Rf in 12 M HCl by liquid-liquid extractions into 0.1 M triisooctylamine in benzene. They also performed a series of liquid-liquid extractions with TBP/benzene [8] to study the effects of HCl-, chloride-, and hydrogen-ion concentration between 8 and 12 M on the extraction of Zr^{4+}, Hf^{4+}, Th^{4+}, Pu^{4+}, and Rf^{4+}. It was found that Rf extraction increases as a function of HCl concentration and that the extraction of Rf is between that of Zr and Hf. In experiments in which the chloride and hydrogen ion were varied, Rf extraction differed from that of the group-4 elements and behaved more like Pu^{4+} [8].

Recently, Bilewicz *et al.* [9] studied the sorption of Zr, Hf, Th, and Rf on cobalt ferrocyanide surfaces and interpreted the results such that the hydrolysis trend in these elements decreases in the order Rf >

Zr = Hf > Th. This is in contradiction with expectations based on the simple ionic model of hydrolysis, for details see Sect. 4. This unexpected trend was attributed [9] to relativistic effects in Rf which split the $6d$ orbitals into two $6\,d_{3/2}$ orbitals and three strongly destabilized $6d_{5/2}$ orbitals. The destabilization of the $6d_{5/2}$ orbitals was believed to cause the promotion energy involving $7s$, $7p$, and $6d_{5/2}$ orbitals to be too high for sp^3d^4 hybridization. This was believed [9] to give Rf a coordination number of 6 rather than 8 in aqueous solutions because 6-coordination requires only $6d_{3/2}$ orbitals while 8-coordination also requires the $6d_{5/2}$ orbitals. A coordination number of 6 would result in a larger hydrolysis constant than otherwise expected. We shall argue against this interpretation in the discussion. Kacher et al. [10] performed some additional chloride extractions into TBP/benzene with Zr, Hf, and Ti. The reported low extraction yields of Hf by Czerwinski et al. [8] could not be reproduced by Kacher et al. [10] who reported that they observed that significant amounts of Hf (more than 50% in some cases) stick to teflon surfaces. (They actually conducted their subsequent experiments with polypropylene equipment because only negligible absorption was observed with polypropylene surfaces.) The Hf results from the Czerwinski et al. experiments [8] were based on on-line data taken at the Cyclotron where the activity was collected on teflon discs which, according to [10], accounts for the seemingly low extraction. Surprisingly, a similar loss due to absorption of Rf in the Czerwinski et al. work [8] was not suspected by Kacher et al., and so the latter authors, based on their new Zr-, Hf-, and Ti-results and on the old [8] Rf results, suggested a revised sequence of extraction into TBP/benzene from around 8 M HCl as Zr > Hf > Rf > Ti. In a parallel study of liquid-liquid extractions of these elements into TBP/benzene from HBr solutions, extraction of Rf was found to be low and was only observed when LiBr was added to increase the bromide concentration beyond 9 M [10]. The extraction behaviour of the group-4 elements into TBP from both HCl and HBr solutions was primarily attributed to their different tendencies to hydrolyze [10].

In hydrofluoric acid solutions, on-line chromatographic studies by Szeglowski et al. [11] indicated that Rf forms anionic fluoride complexes which sorb on anion-exchange columns. Kacher et al. [12] found extraction of Rf into triisooctylamine/xylene from 0.5 M HF and claimed that the extractability in this system decreases in the order Ti > Zr = Hf > Rf in inverse order of the decrease in ionic radii.

The present study of Rf extraction into TBP from HCl solutions was performed in view of the somewhat unsatisfactory situation with the conflicting Hf results in [8, 10] and with the intention to establish an independent set of data characterizing the extraction sequence of Zr, Hf, and Rf at 8 M HCl. This particular concentration was chosen because, as will be enlarged below, the largest differences in extraction between Zr and Hf are observed here, so that a chromatographic

separation of Zr and Hf appeared to be feasible which would allow us to determine the centroid of the elution position of Rf relative to that of Zr and Hf.

2. Experimental

A. Materials

The TBP and other chemicals were purchased from Merck and used as received. Their purity was analytical grade (p.a.). Voltalef™ powder from Lehmann & Voss, Hamburg, was used as inert support for the TBP column material. A range of particle sizes between 30 and 80 μm was selected by sieving. These particles were coated with TBP, weight ratio Voltalef/TBP 5:1, by immersing the Voltalef in a solution of the TBP in cyclohexane and by removing the cyclohexane by evaporation under stirring.

B. Tracer solutions

The isotopes ^{95}Zr and ^{175}Hf were used as tracers. Carrier free ^{95}Zr was purchased from CIS Diagnostik GmbH, Dreieich, and was delivered in 0.5 M oxalic acid. This solution was evaporated to dryness in the presence of H_2O_2 and HCl several times to destroy the oxalic acid. It was then stored in 12 M HCl in a polypropylene flask. ^{175}Hf was obtained as decay product of ^{175}W that was produced by 68 MeV α-particle bombardment of a stack of thin Hf targets on 1.5 μm Al backings at the Cyclotron of the Forschungszentrum Karlsruhe. The Al backings containing the reaction products were dissolved in conc. HCl and the Al was removed on an anion-exchange column (Dowex 1x8, 200 mesh). The ^{175}Hf was eluted in 7 M HCl, evaporated to dryness, dissolved in 12 M HCl, and stored in a polypropylene flask.

C. Isotopes produced on-line

1. ^{261}Rf production

The isotope ^{261}Rf ($t_{1/2}$ = 78 s [13]) was produced via the ^{248}Cm (^{18}O, 5n) reaction at the Philips Cyclotron of the Paul Scherrer Institut, Villigen. The beam energy on target was 101 MeV and the $^{18}O^{5+}$ beam intensity varied between 0.8 and 2.0 μA (electrical). The target material, Cm_2O_3, isotopic composition 95.7% ^{248}Cm, and 4.2% ^{246}Cm, was prepared by electrodeposition of $Cm(NO_3)_3$ in isopropanol on a 2.34 mg/cm^2 Be foil by electrodeposition and by converting the nitrate to the oxide by heating the target to 600°C. The target thickness was determined by α-particle counting to be 450 μg/cm^2 of ^{248}Cm. The products of the ^{18}O bombardment were transported to the chemistry apparatus by a helium KCl gas-jet transportation system at a flow rate of 1.6 l/min.

2. ^{169}Hf production

The isotope ^{169}Hf ($t_{1/2}$ = 3.25 min) was produced via the Gd(^{18}O,xn) reaction at the Philips cyclotron using

the same beam energy as above. The target material, Gd_2O_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, was prepared by electrodeposition as above. [169]Hf was transported to the chemistry apparatus by the same gas-jet transportation system for on-line tracer experiments under identical conditions as in the rutherfordium experiments. The [169]Hf also served to determine the gas-jet transportation yield by implanting it into a Au catcher foil placed directly behind the target and comparing its gamma activity with that at the collection site. The transport yield was 36%.

3. [98]Zr production

[98]Zr ($t_{1/2}$ = 30.7 s) was produced at the Mainz TRIGA reactor by thermal neutron induced fission of [235]U. The 787 keV gamma radiation of the daughter [98g]Nb ($t_{1/2}$ = 2,9 s) was detected which decays in transient equilibrium with [98]Zr. [98]Zr was transported to the chemistry apparatus by a gas-jet transportation system and studied under identical conditions as in the rutherfordium experiments.

D. Radiation detection

Gamma-emitting isotopes were assayed using a high-purity Ge spectrometer system. α-emitting [261]Rf was assayed with passivated ion-implanted planar silicon (PIPS) detectors calibrated with a [212]Pb source milked from [228]Th. The detection efficiency for α-particles was 33%. The time, channel number, and detector number of each incoming event was stored by a list processor driven by the GOOSY data acquisition and analysis software.

E. [95]Zr and [175]Hf liquid-liquid extractions

Liquid-liquid extractions of the Zr and Hf tracers were performed with TBP in toluene (benzene) in the volume ratio 1:1 (1.8 M) with HCl concentrations ranging from 1 to 12 M. 2 ml of the organic phase were contacted with 2 ml aqueous phase containing the tracer activity by shaking for 1 min in polypropylene tubes. Subsequently, 1 ml of the aqueous and 1 ml of the organic phase were removed and counted for activity. From the counts of the organic phase and the aqueous phase the K_d or the percent extraction were obtained. It was verified that the sum of the counts was consistent with the initial activity. In order to study extractions of the tracers into undiluted TBP, 43 mg of the TBP/Voltalef (1:5) powder (7.39 μl of pure TBP) was contacted with 2 ml of the aqueous phase by shaking for 1 min. Here, a 1 ml aliquot of the aqueous phase was counted to determine the K_d which was calculated by taking the ratio of final activity over the initial activity.

F. Extraction chromatography

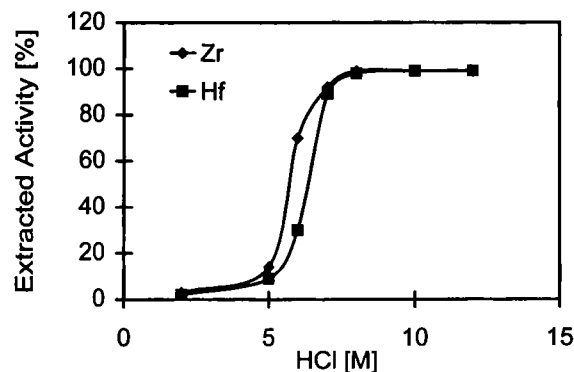Reversed-phase extraction chromatography was performed on 1.6 × 8 mm columns packed with TBP/Vol-

Fig. 1. Percent extraction of Zr and Hf ([95]Zr and [175]Hf) from HCl solutions into TBP/toluene (1:1).

talef (1:5) in the automated HPLC apparatus ARCA II [14]. The flow rate of the aqueous phase was 1 ml/min. The columns were perconditioned with 200 μl of 12 M HCl. Originally, the tracers [95]Zr and [175]Hf were fed onto the column in 180 μl 12 M HCl from a sample loop. In subsequent on-line experiments with [98]Zr at the TRIGA reactor and with [169]Hf and [261]Rf at the Philips cyclotron, the activity was deposited in ARCA II with the KCl aerosol by impaction, dissolved and fed onto the column in 167 μl 12 M HCl. This was followed by the elution of a Hf- and a Zr-fraction in 200 μl of 8 M HCl and 167 μl of 2 M HCl, respectively. These fractions were evaporated to dryness on Ta discs and assayed for gamma or α-activity.

3. Results

Our liquid-liquid extraction data for [95]Zr and [175]Hf from HCl solutions into TBP/toluene (1:1) are shown in Fig. 1. In contrast to the data by Czerwinski et al. [8], we find that Hf, like Zr, is completely extracted from ≥ 8 M HCl. As Czerwinski et al. used TBP/benzene for their extractions, we checked the extraction data for [95]Zr and [175]Hf also with TBP/benzene (1:1) from 8 M HCl; these data are indistinguishable from the TBP/toluene data for 8 M HCl in Fig. 1. Our data qualitatively corroborate the results by Kacher et al. [10], who report about 85% extraction of Hf and nearly complete extraction of Zr from 7.5 M HCl into 0.35 M TBP/benzene. The Hf data by Czerwinski et al. [8] are obviously falsified by absorption.

As our goal was to use undiluted TBP/Voltalef for the chromatographic study of the sequence of extraction of Zr, Hf, and Rf, we also determined the percentage extraction and the K_d-values of Zr and Hf with undiluted TBP/Voltalef (1:5) in batch experiments, see Fig. 2. As compared to the TBP/toluene (benzene) data, nearly complete extraction of both Zr and Hf is shifted to higher HCl molarities as expected, i.e. to ≥ 10 M HCl, and there is a large difference in the percentage extraction of Zr (80%) and Hf (20%) at 8 M HCl which might give a chance for a chromatographic separation of Zr and Hf.
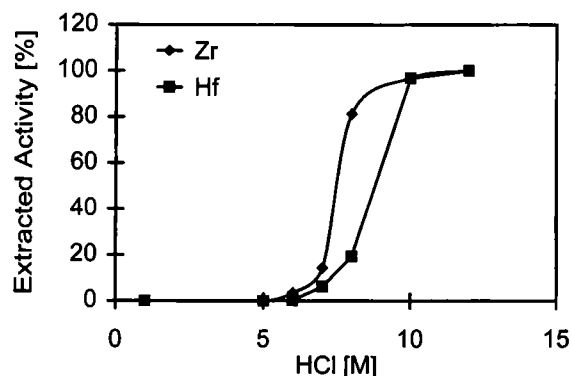
Fig. 2. Percent extraction of Zr and Hf (^{95}Zr and ^{175}Hf) from HCl solutions into undiluted TBP/Voltalef (1:5).

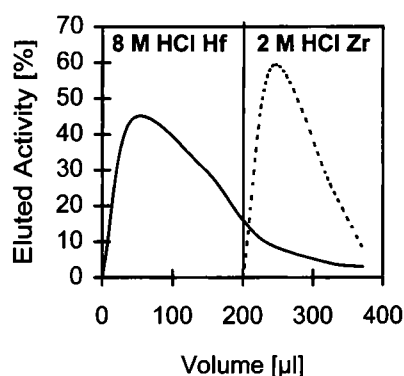**Fig. 3.** Elution curves for ^{169}Hf (8 M HCl) and ^{98}Zr (2 M HCl) from 1.6×8 mm columns filled with TBP/Voltalef (1:5) measured in ARCA II under identical conditions as in the Rf experiments, i.e. the activities were produced on-line and transported to ARCA II by a He/KCl jet, dissolved and fed onto the column in 167 μl 12 M HCl.

Table 1. Correlated ^{261}Rf-^{257}No mother-daughter α-decays

Hf-fraction (8 M HCl)			
$E(\alpha_1)$/MeV	$t(\alpha_1)$/s[a]	$E(\alpha_2)$/MeV	$t(\alpha_2)$/s[b]
8.07	98.9	8.24	10.4
8.22	57.5	8.02	47.1
Zr-fraction (2 M HCl)			
8.13	71.8	8.12	58.0
8.12	14.8	8.12	61.1
8.23	76.8	8.23	25.0

[a] After begin of counting.
[b] After mother decay.

Chromatographic separations of Zr and Hf on TBP/Voltalef columns of 1.6×8 mm in ARCA II were studied in 7.5, 7.7, and 8.0 M HCl after feeding of ^{95}Zr and ^{175}Hf onto the column in 12 M HCl. The best separation was achieved by eluting the Hf in 8.0 M HCl followed by stripping the Zr in 2 M HCl. The elution curves measured with short-lived ^{169}Hf and ^{98}Zr under conditions that were identical to those in the Rf experiments are shown in Fig. 3. In 200 μl of 8 M HCl, 75% of Hf and no Zr are eluted. The following elution in 200 μl of 2 M HCl was almost complete for Zr (93%) and removed the remainder of the Hf from the column. The 75% elution of Hf in 200 μl of 8 M HCl is the expected result according to the relation

$$K_d = \left\{ \frac{100}{\%\text{aq}} - 1 \right\} \frac{V_{\text{aq}}}{V_{\text{org}}} \qquad (2)$$

where %aq is the percentage of activity eluted into the aqueous phase (75±5%), V_{aq} is the volume of the aqueous phase (200 μl minus 35 μl which is the void volume in ARCA including the free column volume [14]), and V_{org} is the volume of the organic phase (1.03 μl). According to Eq. (2), the resulting $K_d = 53^{+15}_{-13}$. This is consistent with the K_d determined

in batch experiments for Hf in 8 M HCl which is 64^{+9}_{-8}. It was the goal of the subsequent Rf experiments to determine the K_d for Rf in 8 M HCl in the same way, i.e. from the number of ^{261}Rf α-decays in the Hf- and the Zr-fraction.

1140 experiments were conducted with ^{261}Rf in ARCA II. The collection time of the aerosol was 90 s. Because of the risk of absorption of group-4 elements on fluoride containing material [10] a titanium slider was used to collect the activity in 798 of the experiments. As some Ti was dissolved by the HCl, the resulting evaporated samples for α-spectroscopy were not ideally weightless resulting in an α-energy resolution of 100 keV. In the subsequent 342 experiments, the Ti slider was replaced by a Kel-F slider. Apparently, this did not reduce (by absorption) the rate at which ^{261}Rf was observed. Due to the resolution of 100 keV in the majority of the experiments, a window of α-energies from 8.0 to 8.65 MeV was used to search for α-decays of ^{261}Rf (8.29 MeV) and its daughter ^{257}No (8.22, 8.27, 8.32 MeV) and for time-correlated pairs of mother-daughter decays. The upper end of the energy window, 8.65 MeV, was selected because of the recent observation of another decay branch of ^{261}Rf at 8.52 MeV [15]. The counting time for each sample was 6 min.

5 αα-mother daughter correlations in the above mentioned energy window were registered, see Table 1. The fact that they are observed both in the Hf-fraction (2) and in the Zr-fraction (3) points to the fact that Rf extraction from 8 M HCl is somewhere between that of Hf and Zr.

In order to determine the probability for random correlations, the total number of α-decays in the considered energy window, 20 in the Hf-fraction and 16 in the Zr-fraction, have to be considered and their time distribution has to be randomly redistributed by a Monte-Carlo method. In the Hf fraction, the number of random correlations predicted in 10000 simulations is 0.15, which means that the probability for the two observed correlations to be random is 1.0%. In the Zr-fraction, the predicted number of random correlations is 0.08 and the resulting probability for the three observed correlations to be random is 0.008%. Thus, the
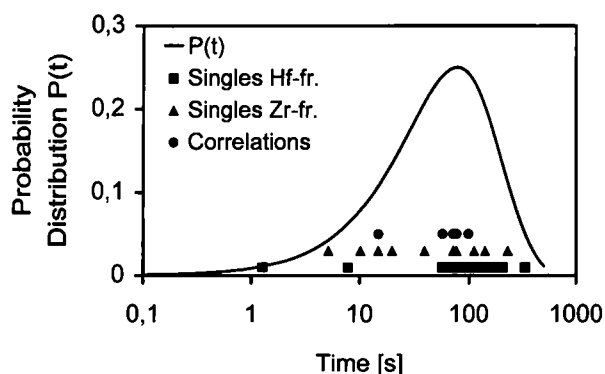
Fig. 4. Time distribution of the α-decays of ^{261}Rf/^{257}No. The solid line is the probability distribution for $t_{1/2} = 78$ s.
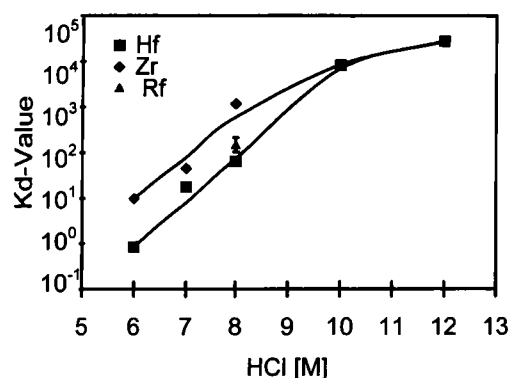

Fig. 5. K_d-values of Zr and Hf in the system undiluted TBP/ Voltalef-HCl (same experimental data as in Fig. 2) with the K_d for Rf at 8 M HCl.

observed correlations of ^{261}Rf- and ^{257}No-decays are likely to be true correlations. The half-life of 28 s resulting from the ^{257}No decay times in Table 1 is in good agreement with the accepted value of 26 s. The time distribution of the singles and correlated events is shown in Fig. 4 together with the probability distribution for α-decays of ^{261}Rf with a half-life of 78 s [13]. The fact that some of the decays are due to the daughter, 26-s ^{257}No, i.e. occur with a certain delay, is ignored in this representation of the data.

Before the number of ^{261}Rf- and ^{257}No-decays in the Hf- and Zr-fraction can be used to calculate the K_d for Rf, a careful consideration of background is in order. The background in the considered energy window from cosmic rays, electronic noise, etc., was determined in long counting intervals before and after the Rf experiment as 7.1 events in all detectors during the complete counting time of 1140×6 min. The number of decays of ^{211m}Po at 8.305 MeV (0.25%) was determined from the α-line of ^{211m}Po at 7.28 MeV (91%) which consisted of 27 events in the sum spectrum of all samples. This adds 0.074 events to the background. Thus, a total of 7.17 background events distributed over all samples, i.e. 3.59 for both the Hf- and the Zr-fraction have to be subtracted. This results in $20 - 3.59 = 16.41$ events for the Hf-fraction and $16 - 3.59 = 12.41$ events in the Zr-fraction. The latter number has to be further corrected because the start of counting of the Zr-fraction was 24 s later than the start of counting of the Hf-fraction. With a half-life of 78 s for ^{261}Rf taken into account, this increases the number of events in the Zr-fraction to 15.36. With these numbers, we arrive at the conclusion that $51.7 + -8.9\%$ of the Rf was eluted into the Hf-fraction in $(200 - 35 = 165)$ μl 8 M HCl. With Eq. (2), this gives a K_d-value of 150^{+64}_{-46}. This value shows that Rf extraction into TBP is larger than that of Hf and we obtain the extraction sequence Zr > Rf > Hf, see Fig. 5, with the K_d-values 1180, 150, and 64 for Zr, Rf, and Hf, respectively.

If one looks at the percentage of extraction in the work of Czerwinski et al. [8] which is ~60% for Rf and ~25% for Hf, and the percentage extraction in the present work, ~52% for Rf and ~25% for Hf, the

data, at first sight seem to be consistent. However, one has to consider the extremely different ratios of volumes of the aqueous and organic phase used in [8] (10 μl : 20 μl) and in the present work (165 μl : 1.03 μl), to realize that significant differences exist: With Eq. (2), K_d-values for Rf and Hf resulting from the data in [8] results as ~0.75 and ~0.17, respectively. In order to compare these with our data the dependence of the equilibrium constant of Eq. (1) on the TBP concentration in the organic phase needs to be taken into account. For $x = 2$ in Eq. (1), one obtains a ratio of distribution coefficients

$$\frac{K_{d1}}{K_{d2}} = \frac{[\text{TBP}]_1^2}{[\text{TBP}]_2^2} \tag{3}$$

for two different experiments using different TBP concentrations. The TBP concentration in [8] was 0.25 M; for our liquid-liquid extraction data in Fig. 1 the TBP concentration was 1.8 M. Thus, the K_{d1} (0.25 M) = 0.17 for Hf in 8 M HCl in [8] translates into an expected K_{d2} (1.8 M) = 8.8 in our work, while the measured value is 49, i.e. different by a factor of ~6. This means that the K_d-value in 8 M HCl for Hf and most probably also that for Rf in [8] are significantly too low.

The K_d-value of 49 in 8 M HCl for Hf in our liquid-liquid extraction data could be used to predict the K_d-value in 8 M HCl for Hf for undiluted TBP which is 3.65 M. Using the same second-order dependence on TBP concentration as in Eq. (3), we expect a K_d-value of 201 for undiluted TBP, while the measured value is 64. This indicates that the K_d-values in undiluted TBP are relatively low because of aggregation effects as mentioned in the introduction.

4. Discussion

The newly established K_d-values and extraction sequence of the group-4 elements into TBP, Zr > Rf > Hf, is at variance with earlier results and conclusions concerning Hf and Rf extraction into TBP [8, 10]. Apparently, both the original Hf and the Rf results [8] were falsified by losses due to absorption of these ele-

ments on teflon surfaces. This remained unobserved as only one phase, the TBP phase, was assayed for the decay of ^{169}Hf and ^{261}Rf. In the present chromatographic experiment, the distribution of the group-4 elements between TBP and 8 M HCl was studied by determining the amount of activity in the 8 M HCl phase and by stripping the remainder of the activity from the organic phase with 2 M HCl. This ensures complete recovery of the activity and results in reliable K_d-values. The present work shows that Rf behaves intermediate between Hf and Zr near the threshold in HCl molarity where extraction of Hf and Zr increases steeply, i.e. around 8 M HCl. It is probably extracted as $RfCl_4 \cdot 2$ TBP.

The conclusion in [10], i.e. Rf (like Ti) does not extract as well as Zr and Hf because it hydrolyses more easily than Zr and Hf, cannot be maintained.

Also, the statement in [10] that "these results tend to confirm the results" of the experiments on sorption of Zr, Hf, and Rf on cobalt ferrocyanide surfaces [9] is misleading as it relies on data [8] which are outrun. Furthermore, the above statement obviously mixes two independent processes: "hydrolysis of cations" and "hydrolysis of complexes". In 6–12 M HCl, the distribution of chloride complexes between the organic and aqueous phases depends on the hydrolysis of the chloride complexes. In the sorption experiments [9], performed at HCl concentrations below 4 M, the sorption depends on the hydrolysis of cations.

Hydrolysis of cations [16] is generally expressed by the following equilibria

$$xM(H_2O)_w^{z+} + y\,OH^- \Leftrightarrow M_xO_u(OH)_{y-2u}(H_2O)_w^{(xz-y)+}$$
$$+ (xw^0 + u-w)H_2O. \tag{4}$$
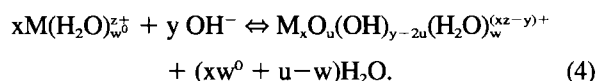
In another way, each step in the formation of a series of mononuclear species can be described as a successive loss of protons

$$M(H_2O)_w^{z+} \Leftrightarrow MOH(H_2O)_{w-1}^{(z-1)+} + H^+. \tag{5}$$
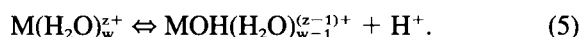
Hydrolysis of complexes, in turn, is expressed generally by the following equilibria:

$$xM(H_2O)_w^{z+} + yOH^- + aA^-$$
$$\Leftrightarrow M_xO_u(OH)_{y-2u}(H_2O)_wA_a^{(xz-y-a)+}$$
$$+ (xw^0 + u-w)H_2O . \tag{6}$$
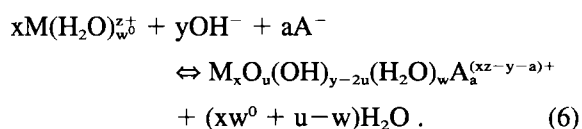
Reactions (4) and (6) are different processes and their constants are not related: Cations of Zr are more hydrolyzed ($\log K_{11} = 0.295$) than cations of Hf ($\log K_{11} = 0.146$) [16], while in the extraction experiments, Zr is better extracted (less hydrolyzed) than Hf [10, this work]. The same is observed for group 5 where Nb as a cation is more hydrolyzed than Ta [16], while in the extraction from HCl solutions, Nb is better extracted than Ta due to the stronger hydrolysis of the latter [17]. Also electrodialysis experiments [18] show that Nb forms anionic complexes in HCl solutions at lower chloride concentrations than Ta, with those of Ta being more hydrolyzed.

It is tempting to discuss the hydrolysis of cations further. In [9], the lower sorption of Rf on cobalt ferrocyanide surfaces was interpreted as Rf being more hydrolyzed than Zr and Hf. Assuming the same coordination number (CN) of water molecules for all the group-4 elements, this result would contradict the simple ionic model of hydrolysis which implies that cations of the same charge and larger ionic radii are less hydrolyzed. As an explanation of the seemingly stronger hydrolysis of Rf, a decrease in CN from 8 to 6 has been supposed [9]. This was thought to be caused by the destabilization of the $6d_{5/2}$ orbitals preventing them from being involved in the chemical bonding with valence orbitals of oxygen of water molecules. From the energies of the spin-orbit (SO) splitted $6d_{3/2}$ and $6d_{5/2}$ orbitals of Rf (see Fig. 3 in Ref. [19]) we see that they are by 2 eV lower than the $7p$ orbitals. Being subjected to a indirect relativistic effect, their SO splitting is not large (about 1 eV) and less than that of the $7p$ orbitals. The SO splitting of the $6p$ orbitals of Pb (about 1.5 eV) is even larger, nevertheless both $6p_{1/2}$ and $6p_{3/2}$ orbitals are involved in bonding. The smaller energy difference for the valence orbitals of Rf cannot be a reason for not attaining a sp^3d^4 hybridization requiring in addition to the $6d_{3/2}$ also the $6d_{5/2}$ orbitals. On the contrary, it is known [20] that increasing relativistic effects in the transactinides result in a close spacing of all the valence levels (the difference between $7s$, $6d$, and $7p$ levels is just 1– 2 eV for Rf), so that the higher CN are easily obtained. For comparison: for Ge, Sn, and Pb, the difference between the valence s and p levels is on the order of 8–10 eV and, for example, for Sn, the promotion energy $s^2p^2 \rightarrow sp^3$ is about 5 eV, and still the sp^3 or sp^3d^2 hybridization is reached giving CN = 4 or 6. In addition, all MO calculations of the light transactinides [21] have shown the $6d_{5/2}$ orbitals to participate even stronger in chemical bonding than $6d^{3/2}$ orbitals since they are more expanded due to relativistic effects and have a higher overlap with the valence orbitals of ligands.

As an example for "relativistically" reduced lower CN, in Ref. [9], complexes of Hg are mentioned. The main feature of compounds of Au, Hg, or Tl having a preference for CN = 2 is a particular shortening and strengthening of two bonds. In [22], the reason for this was said to be a large s-p separation and a preference for sp hybridization instead of sp^n hybridization where $n > 1$. One should not forget that here the question is about a particular stabilization of the $6s^2$ pair and the contraction of the corresponding valence shell due to both relativistic effects and shell-structure effects (completion of the d shell). Even if the bond lengths are generally independent of the shell contraction, in case of Au, Hg, and Tl such a relativistic contraction of the $6s$ shell (and of the $sp_{1/2}$ hybrid orbitals as well since the $6p_{1/2}$ orbitals are also relativistically contracted) influences the metal-ligand bond lengths making them short. The further one goes away from the "gold maximum" the longer get the bond distances. Another

explanation of the special case of Hg, by the way, was a small $5d-6s$ distance [23] which may also be attributed largely to relativistic effects. If to apply all these arguments to the separation of the $6d_{3/2}-6d_{5/2}$ orbitals in the case of Rf, it is hard to see which advantage the $sp^3d^2_{3/2}$ hybridization for CN = 6 should have over $sp^3d^2_{3/2}d^2_{5/2}$ for CN = 8 in terms of bond strengths or bond lengths. Both $d_{3/2}$ and $d_{5/2}$ orbitals are diffuse and destabilized.

Generally, the s-p separation alone cannot explain the advantage of the linear hybridization. In Tl, $6s-6p_{1/2}$ separation is 0.238 a.u. and $6s-6p_{3/2}$ = 0.273 a.u., and Pb is not much larger: $6s-6p_{1/2}$ = 0.291 a.u., and $6s-6p_{3/2}$ = 0.305 a.u. [24]. Nevertheless, $Tl(H_2O)_6^{3+}$ is known to have a preference to form two stronger bonds to two of the water ligands while Pb^{4+} is not.

In Ref. [25], the electronic structures of hexa-hydrated divalent Zn^{2+}, Cd^{2+}, and Hg^{2+} ions have been calculated. The effect of strengthening of two particular metal−oxygen bonds in $Hg(H_2O)_6^{2+}$ was found to be stipulated by the action of the second-order Jahn-Teller effect, resulting in the distortion of the original O_h structure. The latter was due to a smaller value of the energy gap ΔE between occupied and vacant levels (with an excitation energy of 7.2 eV) in the Hg complex in comparison with Zn and Cd (with excitation energies of 12.5 and 11.7 eV, respectively), allowing mixing of these levels by the E_g vibrational mode. The second-order Jahn-Teller effect is known to be active when the energy gap ΔE between occupied and the first vacant MO is small so that the "softening" criterium of the system is fulfilled: $\Delta E < 2a^2/K$ where K is the force constant and $a = dV/dR_0$ with V being the molecular potential and R_0 the internuclear distance at the point of equilibrium. The second order Jahn-Teller effect was also found to be responsible for the strengthening of two bonds in the $Tl(H_2O)_6^{3+}$ compound [26].

One could try to apply these arguments to $Rf(H_2O)_8^{4+}$ vs. $Rf(H_2O)_6^{4+}$. One could suppose a loss of two water molecules due to some distortion of the regular O_h structure. Calculations of different compounds of Rf and other transactinides [21] have shown that ΔE increases from the $4d$ to $5d$ and further to $6d$ elements so that it is hard to foresee a smaller ΔE in $Rf(H_2O)_8^{4+}$ than that in $Zr(H_2O)_8^{4+}$ and $Hf(H_2O)_8^{4+}$ (though the calculations of these complexes would be desirable). In addition, recent calculations [27] of the electronic structure of $M(H_2O)_6^{5+}$ (M = Nb, Ta, Pa, Ha) and study of their hydrolysis have shown that the hydrolysis of these cations follows the sequence Nb > Ta > Ha > Pa being for Nb, Ta, and Pa in agreement with experiment [16]. It turned out that the reason for this is a predominant change in the electrostatic metal-ligand interaction when water molecules are replaced by OH^- groups. Since groups 4 and 5 are very similar, see [21, 23], one can foresee a similar sequence in group 4: Zr > Hf > Rf. Thus, the weaker sorption of

Rf^{4+} on cobalt ferrocyanide surfaces [9] can hardly be explained by its stronger hydrolysis.

Let us come back to the present work in which complex formation has been studied for HCl concentrations between 6 and 12 M. Complex formation and the hydrolysis of complexes are competing processes characterized by the following simplified version of Eq. (6):

$$M(OH)_xCl_{4-x} + xHCl \Leftrightarrow MCl_4 + xH_2O . \tag{7}$$
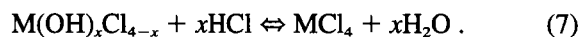
To predict the equilibrium constant for Eq. (7), one has to consider the difference in total energies of the (partially) hydrolyzed species on the left hand side of the equilibrium that are not extracted and of the extractable MCl_4. (It is assumed that the OH^- containing species will not extract into the organic phase because of the strong hydrogen bonding interaction between OH^- and H_2O.) This can be done by quantum-chemical calculations, presently using the DS DV method [29, 21], allowing calculations of the differences in the Coulomb and covalent parts of the binding energy separately. Calculations for Zr, Hf, and Rf are still to be done, but one can already draw qualitative conclusions based on a parallel study of the hydrolysis of chloro complexes of the group 5 elements Nb, Ta, Pa, and Ha [30]. For group 5, the order of complex formation described by equilibria similar to the reaction (7) in 4−12 M HCl solutions was found to be Pa > Nb > Ha > Ta. The reason for this are dominant differences in the Coulomb part of the energy of reaction when OH^- groups are replaced by Cl^- anions.

Earlier calculations [28] of MCl_4 (M = Zr, Hf, and Rf) have shown that the compounds are very similar, which can also be supposed for $M(OH)_xCl_{4-x}$. Knowing the analogy in the electronic structure of the halides and oxyhalides of groups 4 and 5 [21, 30], one can postulate the same order of complex formation Zr > Rf > Hf according to Eq. (7) as it was found for the corresponding group 5 elements. For both group 4 and 5, such a sequence is in full agreement with experimental data for Zr and Hf, and Nb and Ta, respectively, showing that compounds of the $5d$ elements are more hydrolyzed than those of the $4d$ elements and are hence less extracted. For these elements, the hydrolysis of complexes is of opposite order to the order of hydrolysis of the cations which underlines that these processes should not be mixed.

In summary, we have established an extraction sequence of the group-4 elements from 8 M HCl into TBP, Zr > Rf > Hf, which is in qualitative agreement with theoretical considerations on the competition between hydrolysis of the chloro complexes in the aqueous phase and extraction of the chloro complexes into the organic phase.

Acknowledgments

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