Extraction of short-lived zirconium and hafnium isotopes using crown ethers: A model system for the study of rutherfordium

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(Received: ; Accepted:)

Zirconium / Hafnium / Crown ether / Liquid-liquid extraction / Distribution ratio / Separation factor

Summary

The extraction of zirconium and hafnium from hydrochloric acid media was studied using the crown ethers dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DC18C6) and dicyclohexano-24-crown-8 (DC24C8) as extractants. The goal was to find an extraction system that exhibits a high selectivity between the members of group 4 of the periodic table and is suitable for the study of rutherfordium. It was found

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that Zr and Hf are both extracted using DB18C6, DC18C6 and DC24C8. The extraction yield increases with increasing acid concentration and increasing concentration of crown ether. The extracted species most likely consists of an ion-association complex formed between a Zr or Hf chloro complex and a hydronium crown ether complex. Conditions can be found for each extractant that provide for the separation of Zr from Hf. This selective separation between Zr and Hf makes the extraction with crown ethers from HCl well suited to study the extraction behavior of Rf and compare it to the behavior of Zr and Hf. These extraction systems can be used to determine whether the extraction behavior of Rf is similar to Zr, similar to Hf or follows the trend established by the lighter homologs. The extraction kinetics are fast enough for the study of the 78-s isotope ^{261}Rf.

1. Introduction

The development of suitable chemical systems for the study of the properties of the transactinide elements ($Z \geq 104$) presents several challenges. These challenges are mainly due the short half-lives of these elements and the low rates with which they can be produced. Due to the small production cross sections on the order of nano- or even picobarns, the transactinide elements need to be studied one atom-at-a-time. The atom studied cannot interact with other atoms of the same element but instead it only interacts with its surroundings, because no macroscopic amounts of the element are present. To obtain reliable results, it is necessary to select a chemical system in which one atom undergoes the same kind of interaction many times [1]. Liquid-liquid extraction is a good example of such a system, and this technique has been extensively used for the study of the lighter transactinide elements [2].

Reaction kinetics play a major role in the choice of a suitable system. The short half-lives of the isotopes studied means that the experiments have to be restricted to chemical systems that reach equilibrium rapidly. Each new system needs to be tested under conditions similar to those encountered during on-line experiments with transactinide elements and on a comparable timescale.

In the past, the nuclear reactions used for the production of transactinide elements imposed further restrictions. In addition to the transactinide element, a large excess of interfering transfer reaction products were created in the interaction between accelerator beam and target or backing material. This made it

necessary to develop extraction systems that removed all interfering reaction products and left only the element of interest. Consequently, very high separation factors between the element of interest and all other interfering nuclides had to be favored over a high selectivity between the individual homologs of the element being studied.

One of the main motivations for the study of transactinide elements is a strong interest in the influence of relativistic effects on the chemical properties within a group in the periodic table. These effects are predicted to lead to deviations from trends established by the lighter members of the group [3]. To test for these deviations, the chemical properties of the transactinide elements need to be compared to the properties of their lighter homologs. For this reason it would be preferable to concentrate on extraction systems that show a high selectivity between members of one group of the periodic table instead of having to focus on the removal of the multitude of interfering elements.

Recently, the fast, automated liquid-liquid extraction system SISAK was successfully used to study the chemical behavior of element 104, rutherfordium [4, 5]. This was made possible by coupling the SISAK system to the Berkeley Gas-filled Separator (BGS) [6]. The BGS was used to achieve a physical pre-separation of the desired element from the beam and unwanted reaction products. Pre-separation reduced the background due to other reaction products substantially and allowed for an unambiguous detection of rutherfordium atoms. In addition, the absence of interfering reaction products offers a great advantage for the design of extraction systems for future experiments with rutherfordium. It allows the use of different classes of extraction systems that favor selectivity between the members of the same group of the periodic table over efficient separation from elements belonging to other groups of the periodic table. These systems can then be used in future experiments with SISAK or other automated systems, as well as manual extraction experiments.

Crown ethers are part of a class of macrocyclic ligands that exhibit highly selective extraction behavior. This behavior is used in a multitude of applications in analytical and separation chemistry. The coordination chemistry of macrocyclic ligands, especially between crown ethers and alkali and alkaline earth metals has been studied in depth (see [7] for a review), and these ligands are commonly applied to the separation of various metal ions (see [8] for a review).

Here we report on the extraction of zirconium and hafnium from hydrochloric acid media with dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DC18C6) and dicyclohexano-24-crown-8 (DC24C8). The chemical structure of the crown ethers is shown in Figure 1. The goal of the research was to determine whether one of these extractants shows a preference for the extraction of zirconium over hafnium or vice versa. If the crown ethers show a high selectivity between the different members of group 4 of the periodic table, then they might be used as a suitable chemical system for the study of rutherfordium.

As mentioned earlier, the kinetics of the reaction are an important factor in developing suitable extraction systems for chemistry experiments with transactinide elements. The size of the organic molecules used as ligands can have a large effect on the kinetics of the reaction. The use of crown ethers for the separation of zirconium and hafnium has been reported previously in the literature [9, 10], but none of these studies were conducted on a time scale short enough to ensure that the reaction kinetics are fast enough to permit the study of ^{261m}Rf with a half-life of 78 s [11]. For this reason, we studied the extraction in on-line experiments using relatively short-lived isotopes of Zr and Hf produced by an accelerator and pre-separated using the BGS. The goal was to conduct the studies under conditions similar to those encountered during an experiment with rutherfordium.

2. Experimental

2.1 Materials

Dibenzo-18-crown-6 (purum, ≥ 98%) and dicyclohexano-18-crown-6 (purum, ≥ 98%) were purchased from Fluka Chemika. Dicyclohexano-24-crown-8 (97%) was obtained from Aldrich Chemical Company. All crown ethers were used as received. Dichloromethane (A.C.S. reagent, ≥ 99.5 %) was purchased from Sigma-Aldrich, Inc. The hydrochloric acid (puriss.) used for the preparation of solutions was obtained from Fluka Chemika and assayed at 37%. To determine the actual concentration of the acid solutions prepared from the concentrated stock solution, an aliquot was taken from each solution. A few drops of bromothymol blue were added to the aliquots and they were titrated with a standardized 0.98 N sodium hydroxide solution (A.C.S. reagent grade sodium hydroxide in ASTM reagent grade I water) purchased from Aldrich Chemical Company.

2.2 Production and pre-separation of short-lived Zr and Hf isotopes

The on-line experiments were performed at the 88-Inch Cyclotron at Lawrence Berkeley National Laboratory (LBNL) using the isotopes ^{85}Zr ($T_{1/2}$ = 7.9 m) and ^{169}Hf ($T_{1/2}$ = 3.25 m). The isotopes were produced by bombarding a ^{nat}Ge target with a 83.6-MeV $^{18}O^{4+}$ beam and a ^{124}Sn target with a 228.0-MeV $^{50}Ti^{11+}$ beam, respectively. The two beams were delivered by the cyclotron as a "cocktail" beam [12]. This means the two beams were simultaneously injected from the Electron Cyclotron Resonance (ECR) ion source into the cyclotron. By varying the cyclotron frequency, either the $^{18}O^{4+}$ or the $^{50}Ti^{11+}$ beam was accelerated, extracted from the cyclotron and delivered to the target. The use of this ion cocktail and an adjustable target ladder in the BGS containing both the ^{nat}Ge and the ^{124}Sn target allowed the experiments with zirconium and hafnium to be performed almost simultaneously and under virtually identical experimental conditions.

The beam passed through a (40-45)-μg/cm^2 carbon vacuum window at the entrance to the BGS and a negligible amount of He before entering the target. A 20-mm diameter target of 350-μg/cm^2 ^{nat}Ge deposited on a 45-μg/cm^2 carbon backing was used for the production of ^{85}Zr and a 20-mm diameter self-supporting 586-μg/cm^2 ^{124}Sn target was used for the production of ^{169}Hf. Typical beam intensities were 100 particle·nA for the $^{18}O^{4+}$and 15-20 particle·nA for the $^{50}Ti^{11+}$ beam. The zirconium and hafnium reaction products recoiling out of the target were separated from the beam and most unwanted reaction products in the BGS based on their respective magnetic rigidities of 0.92 and 1.56 T·m [13]. The BGS was filled with He at a pressure of 0.7 mbar. After traveling through the BGS, the recoiling atoms passed through a 3.3-μm Mylar window into the 40-mm-deep Recoil Transfer Chamber (RTC) where they were thermalized in helium gas at approximately 1.2 bar [14]. The Hf recoil products have a larger kinetic energy than the Zr recoils, and to ensure that the Hf recoils were completely thermalized in the RTC, they were degraded by passing through two Mylar foils with a total thickness of 5.7-μm before entering the RTC window [13]. The low kinetic energy of the Zr recoils prevented the use of a thicker Mylar foil for the RTC window.

2.3 On-line extraction experiments

After thermalization in the RTC, the recoil products were transported through a 2 mm i.d. and ~ 20 meter long steel capillary to the chemistry setup using a potassium chloride aerosol gas-jet system. The aerosol particles were produced at an oven temperature of 640 ^{o}C and the gas-jet was operated at an average flow rate of 1.6-1.8 L/min. The transport efficiency of the gas-jet system was determined to be about 70% in separate experiments.

The aerosol particles containing the radionuclides were deposited on small platinum foils at the exit of the gas-jet capillary. The aerosol residue was dissolved in either 50 or 100 μL of hydrochloric acid of appropriate concentration. The solution was transferred to a centrifuge cone containing additional 3950 or 3900 μL of the same acid solution. The aqueous phase was mixed with an equal volume of crown ether diluted in dichloromethane. Phases were vigorously mixed for 20 seconds using a vortex mixer and centrifuged for 20 seconds. For the kinetics experiments the mixing time was varied between 10 and 60 seconds, while the time for centrifugation was kept constant at 20 seconds. After phase separation, a 3-mL aliquot was taken from each phase.

Both aliquots were assayed using the same HPGe γ-ray detector to minimize the effect of variations in sample geometry and detector efficiency. The first sample measured was usually the aliqout containing the smaller fraction of Zr or Hf. It was counted for 4 minutes; samples were changed during a 15-second interval and then the second aliquot was counted for 4 minutes. The spectra were saved automatically on a PC and analyzed afterwards using the Genie-2000 Software package from Canberra. Data obtained from the second aliquot measured were corrected for decay. The extraction was repeated five times for each acid and crown ether concentration. The extraction yield and distribution ratio were determined as the weighted mean of the five parallel experiments. The error was determined from the statistical counting uncertainty using standard error propagation techniques. The results are reported at the one sigma level.

3. Results and discussion

3.1 Extraction with dibenzo-18-crown-6

The extraction of zirconium and hafnium from hydrochloric acid with 0.090 M dibenzo-18-crown-6 (DB18C6) was studied over the concentration range from 6.0 to 11.0 M HCl. The results are shown in Figure 2. It can be seen that the extraction yield increases with increasing acid concentration for both elements. The extraction begins at concentrations above 7.5 M for Zr. It reaches a maximum yield of (89±9) % at a concentration of 10.5 M and then stays constant. Compared to Zr, Hf extraction begins at higher acid concentrations. Hf starts to extract at concentrations above 8.5 M HCl and the extraction yield reaches a maximum of (85±3) % at 11.0 M. The extraction yield for zirconium is higher than for hafnium over the whole concentration range studied. The separation factors for Zr over Hf at the concentrations studied are listed in Table 1. The separation factor decreases with increasing acid concentration and the resulting increase in extraction yield for both elements. The separation factors demonstrate that Zr and Hf can be separated from each other using this extraction system.

The increase in extraction yield with increasing acid concentration exhibited by both Zr and Hf results from the increased formation of a negatively charged chloride complex in the aqueous phase. At a hydrochloric acid concentration of 11.0 M Zr and Hf are both only present as a double negatively charged hexachloro complex, but the formation of the hexachloro complex starts already at lower acid concentrations [15].

To obtain further information on the extraction mechanism and the number of crown ether ligands involved in the process, the effect of concentration of DB18C6 on the extraction of Zr and Hf from 9.5 M hydrochloric acid was studied. Figure 3 shows a plot of the logarithm of the distribution ratio K_d as a function of the logarithm of the concentration of DB18C6. The distribution ratio for both elements increases with increasing concentration of extractant. The distribution ratios for Zr are higher than for Hf. To obtain the number of crown ether ligands coordinated to the metal ion, the slope of the increase in K_d was determined by a linear fit. The slope for Zr was determined to be (1.62±0.03) and the slope for Hf was (1.70±0.03). These results indicate that each meal ion in the organic phase is most likely coordinated to two molecules of DB18C6.

As discussed earlier, Zr and Hf are both present as negatively charged chloride complexes at high acid concentrations. These species cannot interact directly with the oxygen atoms of the ligand. The donor atoms of the crown ether usually coordinate to positively charged species, but crown ethers can be used to extract anionic complexes by forming ion-association complexes [16]. Crown ethers such as DB18C6 are

known to form positively charged hydronium complexes by coordinating with a H_3O^+ molecule [17, 18]. The hydronium ions are present in excess at high acid concentrations and their size allows them to fit perfectly into the cavity of the ring. The binding energy of the hydronium complex with 18-crown-6 surpasses even that of alkali ions such as Na^+ or K^+ [19]. The resulting positively charged hydronium crown ether complex can then serve as a counter ion for the anionic zirconium or hafnium hexachloro complex and extract it into the organic phase. The extraction mechanism can be described as follows:

$$DB18C6 + H_3O^+ \rightarrow [DB18C6 \cdot H_3O^+] \quad (1)$$

$$2\,[DB18C6 \cdot H_3O^+] + MCl_6^{2-} \rightarrow [DB18C6 \cdot H_3O^+]_2[MCl_6]^{2-} \quad \text{for M= Zr, Hf} \quad (2)$$

3.2 Extraction with dicyclohexano-18-crown-6

To learn about the influence of side groups attached to the basic 18-crown-6 ring structure, the extraction of zirconium and hafnium from hydrochloric acid was studied with 0.025 M and 0.070 M dicyclohexano-18-crown-6 (DC18C6) and compared to the extraction with dibenzo-18-crown-6. Again the extraction behavior was studied over the concentration range from 6.0 to 11.0 M HCl. The results for 0.025 M DC18C6 are shown in Figure 4 and for 0.070 M DC18C6 in Figure 5.

As in the experiments with DB18C6 the extraction yield increases for zirconium and hafnium with increasing acid concentration. In the experiments with 0.025 M DC18C6 Zr is already slightly (~10%) extracted at the lowest acid concentration studied, while Hf is not extracted until an acid concentration of 7.0 M is reached. The extraction yield for Zr reaches a maximum of (91±8) % at 10.5 M. The extraction yield for Hf is lower than for Zr until acid concentration above 9.5 M are reached. The extraction yield for Hf reaches a maximum of (91±4) % at a concentration of 11.0 M and is as high as the yield for Zr. But even though the maximum extraction yields for Zr and Hf are comparable to the maximum yield determined in the experiments with DB18C6, the extraction yield at lower acid concentrations is higher when using DC18C6 instead of DB18C6.

Increasing the concentration of DC18C6 to 0.070 M leads to an increase in extraction yield at lower acid concentrations. The increase in yield for both elements seems to level off at concentrations around 9.5 M

HCl. At this concentration the extraction yield for Hf is similar to the yield for Zr, considering the uncertainties of the measurement: Zr extraction reaches a maximum of (91±8) %, while Hf extraction reaches a maximum of (97±7) %.

In the on-line experiments, the samples with ^{85}Zr had a lower count rate than the samples with ^{169}Hf. This led to very poor counting statistics in the aqueous phase at conditions where almost all of the Zr is extracted. For this reason the extraction yields for Zr at high crown ether concentrations have a higher uncertainty assigned to them than the extraction yields for Hf. Based on the current data available it is impossible to decide whether the extraction yield for Hf really exceeds the yield for Zr or if this is just an effect of counting statistics.

Table 1 shows the separation factors for Zr over Hf at both crown ether concentrations over the acid concentration range studied. The separation factor reaches a maximum at a concentration of 8.0 M HCl for the experiments with 0.025 M DC18C6, while for the experiments with 0.070 M DC18C6, the maximum is already reached at 7.5 M HCl. Suitable conditions for the separation of Zr and Hf can be chosen at either crown ether concentration. Compared to the Zr/Hf separation with DB18C6, the extraction with DC18C6 has the advantage of reaching high extraction yields for Zr already at low acid concentrations.

Figure 6 shows a plot of the logarithm of the distribution ratio K_d as a function of the logarithm of the concentration of DC18C6. The extractions were performed at a fixed acid concentration of 10.0 M HCl. The distribution ratios for Hf increase with rising concentration of crown ether. For Zr the distribution ratio increases at first, but then levels off at DC18C6 concentrations above 0.040 M.

To obtain the number of crown ether ligands coordinated to the metal ion, the slope of the K_d increase for Hf was determined from a linear fit to be (1.73±0.06). This suggests that each Hf ion in the organic phase is coordinated to two molecules of DC18C6, in good agreement with the extraction mechanism proposed in Section 3.1. Due to the fact that the distribution ratio seems to level off, a similar analysis was not possible for Zr.

3.3 Extraction with dicyclohexano-24-crown-8

To test the effect of the ring size of the ligand, the extraction of zirconium and hafnium from hydrochloric acid was studied using dicyclohexano-24-crown-8 (DC24C8). The extraction yields for the extraction of Zr and Hf with 0.025 M DC24C8 from 8.0, 9.0 and 10.0 M HCl are plotted in Figure 7. For comparison the extraction yields for the extraction with 0.025 M DC18C6 are shown as well. It can be seen that the extraction yields for Zr with DC24C8 are almost the same as for the extraction with DC18C6. The extraction yields for Hf with DC24C8 from 8.0 M and 10.0 M HCl are the same as for the extraction with DC18C6. Only the extraction of Hf from 9.0 M HCl shows a large difference in extraction yield for the different crown ethers. Here the yield is significantly higher for the extraction with DC24C8. But in general, the increased size of the crown does not seem to affect the extraction behavior strongly.

3.4 Extraction kinetics

To ensure that a chemical system is suitable for the study of rutherfordium, the kinetics of the reaction need to be fast. The system has to reach equilibrium in a short time; otherwise it can not be used for the study of short-lived isotopes. The kinetics of the extraction with DB18C6 and DC18C6 were studied by determining the extraction yield as a function of contact time between the two phases. For this purpose the mixing time was varied between 10 and 60 seconds, while the time for centrifugation was kept constant at 20 seconds. Figure 8 shows a plot of the extraction yield vs. mixing time for the extraction of Zr and Hf with 0.090 M DB18C6 and 0.025 M DC18C6 from 10.0 M HCl. The results show that for both elements and both crown ethers the extraction yield does not change significantly over mixing times ranging from 10 to 60 seconds. The complex formation and extraction is already complete after 10 seconds. The extraction systems are fast enough for the study of 78-s ^{261m}Rf.

4. Conclusions

In this work the extraction of zirconium and hafnium from hydrochloric acid media was studied using dibenzo-18-crown-6, dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8 as extractants. The results show that Zr and Hf are extracted by all three crown ethers as soon as the concentration of hydrochloric acid is sufficient to form a metal ion chloro complex. In all systems studied the extraction yield increases

with increasing acid concentration and increasing concentration of crown ether. The extracted species most likely consists of an ion-association complex formed between a Zr or Hf chloro complex and a hydronium crown ether complex.

Conditions can be found for each extractant that provide for the separation of Zr from Hf. This makes the extraction with crown ethers from HCl a suitable system to determine whether Rf shows a behavior more similar to Zr or Hf. It is a good example for an extraction system that focuses on selectivity between the members of one group of the periodic table instead of focusing on the group separation necessary for removal of interfering reaction products. The experiments also showed that the complex formation and extraction is already complete after 10 seconds. The extraction kinetics are fast enough for the study of the 78-s isotope ^{261m}Rf. The favorable kinetics of the extraction together with the fact that conditions for the separation of Zr from Hf exist make the extraction with crown ethers a suitable and interesting system for the study of Rf.

If the extraction behavior of Rf is studied using the same crown ethers and compared to the behavior of Zr and Hf, the results will elucidate the extraction behavior along group 4 of the periodic table. The outcome will show whether the extractability follows a common trend down the group or if there are deviations from the trend established by the behavior of Zr and Hf. Because the extraction of Zr and Hf under the conditions studied depends mainly on the formation of a metal ion chloro complex, the extraction with crown ethers is well suited to obtain information on the stability of the group 4 metal chloride complexes. The experiments will give valuable information on the influence of relativistic effects on the complex formation [20].

The next goal will be an on-line experiment to determine the distribution ratio of rutherfordium as a function of hydrochloric acid and crown ether concentration. The extraction of Rf could, for example, be studied from 8.5 M HCl with 0.025 M DC18C6. At this acid concentration the extraction yield is ~28% for Hf and ~84% for Zr. This means if the extraction yield for Rf is at least as high as that for Hf, then some Rf atoms should be extracted and can be detected in the organic phase. If no rutherfordium can be found in the organic phase, then the extraction yield for Rf must be less than that for Hf. At the same time the extraction yields of Zr and Hf are sufficiently different to distinguish between a Zr-like and Hf-like behavior of rutherfordium.

In addition, further experiments are necessary to confirm the structure of the species extracted and to clarify the extraction mechanism. This could be achieved by complementing the tracer scale extraction experiments with speciation studies of macroscopic amounts of the metal ion in solution using EXAFS or other suitable spectroscopy techniques.

Acknowledgements

The authors would like to thank the staff of the 88-Inch Cyclotron at Lawrence Berkeley National Laboratory, especially the ion source team, for the production of the O/Ti cocktail beam. This work was supported by the Director, Office of Science, Office of High Energy and Nuclear Physics, Division of Nuclear Physics, and the Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Table 1. Separation factors for the separation of Zr from Hf by extraction from hydrochloric acid with 0.090 M dibenzo-18-crown-6 (DB18C6) and 0.025 and 0.070 M dicyclohexano-18-crown-6 (DC18C6). The separation factor is defined as the distribution ratio for Zr divided by the distribution ratio for Hf.

Fig 1. Chemical structure of dibenzo-18-crown-6 (a), dicyclohexano-18-crown-6 (b) and dicyclohexano-24-crown-8 (c).

Fig 2. Extraction of ^{85}Zr and ^{169}Hf into 0.090 M dibenzo-18-crown-6 in dichloromethane as a function of hydrochloric acid concentration.

Fig 3. Distribution ratios for the extraction of ^{85}Zr and ^{169}Hf from 9.50 M HCl as a function of dibenzo-18-crown-6 concentration in dichloromethane. The solid and dashed lines indicate the results of linear regression fits to the Zr and Hf data, respectively. For Zr the slope was calculated as (1.62±0.03) and for Hf as (1.70± 0.03).

Fig 4. Extraction of ^{85}Zr and ^{169}Hf into 0.025 M dicyclohexano-18-crown-6 in dichloromethane as a function of hydrochloric acid concentration.

Fig 5. Extraction of ^{85}Zr and ^{169}Hf into 0.070 M dicyclohexano-18-crown-6 in dichloromethane as a function of hydrochloric acid concentration.

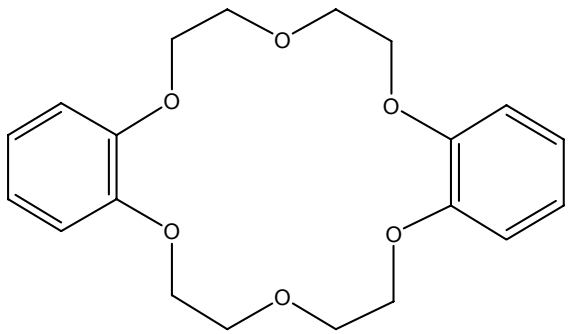
Fig 6. Distribution ratios for the extraction of ^{85}Zr and ^{169}Hf from 10.0 M HCl as a function of dicyclohexano-18-crown-6 concentration in dichloromethane. The dashed line indicates the result of a linear regression fit to the Hf data. The slope was calculated as (1.73±0.06).

Fig. 7. Extraction of ^{85}Zr and ^{169}Hf into 0.025 M dicyclohexano-24-crown-8 in dichloromethane as a function of hydrochloric acid concentration. For comparison the yields for the extraction with 0.025 M dicyclohexano-18-crown-6 are plotted as well.

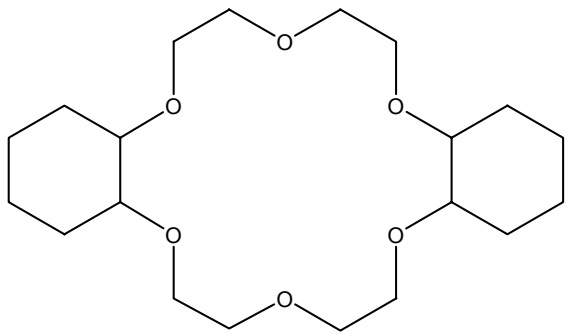
Fig. 8. Extraction yields for Zr and Hf extraction from 10.0 M HCl into 0.090 M dibenzo-18-crown-6 and into 0.025 M dicyclohexano-18-crown-6 as a function of mixing time. The time for centrifugation was kept constant at 20 seconds for all samples.

Table 1.

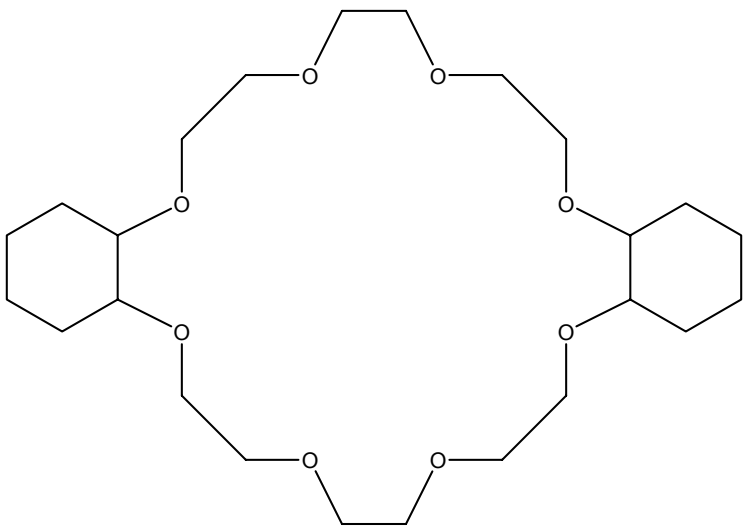
HCl [M]	Separation factor Zr/Hf 0.0900 M DB18C6	Separation factor Zr/Hf 0.0250 M DC18C6	Separation factor Zr/Hf 0.0700 M DC18C6
6.0	---	---	8 ± 3
6.5	---	---	28 ± 4
7.0	---	2.5 ± 0.2	11.1± 0.5
7.5	---	13.7 ±0.7	42 ± 3
8.0	24 ± 5	28 ± 1	14 ± 1
8.5	10 ± 1	12.6 ± 0.7	4.5 ± 0.3
9.0	8.9 ± 0.7	4.3 ± 0.4	1.4 ± 0.1
9.5	5.8 ± 0.3	1.6 ± 0.1	0.70 ± 0.1
10.0	4.7 ± 0.3	1.5 ± 0.2	0.38 ± 0.04
10.5	1.5 ± 0.1	1.3 ± 0.1	0.39 ± 0.04
11.0	1.2 ± 0.1	0.71 ± 0.07	0.16 ± 0.02



(a)



(b)



(c)

Fig. 1.

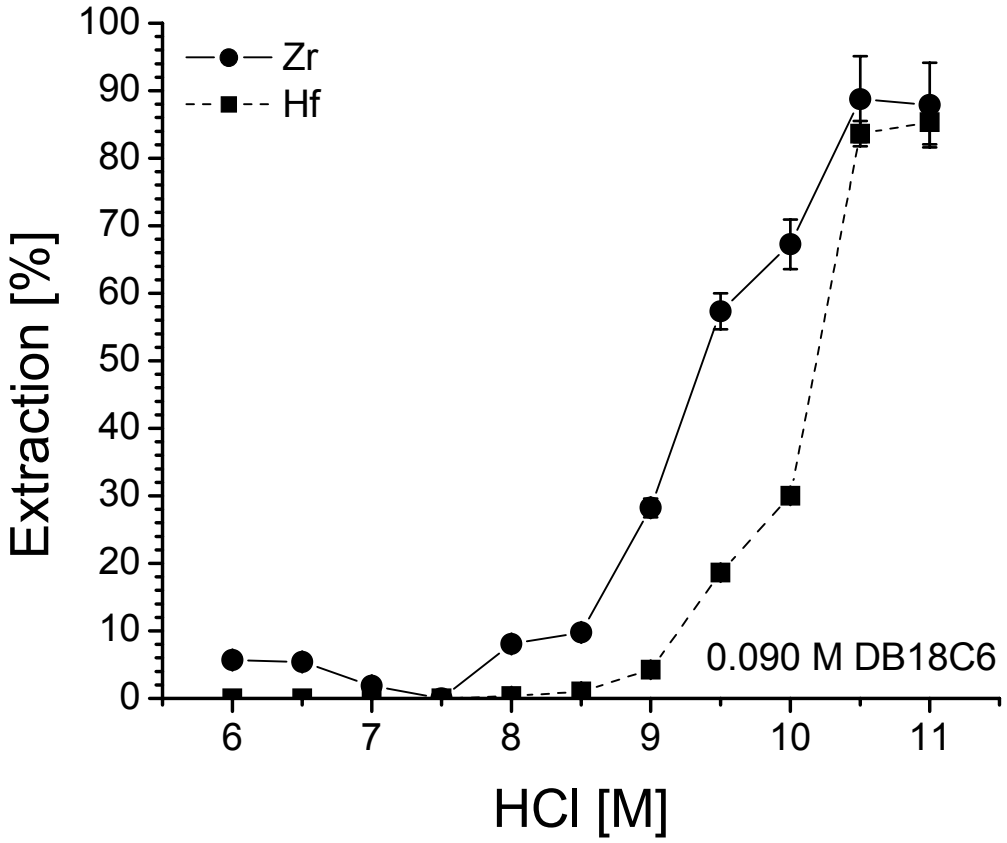

Zr
Hf
Extraction [%]
HCl [M]
0.090 M DB18C6
0
10
20
30
40
50
60
70
80
90
100
6
7
8
9
10
11

Fig. 2.

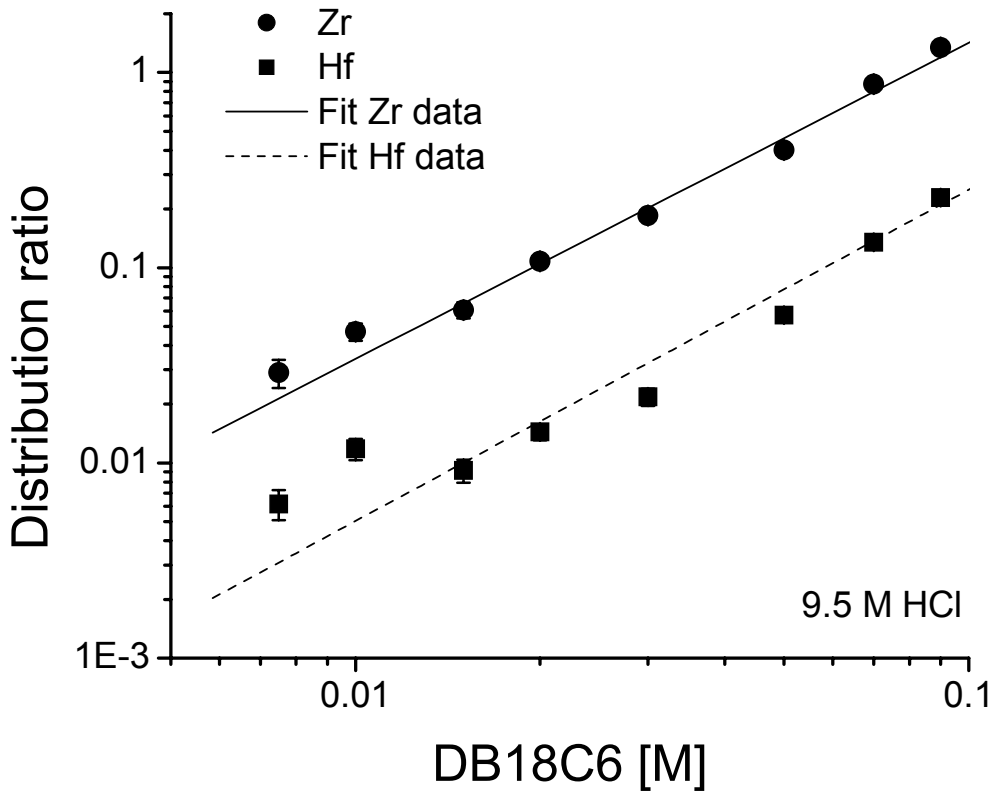

Zr
Hf
Fit Zr data
Fit Hf data
Distribution ratio
1
0.1
0.01
1E-3
9.5 M HCl
0.01
0.1
DB18C6 [M]

Fig. 3.

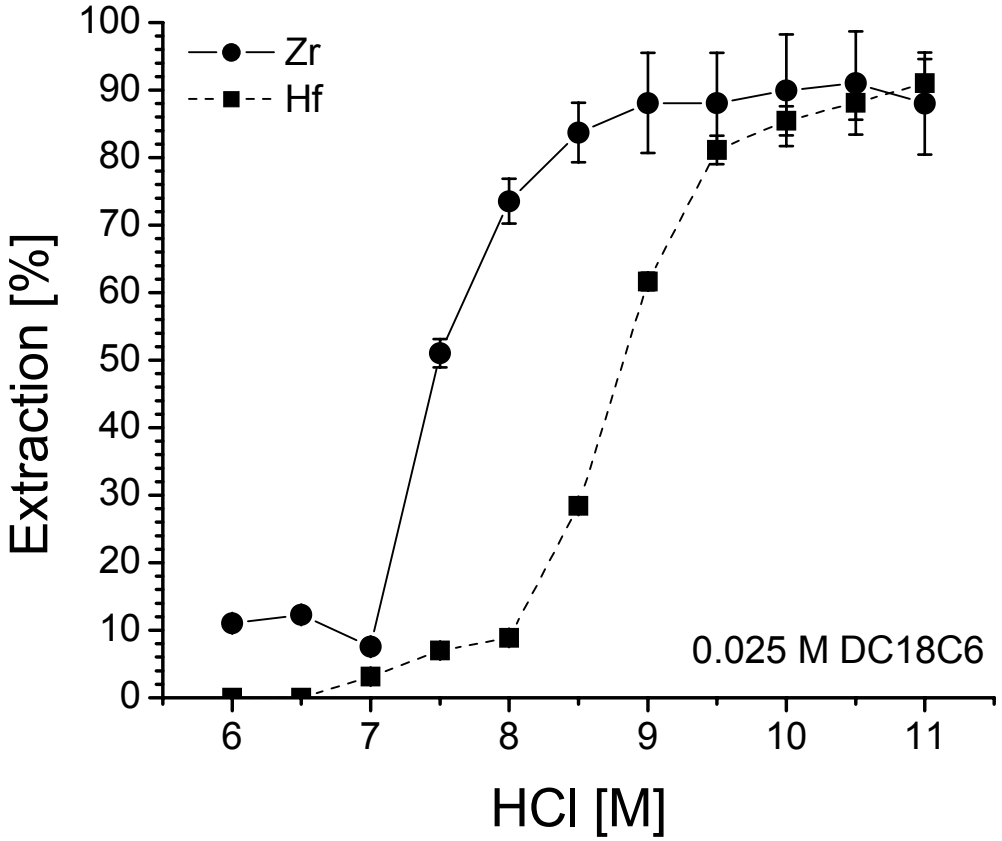

Zr
Hf
Extraction [%]
HCl [M]
0.025 M DC18C6
0
10
20
30
40
50
60
70
80
90
100
6
7
8
9
10
11

Fig. 4.

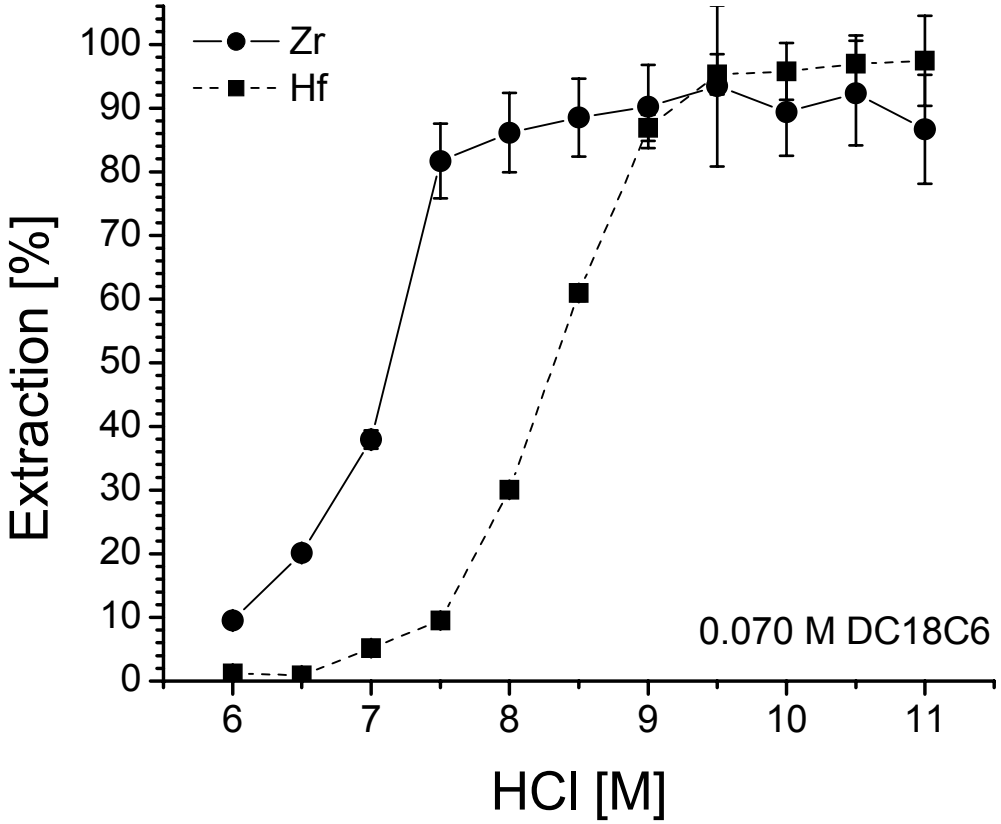

Zr
Hf
Extraction [%]
HCl [M]
0.070 M DC18C6
0
10
20
30
40
50
60
70
80
90
100
6
7
8
9
10
11

Fig. 5.

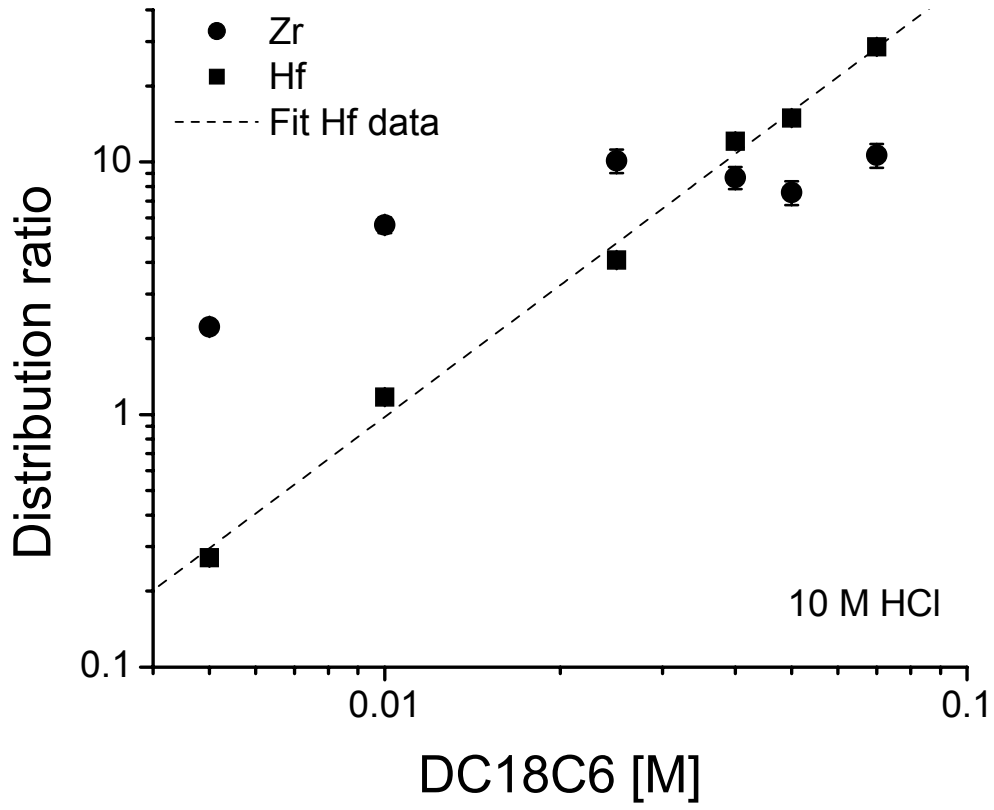

Zr
Hf
Fit Hf data
10
1
0.1
Distribution ratio
10 M HCl
0.01
0.1
DC18C6 [M]

Fig. 6.

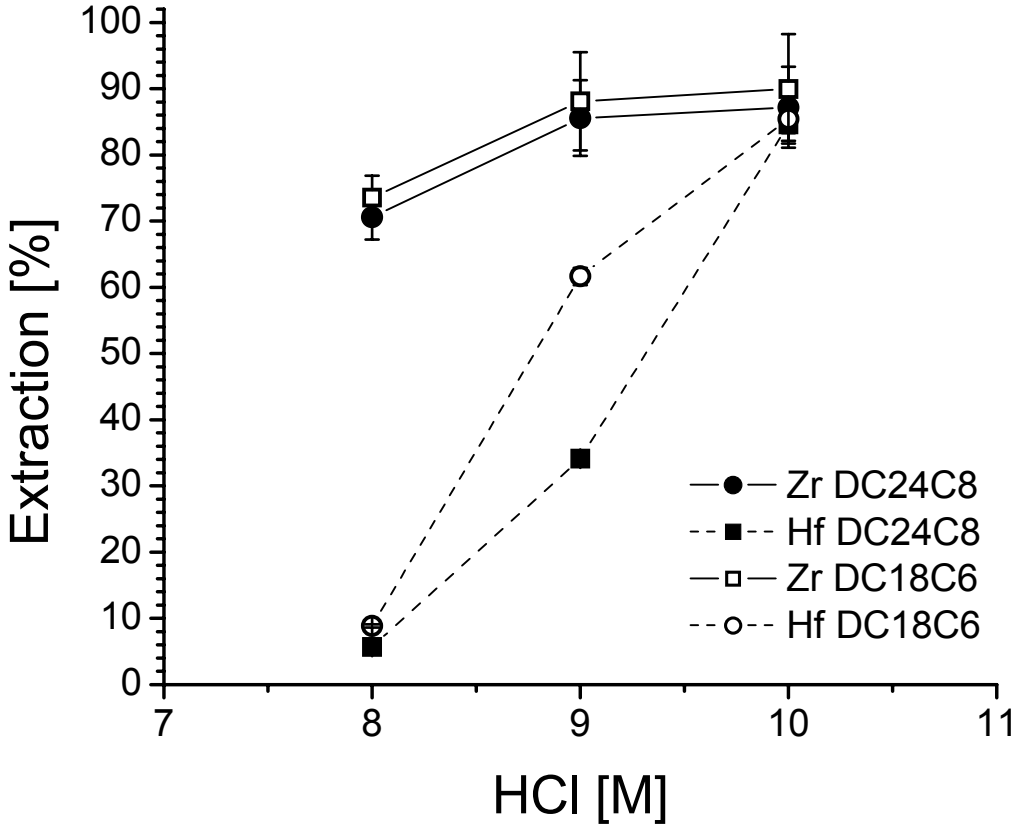

Extraction [%]
HCl [M]
Zr DC24C8
Hf DC24C8
Zr DC18C6
Hf DC18C6
0
10
20
30
40
50
60
70
80
90
100
7
8
9
10
11

Fig. 7.

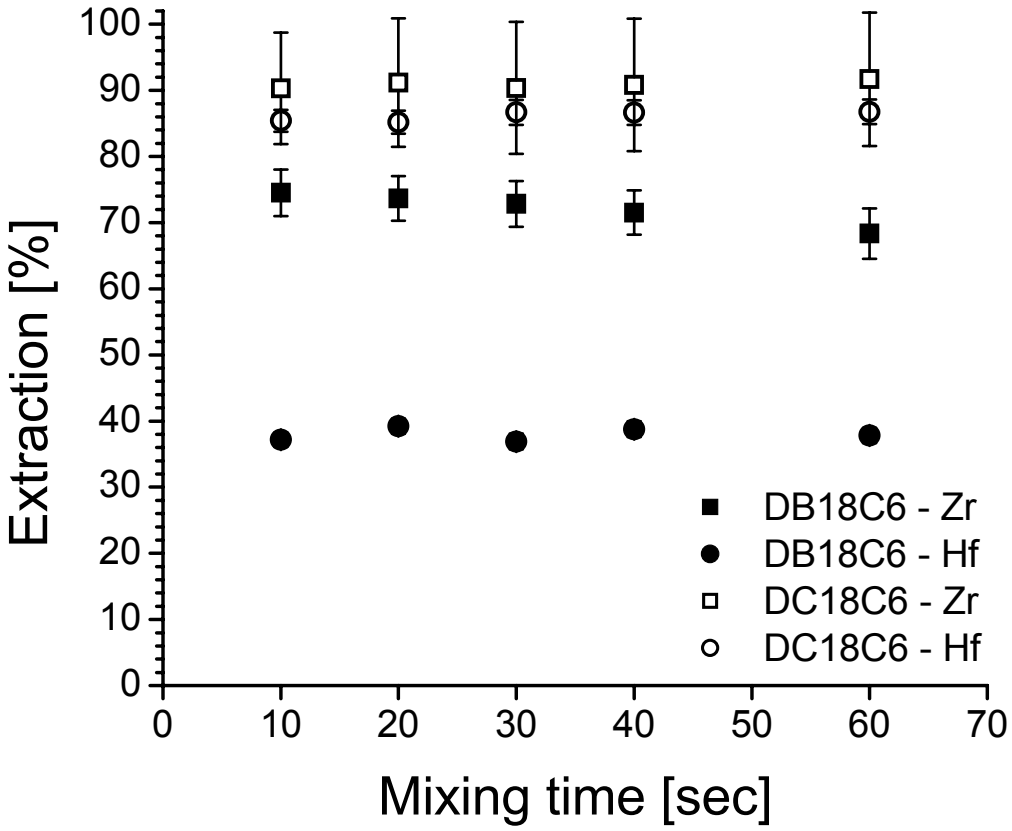

Extraction [%]
Mixing time [sec]
DB18C6 - Zr
DB18C6 - Hf
DC18C6 - Zr
DC18C6 - Hf
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70

Fig. 8.