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Abstract: The extraction of zirconium and hafnium from aqueous HCl solutions by means of Aliquat 336 in organic diluents was systematically studied. The following three aspects were discussed: the extraction dependence on HCl, the Aliquat 336 concentrations, and the nature of diluents. Both of the metals were stripped with deionized water and the influence of phase ratio on the efficiency of the stripping has been investigated. The stoichiometry of the extracted Zr and Hf species from single metal ion were studied and a possible extraction mechanism for the Zr-Hf mixture is discussed in the light of the results obtained.

Keywords: Zirconium, hafnium, HCI, Aliquat 336 concentrations, diluent nature

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INTRODUCTION

The use of Zircaloy in the construction of nuclear fuel elements and other structural components in reactor cores meets many physical and technological requirements essential for the nuclear industry (1). The zirconium metal must contain less than 100 ppm hafnium since hafnium has a high absorption cross-section for thermal neutrons compared to that of zirconium (2). Zircon, the primary ore for nuclear-grade zirconium contains about 65% ZrO_2, 33% SiO_2 and 1% HfO_2. Zirconium and hafnium have similar atomic radii, 1.45 Å and 1.44 Å, respectively) and similar configuration of the valence electrons ($4d^25s^2$ and $5d^26s^2$ for Zr and Hf respectively). Due to their similarity, complicated and expensive separation methods are required to remove the hafnium impurity.

There are three established technologies for the zirconium and hafnium separation (Fig. 1): multiple crystallization of potassium zirconium fluoride, solvent extraction process, and extractive distillation (1–3).

In the tributyl phosphate (TBP) process, sodium zirconate (Na_2ZrO_3), obtained from the caustic soda fusion with zircon sand, is dissolved in concentrated nitric acid. This solution is mixed with TBP in kerosene and the Zr is selectively extracted (4). Zircon sand can be sintered with K_2SiF_6 and KCl to produce $K_2Zr(Hf)F_6$. The multiple crystallization of K_2ZrF_6 allowed to produce nuclear grade Zr as the potassium hafnium fluoride is more soluble than the potassium zirconium fluoride (5). Zircon can also be chlorinated with carbon to produce $SiCl_4$ and crude $ZrCl_4$ containing $HfCl_4$. In Teledyne Wah Chang and Western Zirconium plant (Westinghouse) the

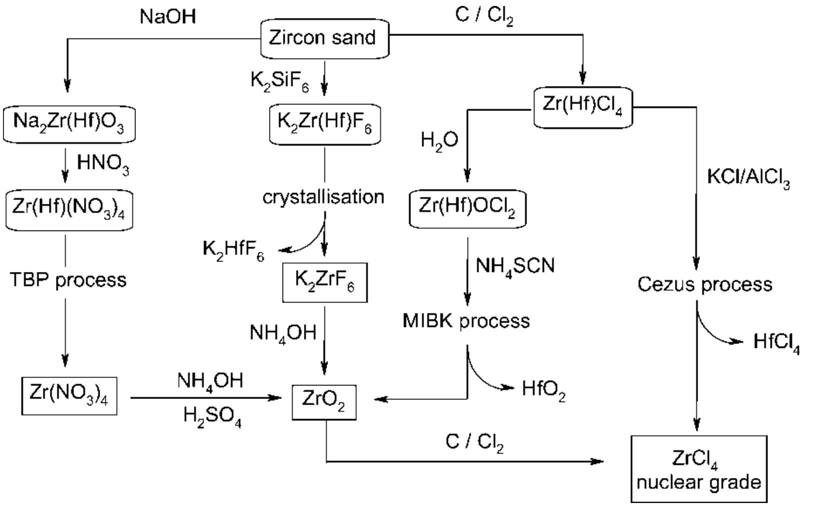

Figure 1. Established technologies for the separation of Zr and Hf.

$ZrCl_4 - HfCl_4$ mixture is converted to the mixture of their oxychlorides and is then processed through a multiple-step solvent extraction process in the presence of NH_4SCN. The hafnium is preferentially extracted as hafnyl thiocyanate using methyl isobutyl ketone (MIBK). The remaining aqueous solution is reacted with sulfuric acid to form the pentazirconyl sulfate, which is precipitated by adjusting the pH with ammonium hydroxide (3, 5). The zirconium hydroxide obtained was dried and calcinated to give Hf-free ZrO_2. A second chlorination leads to the pure $ZrCl_4$. The Cezus plant (Framatome AMP) is based on the extractive distillation with potassium chloroaluminate (mixture of $AlCl_3$ and KCl) as the solvent. The vapors of $ZrCl_4 - HfCl_4$ mixture rise in a counter flow against a descending solution of potassium chloroaluminate saturated with $ZrCl_4 - HfCl_4$ at 350°C. The stream of solvent going downward progressively loses its $HfCl_4$. The $ZrCl_4$ is stripped with nitrogen and is then cooled and condensed (3).

At the end of the 1950s, the USA and then France in 1970s abandoned the TBP process. The crystallization process is simpler and easier, however, it is a batch process. Recently, increasing environmental concern has appeared about the MIBK process due to MIBK solubility in water and flash point and decomposition of the thiocyanate in the presence of hydrochloric acid. Sophisticated technologies and energy consumption required for the extractive distillation process could lead to the search for new zirconium and hafnium separation processes (6). The development of an effective separation method still attracts the attention of many separation chemists; solvent extraction (4, 7), solid/liquid extraction (8–11), and alternative processes (12–15) have recently been proposed.

Chemistry of Zr(IV) and Hf(IV) in Aqueous Media

For both metals, the nature of existing species in aqueous solution is strongly influenced by polymerization and hydrolysis reactions. The chemistry of Zr in aqueous media is dominated by the complexation of Zr^{4+} with OH^-, and where the chloride forms outer-sphere complexes, i.e., $[Zr(OH)_n]^{(4-n)+}$ $(4 - n)Cl^-$ with $n = 1-5$ (16).

In liquid/liquid extraction, the extraction of Zr by using liquid cation exchangers, mostly organophosphorus acids, is quantitative at around 1 M HCl (17). This can be explained by the formation of cationic Zr species such as $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$ and $Zr(OH)_3^+$ (18). However, under these conditions, Zr and Hf show a high tendency to polymerize (19). The formation of polynuclear hydroxo-bridged compounds of Zr in acidic solutions ($[H^+] = 1-2\,mol \cdot L^{-1}$) occurred even in very dilute solutions ($10^{-3}-10^{-4}$ $mol \cdot L^{-1}$) (20) and the same trend was recently observed with Hf (21). Thus, the aqueous reactivity of the elements modify their interaction with the complexing agent (22) and the system has been found to be complicated by the slow change in the composition of the extractable aqueous species on ageing (23, 24).

An increase in hydrochloric acid concentration (up to 7 M) promotes depolymerization (25) while simultaneously hydroxide ions attached to Zr or Hf are displaced by chloride ions (26) to form inner-sphere complexes, Eq. (1) with M = Zr or Hf.

$$[\mathrm{M(OH)_n}]^{(4-\mathrm{n})} + \mathrm{iCl}^- + \mathrm{nH}^+ \leftrightarrows [\mathrm{MCl_i}]^{(4-\mathrm{i})} + \mathrm{nH_2O} \qquad (1)$$

with $i =$ 4, (26) 5, (18) or 6 (27–30).

Thus, at high hydrochloric acid concentration the extraction of Zr or Hf by neutral extractants, (6, 26, 29, 31) or by liquid anion exchangers (LAX) (28, 30, 32–35) is improved. El-Ammouri et al. have shown that the total chloride concentration is the predominant factor controlling Hf extraction, although there must be sufficient acid to prevent hydrolysis and oligomerization reactions (26).

The aqueous chemistry of Zr has been more extensively studied than that of Hf. However, due to their close chemical similarity, the expected behavior of dissolved Hf can often be deduced from the knowledge of analogous Zr solutions.

Some data on the extraction of Zr and Hf from chloride solutions with LAX are available in the literature (30, 32, 34, 36, 37) but most of the experiments have been made using Zr and/or Hf tracers (18, 28, 33, 37–39), a highly diluted solution (30) or with single metal solutions (18, 27, 40).

This paper discusses the liquid-liquid extraction characteristics of Zr and Hf from HCl solutions over a wide concentration range by Aliquat 336 and various parameters such as the kinetics of metal extraction, the nature of the diluent, the initial Zr/Hf ratio, and the stripping of metal from loaded organic phase. The nature of the extractable species has been investigated through a *log-log* analysis from single metal ion solution and from Zr-Hf solution.

EXPERIMENTAL

Materials and Reagents

$ZrCl_4/HfCl_4$ mixtures with different Zr/(Zr + Hf) molar ratio were kindly supplied by Cezus (Framatome-ANP), France. Zr(IV) and Hf(IV) standard solutions ($1000\,\mu g \cdot mL^{-1}$) were obtained from Alfa Aesar. Analytical grade HCl and NaOH standard solutions were obtained from Merck. Aliquat 336 was obtained from Aldrich, toluene and cyclohexane were analytical reagent grade (Acros), the industrial diluents Solvesso 150 (>99% aromatics) and Varsol 80 (25% aromatics) were obtained from ExxonMobil chemical. All organics were used without purification. Deionized water with a resistivity of $>18 M\Omega/cm$ (Milli-Q system, Millipore) was used throughout the experiments.

Extraction Procedure

Hydrochloric acid concentrations were determined by titration using standard NaOH solution. The aqueous phases were prepared by dissolving $ZrCl_4/HfCl_4$ mixtures in solutions containing from 0 to 12 M HCl in volumetric flasks. Known weights of Aliquat 336 (1 to 30% wt) were introduced in volumetric flasks and the diluent weighed to obtain the solvent. The solvent was then saturated with hydrochloric acid solutions having the same concentration as the one from which extraction was carried out. Extraction experiments were carried out at constant volume phase ratio 1:1. The aqueous and organic phases were placed in a flask and then shaken mechanically with a vibrax 100 (Bioblock scientific) shaker for an experimentally determined time required to reach extraction equilibrium. Then, the liquid phases were left to separate. The concentration of Zr and Hf in the aqueous phase was determined by ICP-AES (Spectro D or Jobin Yvon Ultima 2).

The extraction efficiency (*E*), distribution ratio (*D*) and separation factor (*S*) were calculated by using Equations 2 to 4, respectively where *C* refers to the metal concentration in the aqueous phase and the subscripts *i* nd *f* refer to initial and final conditions.

$$E = \frac{(C_i - C_f)}{C_i} \times 100 \tag{2}$$

$$D = \frac{(C_i - C_f)}{C_f} \tag{3}$$

$$S_{(Zr/Hf)} = \frac{D_{Zr}}{D_{Hf}} \tag{4}$$

RESULTS AND DISCUSSION

Kinetics of Metal Extraction

Initial experiments were carried out with a Zr solution containing high levels of Hf (Zr/(Zr + Hf) = 0.71) in 7 M HCl in order to improve the precision of the analysis of Hf (Fig. 2). The apparent equilibration time is 30 min., but 60 min. has been allowed subsequently to ensure equilibration for various experimental parameters.

Influence of HCl Concentration

The extraction of Zr and Hf was investigated with 5% wt Aliquat 336 in toluene over a range of aqueous phase acidity from 0 M to 12 M HCl at 25°C. The extraction of Zr and Hf increases with increasing acidity up-to 8 M for Zr and up-to 11 M for Hf (Fig. 3).

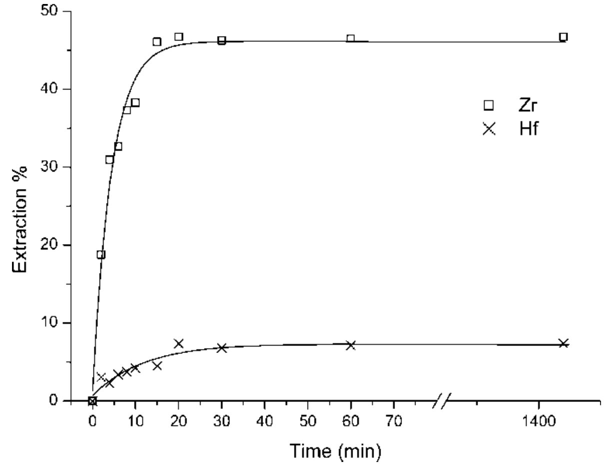

Figure 2. Effect of time on Zr and Hf extraction using 5%wt Aliquat 336 in toluene, [HCl] = 7 M at 25°C, phase ratio = 1. Zr/(Zr + Hf) = 0.71, $[Zr]_i = 2340\,mg \cdot L^{-1}$ and $[Hf]_i = 1800\,mg \cdot L^{-1}$.

The extraction process of Zr and Hf at high chloride concentration with Aliquat 336 may be assumed to be expressed by Eq. (5) were the bar denotes organic phase with M = Zr or Hf:

$$\overline{nR_4N^+Cl^-} + [MCl_i]^{(4-i)} + (i-4)H^+ \rightleftharpoons \overline{nR_4N^+H_{(i-4)}MCl_{i+n}} \quad (5)$$

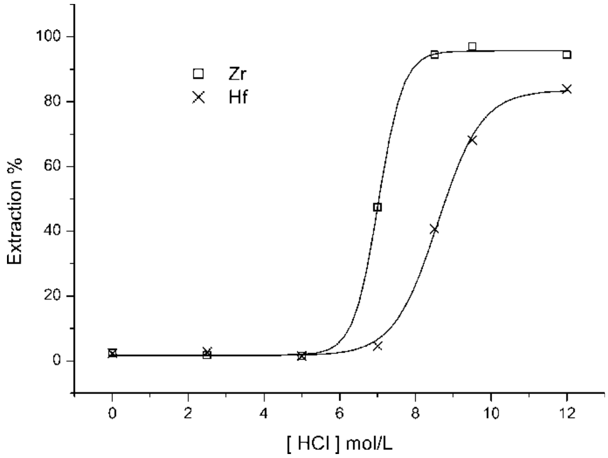

Figure 3. Effect of HCl concentration on Zr and Hf extraction using 5 wt % Aliquat 336 in toluene, phase ratio = 1. Zr/(Zr + Hf) = 0.71, $[Zr]_i = 2340\,mg \cdot L^{-1}$ and $[Hf]_i = 1800\,mg \cdot L^{-1}$ contact time: 60 min at 25°C.

It is also evident from Fig. 3 that Hf has a lower tendency than Zr to form anionic complexes. Thus, at 7 M HCl, Hf is not extracted ($<5\%$) by Aliquat 336 although Zr is extracted (50%) in the organic phase by the LAX. At high chloride concentration (>10 M), both Zr and Hf formed anionic complexes that are extracted by Aliquat 336.

These results, as well as the established processes (Fig. 1), could be rationalized by the Hard-Soft Acid-Base theory (HSAB) (41), Zirconium and hafnium are regarded as hard acids (42), however, values of absolute hardness calculated for Zr and Hf indicate that Hf is less hard than Zr (43). Indeed, in the TBP process, the hard TBP ligand extracts Zr preferentially. In the MIBK process, NCS^-, which is a soft base, forms preferentially a complex with Hf. The Hf complex is thus extracted by the MIBK in the organic phase. In the Cezus process, the hard base, Cl^-, will form inner-sphere complexes with $ZrCl_4$ (i.e., Eq. 1). Thus, $HfCl_4$ could be distilled from the melt. In the liquid/liquid extraction process using LAX, the hard base Cl^- will preferably form inner-sphere anionic complexes with Zr that are extracted in the organic phase by the LAX (Fig. 3).

Effect of Aliquat 336 Concentration

The influence of Aliquat 336 concentration in the organic phase on Zr and Hf separation was examined for 7 M HCl with toluene as solvent (Fig. 4).

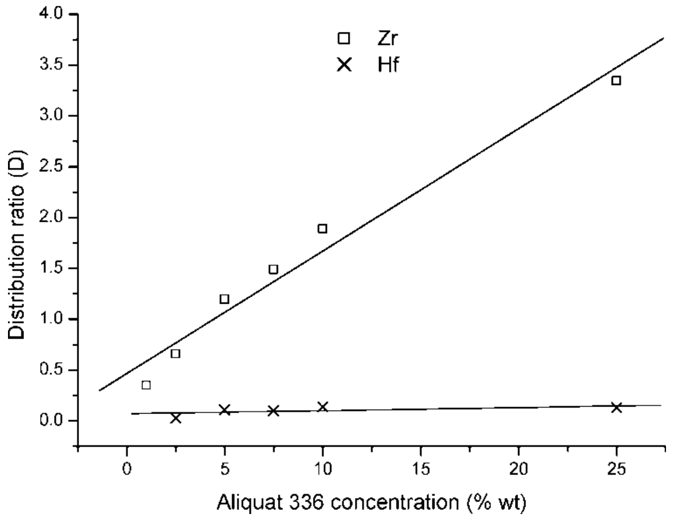

Figure 4. Effect of Aliquat 336 concentration in toluene on Zr and Hf distribution ratio. HCl 7M, phase ratio = 1. Zr/(Zr + Hf) = 0.71, $[Zr]_i = 2340\,mg \cdot L^{-1}$ and $[Hf]_i = 1800\,mg \cdot L^{-1}$ contact time: 60 min, 25°C.

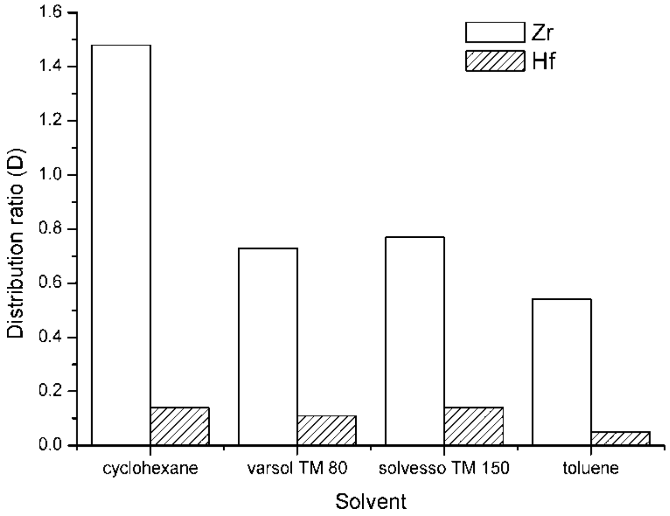

Figure 5. Effect of solvent on Zr and Hf distribution ratio and separation factor using 5% wt Aliquat 336; HCl 7M, phase ratio = 1. $Zr/(Zr + Hf) = 0.71$, $[Zr]_i = 2340\,mg \cdot L^{-1}$ and $[Hf]_i = 1800\,mg \cdot L^{-1}$ contact time: 60 min, 25°C.

A practically constant extraction of Hf was obtained when the concentration of Aliquat 336 was varied from 1 to 31% wt, although a large increase in Zr extraction was observed.

Effect of Organic Solvent

The extraction of Zr and Hf was performed with 5% wt Aliquat 336 in different diluents. Higher extractions and higher selectivities were observed for cyclohexane compared to aromatic diluents (Fig. 5). No difference was observed between Solvesso and Varsol, although the aromatic content was different, 25 and 99%, respectively. However, the formation of a third phase with cyclohexane was observed at high loading which was not observed with aromatic diluents. Thus, toluene has been selected as the diluent of Aliquat 336 for further Zr and Hf separation studies.

Stripping

Deionized water (pH ~ 5) can be used to strip Zr and Hf from the loaded organic solutions. The stripping is quantitative with an organic/aqueous phase ratio of 1 to 0.5 but at lower phase ratios the stripping was not quantitative (Table 1).

Table 1. Influence of the toluene/deionized water phase ratio on Zr and Hf stripping. Extraction: 5 wt% Aliquat 336 in toluene, phase ratio = 1. Zr/(Zr + Hf) = 0.71, $[Zr]_i$= 2340 mg · L^{-1} and $[Hf]_i$= 1800 mg · L^{-1} contact time: 60 min at 25°C. Stripping: deionized water, contact time: 60 min at 25°C

Org./Aq. ratio	Zr stripping (%)	Hf stripping (%)
1	>99	>99
0.5	>99	>99
0.2	95	96
0.1	93	95

Influence of Zr Purity

The influence of Zr/Hf ratio on the Zr/Hf selectivity was studied using 5% wt of Aliquat 336 in toluene. Within experimental error, the calculated selectivity was not influenced by the presence of Hf.

Mechanism of Loading Reaction

To ascertain the nature of the extracted species, we evaluated the distribution ratio (D) with the highest purity metal solution available i.e. Zr 99.98% wt (Zr/(Zr + Hf) = 0.9922) or Hf 99.999% wt (Zr/(Zr + Hf) = 0.0017) while varying the concentration of Aliquat 336 from 1 to 30 wt% in toluene (Figs. 6 and 7). Under our conditions (i.e. 7 M HCl), we were not able to determine the equilibrium concentration of free quaternary ammonium salts in the organic phase. Thus, the exact stoiechiometry of the extracted Zr and Hf species could not be determined. However, under comparable conditions the plots Log $D_{\text{metal ion}}$ *vs* Log of the concentration of Aliquat 336 obtained at a hydrochloric acid concentration of 7 M with single metal ion solution are straight lines whose slopes are equal to 1 within the limits of uncertainty (Figs. 6 and 7). This suggests that, for a single metal solution, the extraction of Zr or Hf from 7 M hydrochloric acid by Aliquat 336 takes place according to the same stoiechiometry. We performed the same experiment under the same experimental conditions with a mixture of Zr and Hf (Zr/(Zr + Hf) = 0.71) (Fig. 8). Under those conditions, the plots Log D_{metalion} *vs* Log of the concentration of Aliquat 336 are straight lines but the observed slopes are equal to 0.6 within the limits of uncertainty.

The data from Fig. 6 to Fig. 8 show that the mechanism of extraction of Zr and Hf from the Cl^- medium is dependent on the Zr/Hf ratio. A slope of 1 was obtained for a pure metal solution although a slope of 0.6 was obtained for both metals with a Zr/(Zr + Hf) molar ratio of 0.71. The change in the mechanism of extraction does not mean that the selectivity of extraction

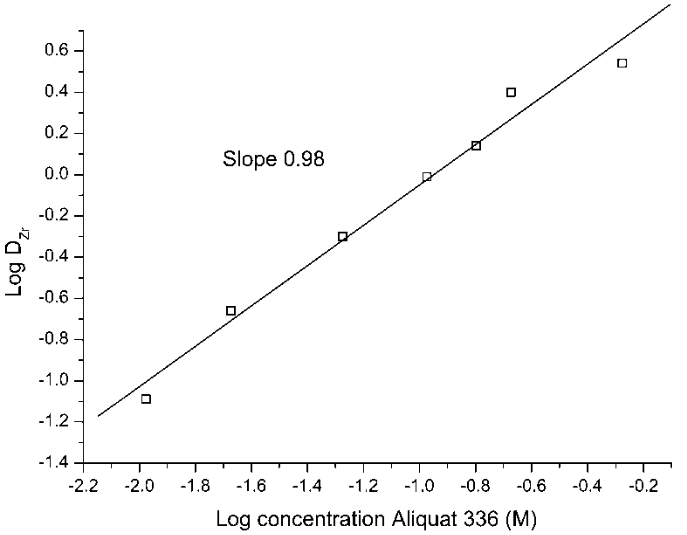

Figure 6. Logarithmic plot of D_{Zr} versus the total concentration of Aliquat 336 for the extraction of single metal Zr solution. Aliquat 336 in toluene, HCl = 7 M, phase ratio = 1. Zr/(Zr + Hf) = 0.9922 using $[Zr]_i = 3900\,mg \cdot L^{-1}$ and $[Hf]_i = 60\,mg \cdot L^{-1}$ contact time: 60 min at 25°C.

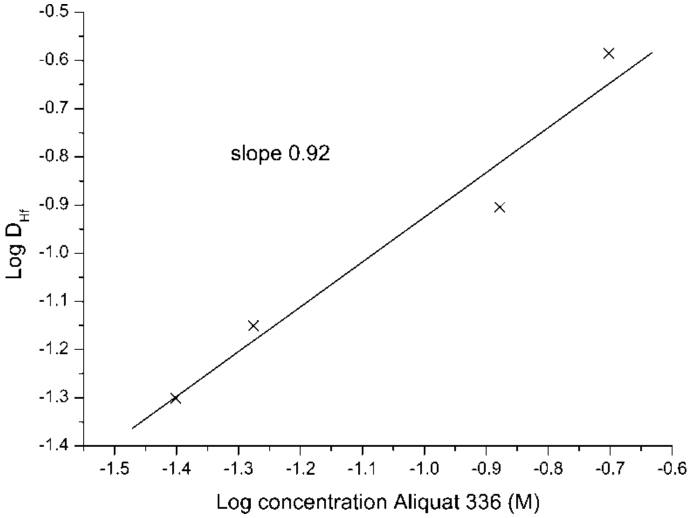

Figure 7. Logarithmic plot of D_{Hf} versus the total concentration of Aliquat 336 for the extraction of single metal Hf solution. Zr/(Zr + Hf) = 0.0017 using Aliquat 336 in toluene, HCl = 7 M, phase ratio = 1. $[Zr]_i = 5\,mg \cdot L^{-1}$ and $[Hf]_i = 5500\,mg \cdot L^{-1}$ contact time: 60 min at 25°C.

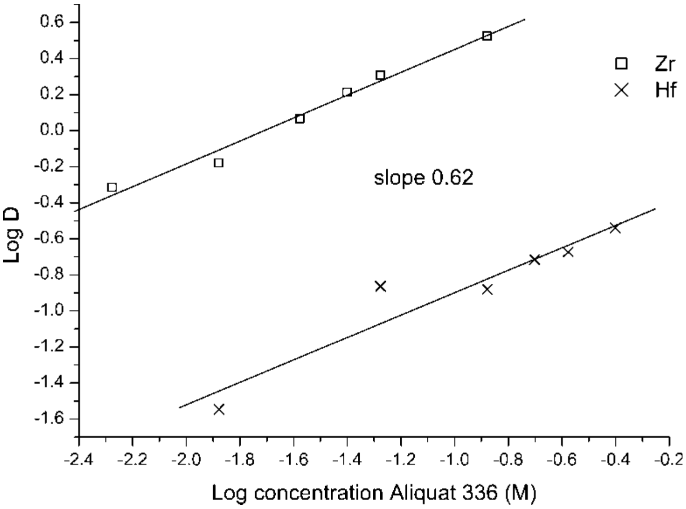

Figure 8. Logarithmic plot of D versus the total concentration of Aliquat 336 for the extraction of Zr/Hf mixture using Aliquat 336 in toluene, HCl = 7 M, phase ratio = 1. Zr/(Zr + Hf) = 0.71 $[Zr]_i = 2340\,mg.L^{-1}$ and $[Hf]_i = 1800\,mg \cdot L^{-1}$ contact time: 60 min at 25°C.

changes in function to the Zr/Hf ratio (see Table 2) but that the extraction process of Zr and Hf cannot be predicted from single metal solutions.

CONCLUSION

From the above results, it is observed that zirconium is extracted with Aliquat 336 in toluene by an anion exchange mechanism. By using the proposed process, it is possible to separate Zr from Hf. The separation requires loading of the zirconium and hafnium tetrachloride in concentrated hydrochloric acid, preventing the formation of polynuclear hydroxo-bridged

Table 2. Influence of Zr purity on the Zr/Hf separation factor using 5% wt Aliquat 336 in toluene, HCl 7 M, $[Zr]_i$ = constant = $2340\,mg \cdot L^{-1}$ and $[Hf]_i$ = variable, phase ratio = 1, contact time: 60 min., 25°C

Zr/(Zr + Hf) ratio	D Zr	D Hf	S Zr/Hf
0.71	1.21	0.11	11 ± 2
0.934	1.70	0.12	14 ± 2
0.986	1.56	0.13	12 ± 2
0.9994	1.63	0.16	10 ± 2

compounds. Zirconium is preferably extracted from hydrochloric acid solutions as an anionic complex. The effect of acid concentration and organic diluent on the separation parameters was examined in order to find the optimum conditions for the present separation system. However, the Zr/Hf system appears to be unique in that the stoiechiometry of the extracted Zr and Hf species from single metal ion solution seems to be different from that obtained with the Zr and Hf mixture. The next step in this study is to attempt to further identify the extracted species involved in these systems.

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