Liquid-Liquid Extraction of Zirconium And Hafnium Oxychloride By Aliquat 336

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Summary: Zirconium and hafnium co-exist in nature, but they have opposite nuclear characteristics. Thus, they have to be separated prior to their transformation into pure metals. Zirconium and hafnium are two of the most important nuclear materials, the chemical similarity of both elements in their metallic and compound states, is greater than that between any other homologous elements in the periodic table. In recent years, the problem of Zr/Hf has acquired significant importance. In this paper it is concerned with the optimum conditions for the extraction and separation of Zr/Hf using aliquat 336/kerosene and using isodecanol as a modifier to prevent the formation of the third phase. The optimum aliquat 336 concentration is 0.1mol/l and a contact time 10 minutes give an extraction efficiency of 93.4 % for Zr(IV) and 77 % for Hf(IV) at pH 1.9, the best diluent to use is kerosene at room temperature. All experiments were carried out at 1:1 organic: aqueous phase ratio.
 Keywords: Liquid-liquid extraction; Zirconium; Hafnium; Aliquat 336.

Introduction

Zirconium and hafnium co-exist in nature, they are two of the most important nuclear materials; the use of zircaloy in the construction of fuel elements and other structural components in reactor cores meets many physical and technological requirements. One advantage of Zr in nuclear applications is its low thermal neutron capture cross-section (0.18 *b/a*), whereas Hf has 640 times higher neutron absorption but they have opposite nuclear characteristics. Thus, they have to be separated prior to their transformation into pure metals. Continuous efforts have been made to develop new extractants for extraction and possible separation of zirconium and hafnium. Conventional solvent extraction technology uses TBP/HNO_3 or MIBK/NaSCN/ HNO_3 [1]. The chemical similarity of zirconium and hafnium, both in their metallic and compound states, is greater than that between any other homolgous elements in the periodic table (the atomic and ionic radii of Zr and Hf are identical: atomic radius: r= 1.45 Å, Hf = 1.44 Å; ionic radius Zr^{4+} = 0.74 Å, Hf^{4+} =0.75 Å [2].

Previous reports have used other extractants for zirconium and hafnium separation [3,4,5]. Among them the most successful has been Cyanex 925 which extracted 61% zirconium and 4% hafnium giving a separation factor 37 [4]. In this study the extraction behavior of zirconium and hafnium has been investigated with aliquat 336 as an alternative for Cyanex 925 and D2EHPA.

Experimental

Materials and chemicals

Aliquat 336, tri-n-octyl-monomethyl ammonium chloride [$(C_8H_{17})_3NCH_3Cl$] (molecular weight: 404.17) was obtained from Aldrich Chemical, USA. Odorless kerosene (non-aromatic) was obtained from Misr Petroleum Company, Egypt. The stock solutions of Zr(IV) and Hf(IV) were 1000 mg/l. All other chemicals were Prolabo products and were used as received.

Liquid-liquid extraction procedure

Batch experiments were carried out by equilibrating equal volumes of Aliquat 336 in kerosene in addition to 5 % isodecanol as modifier, with 6.21×10^{-3}M Zr(IV) and Hf(IV) as determined spectrophotometrically using Alizarin Red S and xylenol orange[6] respectively. The concentration of the Zr(IV) and Hf(IV) in the organic phase was obtained by mass balance. The distribution coefficient, Kd, was taken as the ratio of the concentration of Zr(IV) and HF(IV) in the organic phase to that in the aqueous phase. The separation factor, (SFsx), was calculated from the Eq. (1):

$$SFsx = \frac{Kd\ Zr}{Kd\ Hf} \qquad (1)$$

All the experiments were carried out at room temperature except when effect of temperature on the distribution equilibria was studied.

Results and discussion

Effect of aliquat 336 concentration

The effect of extractant concentrations on the extraction efficiency of Zr(IV) and Hf(IV) were studied in the range 0.02-0.15M at $25 \pm 1^\circ$C. Other

conditions maintained were, A:O ratio 1:1 at room temperature for 10 minutes to attain equilibrium state, the extraction percent of Zr(IV) and Hf(IV) increased steadily with increase in aliquat 336 concentration up to 0.1M. The increase was 70.22–92.12% for Zr(IV) and 60.34-77% for Hf(IV) when aliquat 336 concentration increased from 0.02 to 0.1 M due to the more available sites of extractant for the extraction of Zr(IV) and Hf(IV). Further increase in extractant concentration did not result in any significant increase in percentage extraction of Zr(IV) and HF(IV). In addition, the previous research indicated that the excessive amount of the extractant results in a decrease of the separation factor [7].
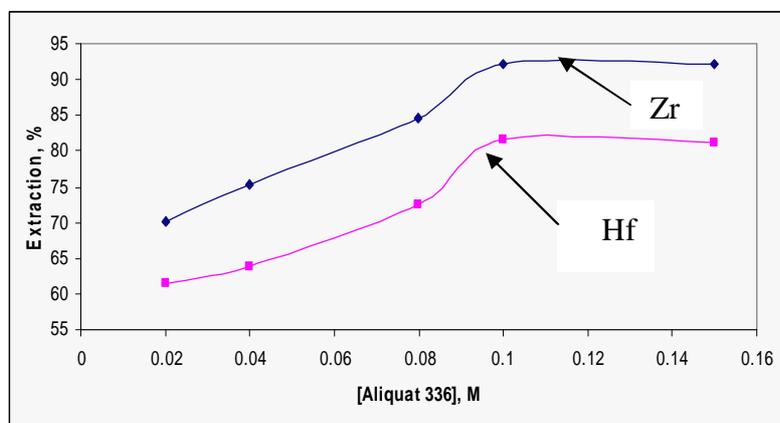

Fig.1. Effect of different concentrations of aliquat 336 on the extraction percent of

   Zr(IV) and Hf(IV).

Effect of equilibration time

The effect of equilibrium time (1-60 min) on the extraction of Zr(IV) was studied using 0.1M aliquat 336 in kerosene/isodecanol while other factors were kept as mentioned before. The results obtained are shown in Fig. 2; it is obvious that the time of 10 minutes is quite adequate for efficient Zr(IV) extraction. The extraction percent was increased from 1-10 minutes and after that slightly decreased may be due to the entrainment of some organic phase droplets into aqueous phase, which causes decrease in the extractive power of extractant.
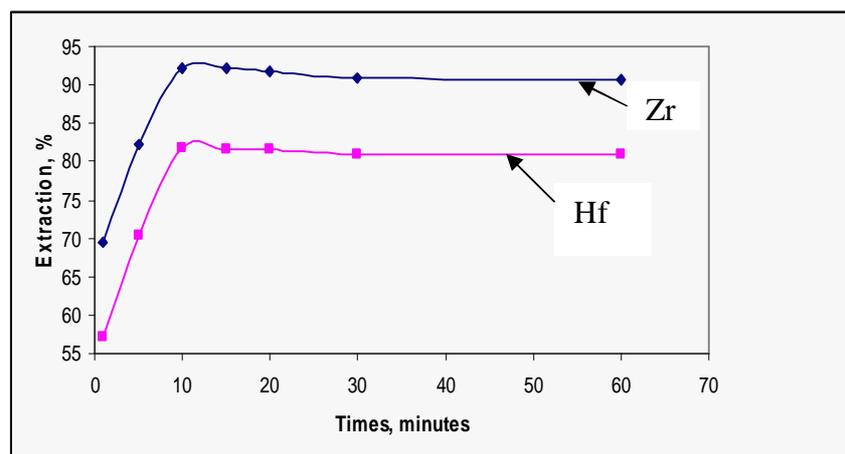
Fig. 2. Effect of contact time on the extraction percent of Zr(IV) and Hf(IV).

Effect of diluents

The diluents themselves are unable to extract metal ions from the aqueous phase, but they greatly affect the extraction behavior of the solvent. The reason is the various interactions that may take place between the diluent and the extractant ranging from that of cavity formation, dipole-dipole interaction, pi-electron interaction, and hydrogen bonding. This is probably due to lower solubility of the extracted species in these diluents as compared with kerosene. Also, probably a function of the different intermolecular diluent:diluent and solvent:diluent interactions that occur in aromatic and non-aromatic diluents. Further, one important factor influencing the extraction of metals by amines is the aggregation of the amine in the organic phase, which is determined essentially by the nature of the diluent [8]. Various aromatic and aliphatic solvents were tested as diluents for the extraction of Zr(IV) and Hf(IV) with 0.1M aliquat 336 in all diluents/isodecanol at an A:O ratio 1:1 for 10 minutes. The results are presented in Table 1. The extraction of Zr(IV) and Hf(IV) were maximum with kerosene, chloroform and carbon tetrachloride as diluents but benzene, p-xylene and toluene proved to be poor diluents. Short equilibrium time and good phase separation was achieved when aliphatic diluents were used compared to aromatic diluents. Considering several factors like cost, environmental and safety aspects and maximum Zr(IV) and Hf(IV) extraction efficiency, kerosene was preferred as the diluent for further Zr(IV) and Hf(IV) extraction studies.

Table (1): Extraction of Zr(IV) and Hf(IV) by aliquat 336 as a function of diluents

Diluents	Dielectric constant	Zr(IV) extraction percent, [%]	Hf(IV) extraction percent, [%]
Benzene	2.30	75.30	56.54
Toluene	2.23	72.36	62.76
P-Xylene	2.28	66.93	60.92
Chloroform	5.10	84.24	74.27
Carbon tetrachloride	2.23	76.69	72.57
Kerosene	2.00	97.52	81.66

0.1M aliquat 336; Phase ratio (Aq:Org) 1:1; time 10 min; room temperature.

Extraction as a function of pH

The percentage extraction of Zr(IV) and Hf(IV) from aqueous chloride medium were studied using 0.1M aliquat 336 in kerosene/isodecanol within the initial pH range 0.4-2.3. The aqueous:organic (A:O) phase ratio maintained was 1:1 and for 10 minutes. As shown in Fig. 3, the extraction of Zr(IV) and Hf(IV) increased with increase in aqueous pH and were reached maximum (94.86%, 81.73%) in the equilibrium pH 1.9 this shows that the equilibrium at that pH is favorable for the formation of ion-pair complex from chloride media, Zr(IV) and Hf(IV) extraction decreased when equilibrium pH was increased from 1.9 to 2.3, Zr(IV) extraction efficiency decreased from 94.86 to

90.45% in case of Hf(IV) extraction efficiency decreased from 81.73 to 74.84 % which may result from the formation of non-extractable metal species as a result of complication with components of aqueous phase.
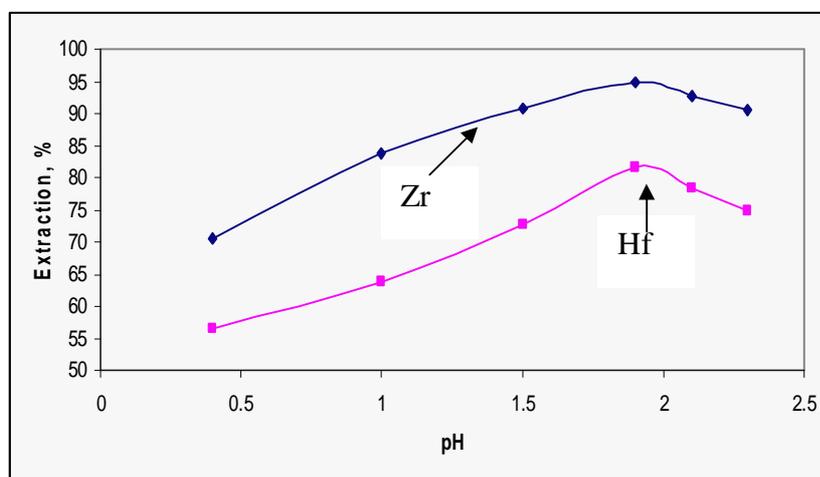

Fig. 3. Effect of pH on the extraction percent of Zr(IV) and Hf(IV).

Effect of stripping agents

Stripping is the reverse of the extraction, so it should be promoted by these factors that affect extraction negatively. Zr(IV) and Hf(IV) stripping from loaded organic solvent, were investigated using stripping agent, HCl, in the range 0.5−6M and A:O ratio of 1:1. The results are presented in Fig. 4. From the results, it is clear that 0.5M HCl is the most effective acid for the quantitative stripping of Zr(IV) in two stages. Zirconium ions can be stripped from zirconium-loaded aliquat 336 solution into 0.5M HCl, where 1M NaOH was added gradually to the obtained strip liquor rich in Zr(IV), $Zr(OH)_4$ is precipitated.
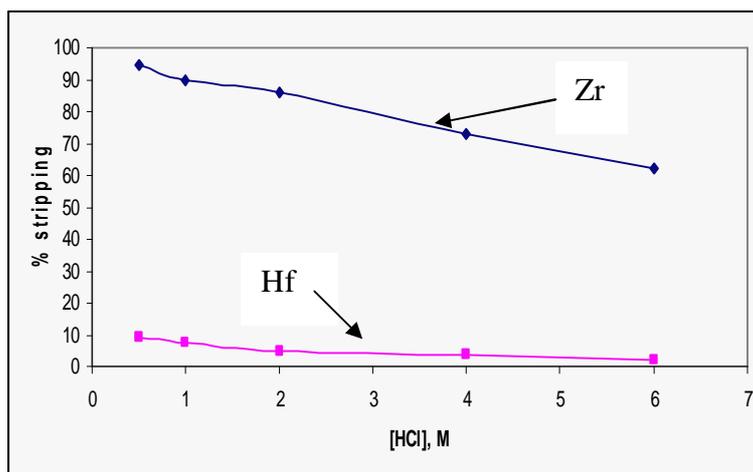
Fig. 4. Effect of different concentrations of HCl on the stripping efficiency of Zr(IV) and Hf(IV).

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