Selective Extraction of Zirconium (IV) from Hafnium (IV) Using Tri-n-Butylphosphate as Extractant

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ABSTRACT

The extraction of zirconium (IV) from hafnium (IV) using tri-n-butyl phosphate (TBP) in kerosene has been investigated. Different parameters affecting the extraction of Zr (IV) from Hf (IV) from nitrate solutions such as TBP, Zr (IV), HNO₃, nitrate, concentration, shaking time, as well as the effect of temperature were studied. The maximum extraction results were obtained at 6 M HNO₃ and 1 M Mg(NO₃)₂ which led to an extraction percentage of 99.7 % for Zr and 52.1 % for Hf. The extraction percent of Zr and Hf increased by increasing the shaking time, TBP, HNO₃, nitrate concentration and temperature. The stripping of the extracted zirconium and hafnium from the loaded organic solution was also carried out using different concentrations of HNO₃.

Key Words: Solvent extraction / tri-n-butylphosphate / Zirconium and Hafnium nitrate/ HNO₃, Mg(NO₃)₂.

INTRODUCTION

Transition earth metals such as zirconium and hafnium ores are found in the earth crust. The most common of these ores are zircon (zirconium silicate (ZrSiO₄) and baddiliite (Zirconia-ZrO₂) (3). The two elements are found in zircon at a ratio about 50 to 1. The mineral zircon is widely distributed in the earth’s crust as a component of igneous, metamorphic and sedimentary rocks and found in the form of heavy residues of rocks or beach sand. In fact, the beach sand zircon is usually associated with ilmenite, rutile, magnetite and monazite (2). Zircon is a co-product or byproduct of the mining and processing of heavy-mineral sand for the titanium minerals, ilmenite and rutile, or tin minerals (3). Zirconium (Zr) is an element having wide applications in modern technology. Among the applications of zirconium alloys, is their use in the nuclear area as structural materials. Due to the similarity of Zr and Hf in chemical and physical properties, hafnium (Hf) is commonly found in nature associated with zirconium minerals and the separation of them is difficult (4, 5). Zirconium is employed in nuclear reactors as a structural and a nuclear fuel cladding material owing to its excellent resistance to corrosion and low neutron absorption cross-section. On the other hand, hafnium is used as a control rod material in water cooled nuclear reactors and rectifiers (6). However, for the application of Zr in nuclear reactors it is necessary to lower the levels of Hf to less than 100 ppm. Therefore, the separation of these elements is of a great importance for the use of zirconium tubes containing nuclear fuel (3). In this context, the separation of zirconium and hafnium requires elaborated processes as: fractional crystallization, solvent extraction (7, 8), molten salt distillation (9) and ion exchange (10-12). Solvent extraction is an operation used in industry for purification, separation or concentration of several species; through this technique it is possible to separate various metals (13-15) and obtain products of high purity. Some studies in the literature report the use of solvent extraction with tri-butyl phosphate (TBP) for the separation of the pair Zr / Hf (16-20). It is known that TBP gradually undergoes destruction in acid medium with the formation of di-butylphosphoric acid (HDBP) from nitric acid solution as a main product of hydrolysis. The presence of HDBP in many extraction systems is a very negative factor because with some metals, specifically zirconium and hafnium, it forms very stable compounds which cause a definite difficulty in the extraction process and in the phase separation (21).
This compound can be decomposed or dissolved by the addition of complexing reagents such as solution of concentrated alkali, and hydrogen peroxide (22). To avoid the presence of an aggressive medium, the present work is directed to the addition of some salting out reagents such as Mg(NO₃)₂ and NaNO₃ as a trial for better separation of zirconium from hafnium from nitrate medium.

**EXPERIMENTAL**

**Chemicals and Reagents**

Most of the used chemicals are of analytical grade. The extractant tri-n-butyl phosphate (TBP) was obtained from Fluka. Odourless kerosene (non-aromatic) was obtained from Misr Petroleum Company, Egypt. The zirconium and hafnium nitrates are products of Prolabo.

**Procedure**

Stock solutions of zirconium and hafnium were prepared by dissolving the necessary amounts of Zr(NO₃)₄ and Hf(NO₃)₄ in double distilled water. The concentration of Zr and Hf in the aqueous phase was determined spectrophotometrically (23) using a Shimatzu UV-160A. Batch experiments were carried out by shaking equal volumes of 30% TBP in kerosene with 100 ppm Zr and Hf in aqueous solution of different concentrations of nitrate ions (NaNO₃ or Mg(NO₃)₂) and HNO₃ with ratio A/O = 1 in stoppered glass bottles using a thermostated shaking water bath adjusted at 25±1 °C. After equilibration and phase separation, a suitable volume of the aqueous phase was spectrophotometrically measured. The concentration of the metals in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after extraction. The distribution ratio D was calculated as the ratio of the concentration of ions in the organic to that in the aqueous phase at equilibrium. From the D values, the extraction percentage was obtained by using the relation Ex% = D x 100/[D + (Vaq/Vorg)] where Vaq and Vorg are the volume of aqueous and organic phases, respectively (24). Stripping percentage was calculated using the relation, % stripping = [C_s / (C_0 − C)] x 100, where C_0 is the original Zr or Hf ions concentration in the aqueous phase before extraction, C is the Zr or Hf ions concentration in the aqueous phase after extraction and C_s is the Zr or Hf ions concentration in the aqueous phase after stripping.

**RESULTS AND DISCUSSION**

**Effect of Extraction Time**

The effect of extraction time (5-120 min.) on the extraction of 100 ppm of either Zr or Hf from 1M Mg(NO₃)₂ and 3M HNO₃ solution by 30% TBP in kerosene is shown in Fig. (1). The extraction percent of Zr reaches equilibrium after 5 min., while that of Hf increase with increase in time till 30 min. after which it reaches equilibrium. This difference in equilibrium time for both metals could be used for their selective separation on kinetic basis (25).

![Fig. (1): Effect of shaking time on the extraction of 100 ppm Zr and 100 ppm Hf from 1 M Mg(NO₃)₂ and 3M HNO₃ solution using 30% TBP in kerosene](image)
Effect of TBP Concentration in Kerosene

The effect of TBP/kerosene concentration on the extraction of 100 ppm Zr and Hf ions from 1 M Mg(NO$_3$)$_2$ and 3M HNO$_3$ to the organic solution was studied in the range 2.5-35%. The results shown in Fig. (2) illustrate that the extraction percent of both elements increased with increasing TBP concentration and reaches maximum at a TBP concentration of 35%. The extraction percentage of both elements were calculated and are listed in Table (1). The TBP ratio 30% was used during all experiments.

![Fig. (2): Effect of TBP concentration in kerosene on the extraction of 100 ppm Zr and Hf from 1 M Mg(NO$_3$)$_2$ and 3 M HNO$_3$ solution](image)

**Table (1):** The Percentage of extraction of 100 ppm zirconium and 100 ppm hafnium with different concentrations of TBP in kerosene from 1M Mg(NO$_3$)$_2$ and 3 M HNO$_3$ solution

<table>
<thead>
<tr>
<th>TBP in kerosene (%)</th>
<th>% extraction of Zr ions</th>
<th>% extraction of Hf ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>9.66</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>19.68</td>
<td>10</td>
</tr>
<tr>
<td>25</td>
<td>40.61</td>
<td>15</td>
</tr>
<tr>
<td>30</td>
<td>68.16</td>
<td>20</td>
</tr>
<tr>
<td>35</td>
<td>71.38</td>
<td>25</td>
</tr>
</tbody>
</table>

Effect of Nitric Acid Concentration:

The effect of nitric acid concentration (0.5-6M) on the extraction of Zr and Hf from 1 M Mg(NO$_3$)$_2$ solution in aqueous phase by 30% TBP in kerosene is shown in Fig. (3). This figure indicates that the extraction for both elements increases with increasing nitric acid concentration \(^{(26)}\). The maximum extraction percentage for Zr and Hf ions was obtained at 6 M HNO$_3$ and reaches about 99.5 % of Zr(IV) together with 52 % of Hf (IV), the data are also listed in Table (2).
Fig. (3): Effect of HNO$_3$ concentration on the extraction of 100 ppm Zr and Hf from 1 M Mg(NO$_3$)$_2$ using 30% TBP in kerosene

Table (2): The percent of extraction of 100 ppm Zr and Hf from 1M Mg(NO$_3$)$_2$ and different concentrations of nitric acid solution using 30% TBP/ kerosene

<table>
<thead>
<tr>
<th>Concentration of HNO$_3$ (M)</th>
<th>% extraction of Zr ions</th>
<th>% extraction of Hf ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>47</td>
<td>5</td>
</tr>
<tr>
<td>1.0</td>
<td>52</td>
<td>7.7</td>
</tr>
<tr>
<td>2.0</td>
<td>62</td>
<td>12.8</td>
</tr>
<tr>
<td>3.0</td>
<td>68</td>
<td>20</td>
</tr>
<tr>
<td>3.5</td>
<td>70</td>
<td>32.8</td>
</tr>
<tr>
<td>4.0</td>
<td>76</td>
<td>41.9</td>
</tr>
<tr>
<td>5.0</td>
<td>90</td>
<td>48.5</td>
</tr>
<tr>
<td>6.0</td>
<td>99.5</td>
<td>52.1</td>
</tr>
</tbody>
</table>

Effect of Nitrate Concentration

The effect of sodium or magnesium nitrate concentration (0.25-2 M) on the extraction of Zr and Hf from 3 M HNO$_3$ solution by TBP in kerosene is shown in Figs.(4A-B). From these figures, it is clear that no significant extraction was observed for both elements in case of using NaNO$_3$ in the aqueous phase. Meanwhile, the extraction % for both elements increased with the increase in Mg(NO$_3$)$_2$ concentration. This may be due to that Mg ions suppress the hydrolysis and condensation of either zirconium and hafnium ions which facilitates the extraction of these ion complexes into the organic phase $^{27}$. The maximum extraction percent for Zr and Hf ions was obtained at 2 M Mg(NO$_3$)$_2$ concentrations.
**Fig. (4):** Effect of nitrate ion concentration on the extraction of (A) 100 ppm Zr and (B) 100 ppm Hf from 3M HNO₃ solution using 30% TBP in kerosene

**Table (3):** The percentage of extraction of 100 ppm zirconium and hafnium from 3M HNO₃ solution at different concentrations of magnesium nitrate using 30% TBP / kerosene

<table>
<thead>
<tr>
<th>Concentration of Mg(NO₃)₂ (M)</th>
<th>% extraction of Zr ions</th>
<th>% extraction of Hf ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>28.9</td>
<td>2</td>
</tr>
<tr>
<td>0.50</td>
<td>48</td>
<td>3.5</td>
</tr>
<tr>
<td>0.75</td>
<td>52.7</td>
<td>10.5</td>
</tr>
<tr>
<td>1.00</td>
<td>68</td>
<td>20</td>
</tr>
<tr>
<td>1.25</td>
<td>85.3</td>
<td>25</td>
</tr>
<tr>
<td>1.50</td>
<td>86.3</td>
<td>28</td>
</tr>
<tr>
<td>2.00</td>
<td>96.9</td>
<td>30</td>
</tr>
</tbody>
</table>

Table (3) shows that a maximum extraction of about 97% for zirconium together with about 30% of hafnium was obtained at 2M Mg(NO₃)₂ concentration. Since it is not preferred to use a relatively concentrated acid, it is recommended to use 3M HNO₃ solution containing 2M Mg(NO₃)₂ for separation of about 97% of Zr(IV) together with 30% of Hf(IV) as given in Table (3).

**Effect of Metal Ions Concentration**

The effect of the initial ions concentration was performed in the concentration range 25-200 ppm at 25°C for the extraction of Zr and Hf from 1 M Mg(NO₃)₂ and 3 M HNO₃ in solution by 30% TBP in kerosene. From the results shown in **Fig. (5)**, it is clear that the extraction percent of the two elements decreased with increasing the initial ions concentration, which may be due to the formation of other zirconium or hafnium species which are not extracted or the insufficient capacity of the used TBP concentration (28). The maximum extraction percent was obtained for 25 ppm of Zr (100%) and Hf (50%).
Fig. (5): Effect of metal ions concentration on the extraction of Zr and Hf from 1 M Mg(NO$_3$)$_2$ and 3M HNO$_3$ solution using 30% TBP in kerosene

3.6 Effect of Temperature

The effect of temperature on the extraction of 100 ppm Zr and Hf from 1 M Mg(NO$_3$)$_2$ and 3M nitric acid by 30% TBP in kerosene was investigated in the range 15 – 45°C. The results represented in Fig. (6) show the increase in the extraction process with the increase in temperature from 15 to 25°C followed by a continuous decrease in ions extraction at the higher temperature, therefore, the extraction of both ions was carried out at 25°C.

Fig. (6): Effect of temperature on the extraction of 100ppm Zr and Hf from 1 M Mg(NO$_3$)$_2$ and 3 M HNO$_3$ solution using 30% TBP in kerosene

Applying Van’t Hoff equations, the thermodynamic parameters, ΔH°, ΔS° and ΔG° were found to be 4.305 kJ·mole$^{-1}$ and 18.22 mole$^{-1}$ JK$^{-1}$·500.4 kJ/mole for zirconium and 5.882 kJ·mole$^{-1}$ and 4.5 mole$^{-1}$ JK$^{-1}$·5477.6 kJ/mole for hafnium. The temperature effect on both metals extraction could be
evaluated in terms of their thermodynamic parameters as the positive values of the enthalpy change ($\Delta H$) for both zirconium and hafnium indicate that the extraction process is endothermic and the positive entropy change ($\Delta S$) indicates the increase in the randomness of the system during extraction. The negative value of the free energy change ($\Delta G^\circ$) in case of zirconium indicates that the reaction is spontaneous and the extraction process is facilitated.

**Stripping**

The loaded organic phase was stripped by the back extraction of the metals to the aqueous phase which is required for commercial extraction processes. Regeneration of the solvent was achieved by treating the solvent with acid or alkali solution. Stripping investigations of Zr and Hf from the loaded organic solution indicated that Zr and Hf could be stripped using different concentrations of nitric acid (0.01-0.5M). Complete stripping of Zr and Hf from the loaded TBP/kerosene solution was reached when using the mentioned concentrations of acid.

**CONCLUSIONS**

- TBP could extract Zr (IV) and Hf (IV) from aqueous HNO$_3$ acid medium containing Mg (NO$_3$)$_2$.
- The increase in nitric acid and nitrate ion concentration increased the extraction of Zr (IV) and Hf (IV).
- The extraction equilibrium of Zr (IV) was reached after 5 min., while the extraction equilibrium of Hf (IV) was reached after 30 min.
- The increase in temperature increased the extraction of Zr (IV) and Hf (IV).
- The thermodynamic parameters were calculated for the two elements. The positive values of the enthalpy change ($\Delta H$) for both zirconium and hafnium indicate that the extraction process is endothermic and the positive entropy change ($\Delta S$) indicates the increase in the randomness of the system during extraction. The negative value of the free energy change ($\Delta G^\circ$) in case of zirconium indicates that the reaction is spontaneous and the extraction process is facilitated.
- Zirconium and Hafnium ions could be stripped from the loaded organic solution using nitric acid, and complete stripping was obtained when using 0.01 M nitric acid. Based on the obtained results, the optimum conditions for good separation of Zr from Hf using TBP in kerosene are as follows: aqueous medium, 3M HNO$_3$ + 2M Mg(NO$_3$)$_2$, time of shaking is 5 min. and temperature of 25°C.

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