

## 황산용액에서 양이온계 추출제 및 TBP와의 혼합추출제에 의한 지르코늄(IV)과 haf늄(IV)의 용매추출

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### Solvent Extraction of Zr(IV) and Hf(IV) from Sulfuric Acid Solutions by Acidic Extractants and Their Mixtures with TBP

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#### 요 약

황산용액에서 양이온 추출제인 Versatic acid, LIX 63 및 Cyanex 301을 사용하여 지르코늄(IV)과 haf늄(IV)의 분리실험을 수행했다. 진한 황산용액에서 Versatic acid와 LIX 63으로 두 금속을 분리할 수 없으나, Cyanex 301에 haf늄(IV)이 선택적으로 추출되었다. 그러나 Cyanex 301에 의한 두 금속의 추출율은 D2EHPA에 비해 매우 낮았다. TBP를 Cyanex 301과 D2EHPA에 혼합하면 두 금속의 추출과 분리에 역효과를 보였다. 염산, 질산 및 황산용액에서 상기 추출제에 의한 두 금속의 추출반응과 분리효율의 차이점을 고찰하였다.

**주제어** : 지르코늄, haf늄, 분리, 황산, 양이온계 추출제

#### Abstract

Separation of Zr(IV) and Hf(IV) from sulfuric acid solutions was investigated by extraction with several acidic extractants such as Versatic acid, LIX 63, and Cyanex 301. From strong sulfuric acid solutions, the separation of Zr(IV) and Hf(IV) by Versatic acid and LIX 63 was not possible, while selective extraction of Hf(IV) over Zr(IV) was obtained with Cyanex 301. However, the extraction percentage of the two metals was much lower compared to that by D2EHPA. Mixing of TBP with Cyanex 301 and D2EHPA led to negative effect on the extraction and separation of the two metal ions. The difference in the extraction reaction and separation selectivity between HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> media with each extractant was discussed.

**Key words** : Zirconium, Hafnium, Separation, Sulfuric acid, Acidic extractants

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## 1. Introduction

Zirconium and hafnium are normally associated together in nature as the minerals, zircon ( $ZrSiO_4$ ) and baddeleyite ( $ZrO_2$ ).<sup>1)</sup> Although their chemical properties are almost identical, they exhibit opposite nuclear characteristics. In nuclear applications, zirconium has low thermal neutron capture cross-section, while the neutron absorption capacity of hafnium is 640 times stronger than that of zirconium.<sup>2)</sup> As a nuclear material, zirconium should have a very low content of hafnium less than 100 ppm.<sup>3)</sup> Therefore the separation of hafnium from zirconium is very important in the manufacture of nuclear grade zirconium. At present, solvent extraction is commercially used to separate the two metals.

Conventionally, two different solvent extraction techniques are employed for the separation of Zr(IV) and Hf(IV): (1) MIBK – thiocyanic - hydrochloric acid process;<sup>4,5)</sup> and (2) TBP - nitric acid process.<sup>6,7)</sup> Hf(IV) is preferentially extracted over Zr(IV) as hafnyl thiocyanate in the MIBK process, while TBP has a selectivity for Zr(IV). In developing a separation process, selective extraction of a minor element (Hf(IV)) from major one (Zr(IV)) is more desirable in terms of economics. Up to now, Zr(IV) is selectively extracted into organic phase over Hf(IV) in most of the reported separation systems, except MIBK separation system. Nonetheless, MIBK process has some disadvantages, such as high aqueous solubility and low flash point of the solvent (MIBK) and environmental issues of the cyanide by-products.<sup>8)</sup> This motivates researchers to develop a new process to selectively extract Hf(IV) over Zr(IV).

The investigation on the separation and extraction behavior of Zr(IV) and Hf(IV) from hydrochloric, nitric and sulfuric acid solutions by using cationic, neutral and amine-based extractants have been investigated in our previous work.<sup>8-15)</sup> Based on this work, it was demonstrated that Zr(IV) is selectively extracted over Hf(IV) from strong hydrochloric or nitric acid solutions by cationic, neutral and amine extractants.<sup>9-13)</sup> On the other hand, selective extraction of Hf(IV) over Zr(IV) occurs from only strong sulfuric acid solutions (1- 4 M) by using acidic organophosphorus extractants.<sup>8,14)</sup>

In this work, solvent extraction experiments were carried out from sulfuric acid solutions by using several acidic extractants, such as Versatic acid, LIX 63, Cyanex 301 and their mixtures with TBP. Moreover, the extraction reactions and separation selectivity between Zr(IV) and Hf(IV) from hydrochloric, nitric and sulphuric acid solutions were also discussed.

## 2. Experimental

### 2.1. Materials

The commercial extractants Versatic acid, Cyanex 301 were purchased from Cytec Canada Inc. LIX 63 was purchased from BASF CO., and TBP was supplied by Yakuri pure chemical Co., Ltd. These reagents were used without any further purification. Kerosene (Daejung Chemicals and Metals CO., Ltd., Korea) was used as a diluent and all the other chemicals used were of analytical grade. The mixed feed solutions of Zr(IV) and Hf(IV) was prepared by dissolving the necessary amounts of  $Zr(SO_4)_2 \cdot 4H_2O$  (Alfa Aesar, Johnson Matthey Company, 98+%) and  $Hf(SO_4)_2$  (Alfa Aesar, Johnson Matthey Company, 99.9%) in doubly deionized water. In our experiments, the concentration of Zr(IV) and Hf(IV) in the stock solutions was kept at 0.2 g/L. Reagent  $H_2SO_4$  was used to adjust the acidity of the solution. Since the composition of Zr(IV) and Hf(IV) may continuously change owing to hydrolysis and polymerization reaction,<sup>16)</sup> freshly prepared solutions of Zr(IV) and Hf(IV) were used in these experiments.

### 2.2. Methods

The general extraction and stripping experiments were carried out by shaking equal volumes (20 mL) of the aqueous and organic phases for 30 min in a 100 mL screwed cap bottle using a wrist action shaker (Burrell model 75, USA). After equilibrium, the contents were allowed to undergo phase disengagement. All the extraction experiments were carried out at ambient temperature. The concentration of metal in the aqueous phase was measured by ICP-OES (Spectro Arcos). The concentration of metal in the organic phase was obtained by mass balance. The extraction percentage was

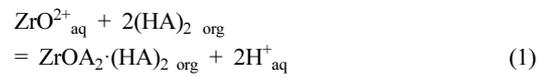
calculated as the ratio of the mass of metal extracted into the organic phase to the initial mass of metal in the aqueous phase before extraction.

### 3. Results and Discussion

#### 3.1. Solvent extraction of Zr(IV) and Hf(IV) by Versatic acid

Experiments were performed to test the extraction and separation behavior of Zr(IV) and Hf(IV) from 0.1 to 3 M sulfuric acid solutions with several acidic extractants, such as Versatic acid, LIX 63 and Cyanex 301. In these experiments, the concentration of Zr(IV) and Hf(IV) in the aqueous solutions was kept at 0.2 g/L. The extraction results by using 0.1 M Versatic acid and LIX 63 are displayed in Table 1. Table 1 indicated that the extraction efficiency of Zr(IV) and Hf(IV) was low with both Versatic acid and LIX 63 in the sulfuric acid concentration ranges employed in this work. For Versatic acid, the extraction percentage of Zr(IV) and

Hf(IV) at 0.1 M sulfuric acid concentration was 12.1 and 17.3%, respectively, and then decreased to nearly nil with the further increase of H<sub>2</sub>SO<sub>4</sub> concentration. Moreover, it is noticed that the percentage extraction of Hf(IV) seemed to be higher than that of Zr(IV) by Versatic acid. Lee et al. reported<sup>17)</sup> that Zr(IV) and Hf(IV) could be extracted by Versatic acid following cation exchange extraction mechanism from dilute hydrochloride solutions (pH around 2), as shown in Table 2. The extraction reaction with Versatic acid was suggested to be as:<sup>17)</sup>



where (HA)<sub>2</sub> represents dimeric form of Versatic acid.

In previous work,<sup>15)</sup> poor extraction of Zr(IV) and Hf(IV) by Versatic acid is also observed from 1 to 4 M strong HCl solutions. It might be inferred that the extraction of Zr(IV) and Hf(IV) by Versatic acid follows cation exchange reaction from both chloride and sulfate solutions. In the extraction of metal ions from strong acid solutions, the dissociation of Versatic acid is depressed and thus Zr(IV) and Hf(IV) were not extracted efficiently.

#### 3.2. Solvent extraction of Zr(IV) and Hf(IV) by LIX 63

In the case of chelating extractant - LIX 63, the extraction percentage of both Zr(IV) and Hf(IV) was

**Table 1.** Extraction of Zr(IV) and Hf(IV) from H<sub>2</sub>SO<sub>4</sub> solutions with 0.1 M Versatic acid and LIX 63 in kerosene

[H <sub>2</sub> SO <sub>4</sub> ], M	0. 1M Versatic acid		0. 1M LIX 63	
	Zr-%EX	Hf-%EX	Zr-%EX	Hf-%EX
0.1	12.1	17.3	2.7	3.6
0.5	1.4	3.2	0.9	1.3
1	1.1	0.2	0.1	0
2	0.4	0.1	1.3	0.6
3	0.1	0	0	0

**Table 2.** Extraction and separation behaviours of Zr(IV) and Hf(IV) from various media with Versatic acid and LIX 63

Extractant	Media	Acidity	Extraction mechanism	Selectivity	Ref.
Versatic acid	HCl	pH=1.4-2.3	Cation exchange	-	16
		1-4 M	Low extraction efficiency		17
	HNO <sub>3</sub>	-	-	-	-
	H <sub>2</sub> SO <sub>4</sub>	0.1-3 M	Cation exchange	Hf over Zr	This work
LIX 63	HCl	1-4 M	Low extraction efficiency		10
	HNO <sub>3</sub>	0.5-4 M	Solvation	Zr over Hf	12
	H <sub>2</sub> SO <sub>4</sub>	0.1-3 M	Low extraction efficiency		This work

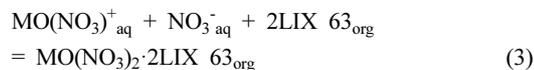
**Table 3.** Chemical structures and pK<sub>a</sub> values for the acidic extractants

Extractant	Structure	pK <sub>a</sub>
Versatic acid	$\begin{array}{c} R_1 \\   \\ R_2-C-COOH \\   \\ R_3 \end{array}$	4.8
LIX 63	$\begin{array}{c} R'' \\   \\ R'-C-C-R'' \\   \quad \quad \quad    \\ O \quad \quad \quad N \\   \quad \quad \quad / \quad \backslash \\ H \quad \quad \quad O \quad \quad H \end{array}$	7.33
Cyanex301	$\begin{array}{c} R \\ \diagup \\ P \\ \diagdown \\ R \end{array} \begin{array}{c} S \\ / \\ SH \end{array}$	2.61
D2EHPA	$\begin{array}{c} RO \\ \diagup \\ P \\ \diagdown \\ RO \end{array} \begin{array}{c} O \\    \\ O \\   \\ OH \end{array}$	3.24

\*R is the alkyl groups.

negligible in the sulfuric acid concentration range employed in this work (Table 1). The extraction results obtained from strong H<sub>2</sub>SO<sub>4</sub> solutions are consistent with those from strong HCl solutions.<sup>15)</sup> Table 2 indicates that the extraction percentage of both Zr(IV) and Hf(IV) from these two acidic solutions was low. The acid dissociation constant (pK<sub>a</sub> value) of LIX 63 is 7.33 (Table 3). It is the highest value among the listed acidic extractants, indicating that the dissociation of LIX 63 in aqueous phase is more difficult than that of others. If cation exchange is responsible for the extraction reaction in chloride and sulfate media, the low extraction efficiency obtained from strong H<sub>2</sub>SO<sub>4</sub> and HCl solutions by LIX 63 might be plausible.

However, a different extraction behaviour of Zr(IV) and Hf(IV) by LIX 63 was observed from nitric acid solutions. Wang et al. reported<sup>12)</sup> that Zr(IV) was selectively extracted over Hf(IV) by LIX 63 from 0.5 to 4 M HNO<sub>3</sub> solutions; and solvation reaction is responsible for the extraction. The extraction reaction for Zr(IV) and Hf(IV) by LIX 63 from nitric acid solutions can be represented as:<sup>12)</sup>

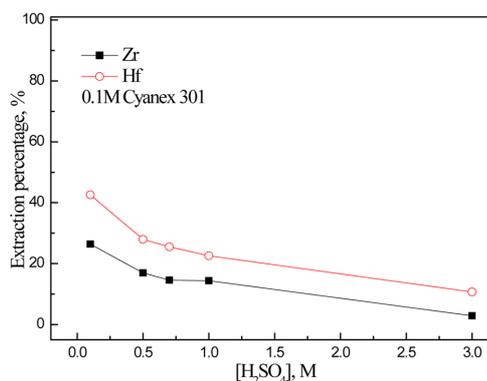


where MO(NO<sub>3</sub>)<sup>+</sup> represents monovalent cationic species of Zr(IV) or Hf(IV) in HNO<sub>3</sub> solution.

Since Zr(IV) and Hf(IV) have high charge and small radius, they have a great tendency to form complexes with anions in aqueous solutions. In strong acidic solutions, Zr(IV) and Hf(IV) form diverse complexes with Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, respectively.<sup>18,19)</sup> The difference in the extraction behaviour with hydrochloric, nitric and sulfuric acid solutions might be ascribed to the difference in the complex formation behaviour of the metal ions with each anion in the aqueous phase.

### 3.3. Solvent extraction of Zr(IV) and Hf(IV) by Cyanex 301

Cyanex 301 is one kind of dithiophosphinic acid extractant. The effect of H<sub>2</sub>SO<sub>4</sub> concentration on the extraction and separation of Zr(IV) and Hf(IV) using 0.1 M Cyanex 301 is depicted in Fig. 1. As shown in this figure, extraction percentage of both metal ions decreased with the increase of H<sub>2</sub>SO<sub>4</sub> concentrations from 26.4 to 2.9% for Zr(IV) and from 42.6 to 10.7% for Hf(IV), respectively. In terms of separation of Zr(IV) and Hf(IV), Hf(IV) was selectively extracted over Zr(IV) in the sulfuric acid concentration range of 0.3 to 3 M. But high separation efficiency between Zr(IV) and Hf(IV)



**Fig. 1.** Extraction of Zr(IV) and Hf(IV) from H<sub>2</sub>SO<sub>4</sub> solutions by 0.1 M Cyanex 301 in kerosene

**Table 4.** Extraction and separation behaviours of Zr(IV) and Hf(IV) from various media with Cyanex 301

Extractant	Media	Acidity	Extraction mechanism	Selectivity	Ref.
Cyanex 301	HCl	0.005-0.1 M	Cation exchange	Hf over Zr	20,21
	HNO <sub>3</sub>	-	-	-	-
	H <sub>2</sub> SO <sub>4</sub>	0.1-3 M	Cation exchange	Hf over Zr	This work

was not attained by using Cyanex 301 in H<sub>2</sub>SO<sub>4</sub> solution. A comparison of the extraction and separation behaviour from various acidic solutions by using Cyanex 301 is displayed in Table 4. Extraction behavior of Zr(IV) and Hf(IV) with Cyanex 301 from HCl solutions has been investigated.<sup>20,21)</sup> Cation exchange reaction is responsible for the extraction of Zr(IV) and Hf(IV) by Cyanex 301 from HCl solution:<sup>20,21)</sup>



where M represents Zr or Hf and HB refers to the monomeric form of Cyanex 301.

In this study, the decrease in the extraction with the increase of the sulfuric acid concentration implied that cation exchange is also responsible for the extraction by Cyanex 301 from strong sulfuric acid medium.

Table 3 shows the chemical structures and the pK<sub>a</sub> values of several acidic extractants. The pK<sub>a</sub> values increase in the order of: Cyanex301 < D2EHPA < Versatic acid < LIX 63, implying that the dissociation of Cyanex 301 and D2EHPA can take place in stronger acidic solutions compared to Versatic acid and LIX 63. The extraction results obtained from this work and reported work indicate that Zr(IV) and Hf(IV) could be extracted by Cyanex 301 and D2EHPA from strong sulfuric acid solutions, while the extraction by using Versatic acid and LIX 63 is difficult. It is in good agreement with the sequence of pK<sub>a</sub> values.

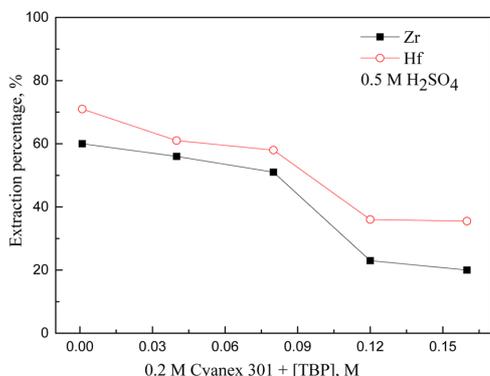
The extraction efficiency of D2EHPA for Zr(IV) and Hf(IV) is higher than that of Cyanex 301. The extraction percentage of Zr(IV) and Hf(IV) was around 20% by extraction with 0.1 M Cyanex 301 from 1 M sulfuric acid solution, while quantitative extraction of both metal ions was obtained with 0.05 M D2EHPA under the same condition.<sup>8)</sup> In terms of the chemical structure,

the functional groups of Cyanex 301 and D2EHPA are in the thiophosphoryl group (-PSSH) and phosphoryl group (-POOH), respectively. They are powerful electron-donating groups. However, oxygen belongs to hard Lewis base, while sulfur is a soft base. On the basis of the HSAB theory, Zr(IV) and Hf(IV) are classified as hard Lewis acids, forming stronger bonds with hard base. As a result, extraction of Zr(IV) and Hf(IV) by D2EHPA is more effective than that by Cyanex 301, although Cyanex 301 possesses a lower pK<sub>a</sub> value than D2EHPA.

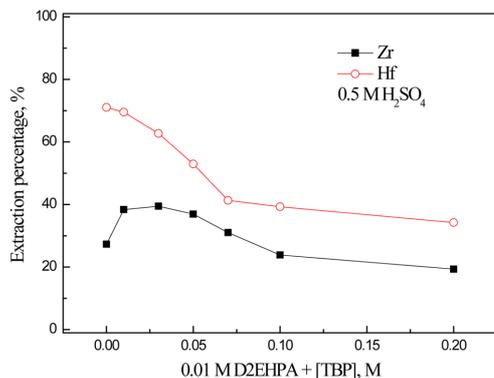
#### 3.4. Solvent extraction of Zr(IV) and Hf(IV) by mixtures of Cyanex 301 + TBP and D2EHPA + TBP

It has been reported that neutral extractants, such as TOPO are used jointly with acidic extractants such as D2EHPA for synergistic extraction of gold or uranium.<sup>22-24)</sup> Wang et al. reported<sup>10)</sup> that a mixture of organophosphorous acidic extractants and TOPO has some advantage in the extraction and separation of Zr(IV) and Hf(IV) from HCl solutions. In order to improve the extraction and separation efficiency between Zr(IV) and Hf(IV) from sulphuric acid solution, neutral extractant, TBP, was mixed with Cyanex 301 and D2EHPA, respectively. The effect of TBP concentration on the extraction of Zr(IV) and Hf(IV) in the presence of Cyanex 301 or D2EHPA at 0.5 M H<sub>2</sub>SO<sub>4</sub> was investigated, and the results are presented in Figs. 2 and 3. The concentration of Cyanex 301 and D2EHPA was fixed at 0.2 and 0.01 M, respectively, while the concentration of TBP in the mixed extractants was varied from 0.01 to 0.2 M.

Figure 2 shows that extraction of Zr(IV) and Hf(IV) metal ions decreased with the increased concentration of TBP in the mixed systems, from 57.2 to 20.0% for Zr(IV) and from 61.7 to 34.7% for Hf(IV). It was



**Fig. 2.** Extraction of Zr(IV) and Hf(IV) from 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions by mixture of Cyanex 301 and TBP in kerosene.



**Fig. 3.** Extraction of Zr(IV) and Hf(IV) from H<sub>2</sub>SO<sub>4</sub> solutions by mixture of D2EHPA and TBP in kerosene.

noticed that the percentage extraction of Hf(IV) was higher than that of Zr(IV) by using the mixture of Cyanex 301 and TBP. In terms of separation, significant improvement on the separation of these two metal ions was not observed by the addition of TBP into Cyanex 301. Fig. 3 shows the extraction behavior of Zr(IV) and Hf(IV) in 0.5 M sulfuric acid solutions with the mixture of D2EHPA and TBP. The extraction percentage of Zr(IV) decreased steadily while that of Hf(IV) increased at first and then decreased with the increase of the added TBP concentration in the mixtures. The depression in the extraction of Zr(IV) and Hf(IV) by the mixtures of Cyanex 301 + TBP and D2EHPA + TBP may be related to the mutual interaction in the

organic phase. In terms of separation efficiency, mixing of TBP with D2EHPA led to some negative effect on the separation of the two metal ions compared to single D2EHPA under the same experimental condition.

#### 4. Conclusions

Solvent extraction of Zr(IV) and Hf(IV) was carried out from sulfuric acid solutions by several acidic extractants (Versatic acid/LIX 63/Cyanex 301). Moreover, the extraction and separation of the two metals by cationic extractants from HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> solutions were discussed on the basis of the complex formation behaviour and the pK<sub>a</sub> value of the extractant. Zr(IV) and Hf(IV) could be extracted by Versatic and LIX 63 from only weak acid solutions (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>), due to their relatively high pK<sub>a</sub> values compared to other kinds of extractants. On the other hand, extraction of Zr(IV) and Hf(IV) with Cyanex 301 took place in strong sulfuric acid solutions, following a cation exchange mechanism. Selective extraction of Hf(IV) over Zr(IV) was attained using single Cyanex 301 and mixtures of Cyanex 301 + TBP, D2EHPA + TBP. Compared to single Cyanex 301/D2EHPA, mixture of TBP with Cyanex 301 or D2EHPA exhibited antagonism on the extraction and separation of Zr(IV) and Hf(IV).

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