

## Selective Extraction of Hafnium over Zirconium with Dialkylphosphinic Acids from H<sub>2</sub>SO<sub>4</sub> Media

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Designing highly efficient dialkylphosphinic acid extractant for zirconium/hafnium separation relies on systematic structure-property studies. In this paper, dialkylphosphinic acids with different substituents at  $\beta$ -C,  $\gamma$ -C and  $\delta$ -C for zirconium and hafnium extraction and separation from H<sub>2</sub>SO<sub>4</sub> media were investigated. The results show that substituents at  $\beta$ -C,  $\gamma$ -C and  $\delta$ -C reduce the extraction ability of dialkylphosphinic acids for both zirconium and hafnium. The substituent effect at  $\beta$ -C is greater than that at  $\gamma$ -C and  $\delta$ -C. The larger steric hindrance of the substituents (ethyl > methyl > H), the weaker extraction ability of the dialkylphosphinic acids. The zirconium and hafnium separation behavior is related to the extraction ability of dialkylphosphinic acids. Dialkylphosphinic acids with stronger extraction ability show better zirconium/hafnium separation performance at higher acidity of 2.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, while those with weaker extraction ability show better zirconium and hafnium separation performance at lower acidity of 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. The highest hafnium/zirconium separation factor ( $\beta_{\text{Hf/Zr}}$ ) in the current study occurs with (2-ethylhexyl)(2,4,4-trimethylpentyl)phosphinic acid (USTB-1), which reaches 19.2.

**Keywords:** zirconium, hafnium, solvent extraction, separation, dialkylphosphinic acids

### Introduction

Zirconium and hafnium are indispensable rare metal materials in the atomic energy industry. The big difference in their thermal neutron capture cross-sections (TNCCS) leads to their totally different applications in atomic energy fields. Highly purified zirconium with TNCCS of only 0.18 b (1 b = 10<sup>-24</sup> cm<sup>2</sup>) is used as structural materials of nuclear reactors and uranium fuel rod cladding materials, etc. On the contrary, highly purified hafnium has large TNCCS of 105 b.<sup>1</sup> Therefore, hafnium is a preferred control material for small thermal reactors. At present, nearly all the water-cooled reactors of atomic submarines, nuclear-powered aircraft carriers, etc., utilize hafnium as control rods.<sup>2-4</sup>

However, zirconium and hafnium always coexist in nature. They must be separated profoundly to obtain highly purified zirconium (containing < 100 ppm hafnium) and hafnium (> 96%) before their nuclear-related applications.<sup>4</sup>

Unfortunately, zirconium and hafnium have very similar physico-chemical properties, which makes it very hard to separate them completely.<sup>1,2</sup> Solvent extraction is the main way of separating zirconium and hafnium to obtain their nuclear grade products. The commercialized zirconium/hafnium separation systems are methyl isobutyl ketone (MIBK)-HSCN, tributyl phosphate (TBP)-HNO<sub>3</sub>-HCl and trioctyl amine (TOA)-H<sub>2</sub>SO<sub>4</sub>. MIBK-HSCN system alone produces about two thirds of the global zirconium sponge.<sup>2,5</sup> However, MIBK has a high solubility in water (19.1 g L<sup>-1</sup> at 20 °C), a low flashing point (15.6 °C) and a strong smell.<sup>6</sup> Therefore, MIBK-HSCN system has the drawbacks of high extractant loss and high inflammability. Besides, it generates wastewater with high concentrations of ammonia and nitrogen compounds, SCN<sup>-</sup>, CN<sup>-</sup> and organic matter. The nuclear grade zirconium sponges produced by TBP-HNO<sub>3</sub>-HCl and TOA-H<sub>2</sub>SO<sub>4</sub> systems only share a small global market. TBP-HNO<sub>3</sub>-HCl system costs twice as much as MIBK-HSCN to produce zirconium sponge. Besides, it needs high acidity and easily emulsifies during extraction. TOA-H<sub>2</sub>SO<sub>4</sub> system has the shortage of

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low extraction capacity, long process and poor zirconium/hafnium separation performance.<sup>3,5,7</sup>

To seek more efficient and eco-friendly zirconium/hafnium separation systems, various commercialized extractants as well as novel compounds were studied on zirconium/hafnium extraction and separation, such as neutral extractants (trioctyl-phosphine oxide (TOPO/Cyanex 921),<sup>8</sup> Cyanex 923<sup>9</sup> and Cyanex 925),<sup>10</sup> organophosphorus extractants (di-(2-ethylhexyl)phosphoric acid (D2EHPA/P204),<sup>11,12</sup> 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA/PC88A/P507),<sup>13,14</sup> Cyanex 272<sup>15,16</sup> and Cyanex 572),<sup>17</sup> thio-organophosphorus extractants (Cyanex 301,<sup>18</sup> Cyanex 302),<sup>19</sup> oximes (LIX 63,<sup>20</sup> LIX 84 IC),<sup>21</sup> amine-based extractants (Aliquat 336, Alamine 336, TOA/Alamine 300, Alamine 308, etc.),<sup>22-24</sup> diisobutyl ketone (DIBK),<sup>6</sup> *N,N,N',N'*-tetraoctyldiglycolamide (TODGA),<sup>25</sup> *N,N*-*n*-octylamine di(methylenephosphinic acid) (OADMPPA),<sup>26</sup> bis(2-ethylhexyl)-1-(2-ethylhexylamino) propylphosphonate (BEAP)<sup>27</sup> and isoxazolones.<sup>28</sup> Hf is the minor element in natural resources, as its content is only 1-3% compared to that of Zr.<sup>29</sup> Therefore, selectively extracting hafnium over zirconium has many advantages, such as low cost, low reagent consumption, small equipment dimension and less pollution problems. However, above the mentioned extractants, only a few can selectively extract the minor hafnium over the major zirconium.

Organophosphorous acids, of which typical commercial products are D2EHPA, EHEHPA, and Cyanex 272, selectively extract the minor hafnium over zirconium from H<sub>2</sub>SO<sub>4</sub> media. They have much stronger extraction ability for zirconium and hafnium than MIBK. They also have higher boiling points and flashing points, and lower solubility in water (see Table 1). Besides, organophosphorous acid-H<sub>2</sub>SO<sub>4</sub> systems have no problems of HSCN oxidation. It is the most promising kind of extractants to explore new zirconium/hafnium separation systems with commercial prospects.

The current studies on zirconium/hafnium separation by organophosphorous acids are limited to D2EHPA,<sup>11,12</sup> EHEHPA,<sup>13,14</sup> Cyanex 272,<sup>15,16</sup> Cyanex 572 (a mixture of EHEHPA and Cyanex 272),<sup>17</sup> diisooctylphosphinic acid (Dio-PA)<sup>32</sup> and diphenyl phosphate (DPPA).<sup>32</sup> D2EHPA

has strong extraction ability for zirconium and hafnium, which leads to hard stripping of the extracted hafnium. Most importantly, its hafnium/zirconium separation factor ( $\beta_{\text{Hf/Zr}}$ ) is only 2-3 in industrial production scale, much lower than that of MIBK-HSCN system ( $\beta_{\text{Hf/Zr}} = 4-5$ ).<sup>7</sup> DPPA has even much stronger extraction ability than D2EHPA, while Dio-PA has nearly equivalent extraction ability to D2EHPA.<sup>32</sup> Their hafnium/zirconium separation factors have not been reported. Many studies<sup>33-35</sup> show that di-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) has weaker extraction ability and better separation performance for similar metals (such as Co/Ni, rare earths) than D2EHPA and EHEHPA. We can expect more efficient extraction for zirconium/hafnium separation from dialkylphosphinic acids. In addition, dialkylphosphinic acids have no O-P bond and will not hydrolyze in acidic media. They are more stable in acidic media than D2EHPA and EHEHPA. Designing highly efficient dialkylphosphinic acid extractant for zirconium/hafnium separation relies on systematic structure-property studies. As far as we know, there has not been such research yet.

For dialkylphosphinic acids, their performances mainly depend on two factors: the number of carbon atoms and the branches. The former mainly determines the extractant solubility in water, while the latter determines the extractant extraction ability, selectivity, stripping, etc. The carbon atoms of commercial organophosphorous acid extractants D2EHPA, EHEHPA, Cyanex 272, Cyanex 301 and Cyanex 302 are all 16, which means 16 is the proper number of carbon atoms for dialkylphosphinic acid extractants. As to the branches, based on our previous studies, the substituents at  $\alpha$ -C lead to too weak extraction ability.<sup>36</sup> Therefore, the effect of substituents at  $\beta$ -C,  $\gamma$ -C and  $\delta$ -C on zirconium/hafnium extraction and separation performance are more important.

In this work, seven dialkylphosphinic acids were synthesized in our lab or kindly provided by others. They all have 16 carbon atoms with different substituents at  $\beta$ -C,  $\gamma$ -C or  $\delta$ -C. Their name, structure, molecular formula and the reported  $pK_a$  are summarized in Table 2. Their zirconium/hafnium extraction and separation behaviors from H<sub>2</sub>SO<sub>4</sub> media were investigated. The relationship between the

**Table 1.** Comparison of some characteristics shown by MIBK, D2EHPA, EHEHPA and Cyanex 272<sup>30,31</sup>

Extractant	Boiling point / °C	Flashing point / °C	Solubility in water	Media	Selectivity
MIBK	116.5	15.6	19.1 g L <sup>-1</sup> at 20 °C	HSCN	Hf over Zr
D2EHPA	393.44	191.75	insoluble	H <sub>2</sub> SO <sub>4</sub>	Hf over Zr
EHEHPA	390.6	196	insoluble	H <sub>2</sub> SO <sub>4</sub>	Hf over Zr
Cyanex 272	> 300	> 108	38 mg L <sup>-1</sup> (pH = 3.7)	H <sub>2</sub> SO <sub>4</sub>	Hf over Zr

MIBK: methyl isobutyl ketone; D2EHPA: di-(2-ethylhexyl)phosphoric acid; EHEHPA: 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester; Cyanex 272: di-(2,4,4-trimethylpentyl)phosphinic acid.

**Table 2.** Name, structure, molecular formula and  $pK_a$  of dialkylphosphinic acids

No.	Name	Structure	Molecular formula	$pK_a$
P208	di-( <i>n</i> -octyl)phosphinic acid		$C_{16}H_{33}PO_2$	4.96 <sup>37</sup>
INET-1	( <i>n</i> -octyl)(2,4,4-trimethylpentyl)phosphinic acid		$C_{16}H_{33}PO_2$	not known
P218	di-(2-methylheptyl) phosphinic acid		$C_{16}H_{33}PO_2$	5.42 <sup>37</sup>
USTB-1	(2-ethylhexyl)(2,4,4-trimethylpentyl)phosphinic acid		$C_{16}H_{33}PO_2$	5.73 <sup>38</sup>
P227	di-(2-ethylhexyl)phosphinic acid		$C_{16}H_{33}PO_2$	5.68, <sup>38</sup> 5.61 <sup>37</sup>
P218	di-(2-methylheptyl) phosphinic acid		$C_{16}H_{33}PO_2$	5.42 <sup>37</sup>
P2132	di-(2-methyl-3-ethylpentyl) phosphinic acid		$C_{16}H_{33}PO_2$	not known
Cyanex 272	di-(2,4,4-trimethylpentyl) phosphinic acid		$C_{16}H_{33}PO_2$	5.68, <sup>38</sup> 5.58 <sup>37</sup>

structure and their extraction ability and selectivity for zirconium and hafnium were revealed.

## Experimental

### Reagents

Dialkylphosphinic acids P208, P218, P2132, INET-1 and USTB-1 were synthesized in our lab.<sup>36,38,39</sup> P227 ( $\geq 93\%$ ) and Cyanex 272 ( $\geq 85\%$ ) were kindly provided by Shanghai Institute of Organic Chemistry (Chinese Academy of Sciences) and Cytec Industries (Shanghai) Co., Ltd (China), respectively. P208 was further purified through recrystallization, while other extractants were all further purified through cobalt salt precipitation method. *n*-Octane was of chemical purity (C.P.) (Sinopharm Chemical Reagent Co., Ltd, Beijing, China). ZrCl<sub>4</sub> (99.9%) and HfCl<sub>4</sub> (99.5%) were both bought from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Concentrated H<sub>2</sub>SO<sub>4</sub> was analytical reagent (A.R.) (Beijing Chemical Works, Beijing, China).

The zirconium and hafnium feed solutions were prepared by dissolving ZrCl<sub>4</sub> and HfCl<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> solution with different concentrations and diluting to volume in 1-L volumetric flasks. The H<sub>2</sub>SO<sub>4</sub> solutions were prepared by precisely diluting the concentrated H<sub>2</sub>SO<sub>4</sub> with deionized water. The H<sub>2</sub>SO<sub>4</sub> concentrations were confirmed by titration with standard NaOH solution, which were 0.25, 0.51, 0.75, 1.02, 1.49 and 2.01 mol L<sup>-1</sup>, respectively. The feed solutions were let stand more than 24 h after preparation and then the extraction were carried out. The concentrations of zirconium and hafnium in the feed solutions were  $64 \pm 2$  and  $68 \pm 4$  mg L<sup>-1</sup>, respectively.

The organic phases were 10 mmol L<sup>-1</sup> of each corresponding dialkylphosphinic acid. They were prepared as follows: (i) preparation of 0.1 mol L<sup>-1</sup> dialkylphosphinic acid: 2.90  $\pm$  0.01 g of the corresponding dialkylphosphinic acid was dissolved in *n*-octane and diluted to volume in a 100-mL volumetric flask; (ii) stepwise dilution: 10 mL of the obtained 0.1 mol L<sup>-1</sup> of dialkylphosphinic acid was measured and diluted to 100 mL in another 100 mL volumetric flask.

### Instrumentation

A Multi-tube Vortexer UMV-2 (Usun Technologies Co., Ltd., Beijing, China) was used for mixing aqueous-organic phases (2500 r min<sup>-1</sup> for 20 min). A Guanghe TD4C Low Speed Tabletop Centrifuge (Jintan Liangyou Instrument Co., Ltd., Changzhou, Jiangsu Province, China) was used for accelerating phase separation (3000 rpm

for 5 min). An iCAP 7400 inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Fisher Scientific, Waltham, MA, USA) was adopted to determine the zirconium and hafnium concentrations in aqueous solutions. The parameters during Zr and Hf determination were as follows: the plasma power was 1150 W; the wavelengths for Zr, Hf determination were 339.198 and 339.980 nm, respectively; the pump speed was 50 rpm; the auxiliary gas flow rate was 0.5 L min<sup>-1</sup>; the nebulizer or carrier gas flow rate was 0.6 L min<sup>-1</sup>; the plasma view was axial and the sample washing time was 30 s.

### Extraction procedure

Certain volumes (4 mL/2 mL at A/O (phase ratio, namely the volume ratio of aqueous phase to organic phase) = 2, and 3 mL/3 mL at A/O = 1) of aqueous feed solution and extractant organic solution were sealed in a 10-mL centrifugal tube and oscillated on the Multi-tube Vortexer at 2500 rpm for 20 min, which was sufficient to reach extraction equilibrium.<sup>40</sup> Then, the mixture was centrifugated at 3000 rpm for 3 min to accelerate phase separation. After that, the aqueous phase was separated for zirconium and hafnium concentration analysis with ICP-OES. All the samples were measured 3 times, and we took the average value as the final result. Zirconium and hafnium concentration in the organic phase was calculated on the basis of mass balance (equation 1). The calculation equations of zirconium/hafnium extraction percentage (E), distribution ratio (D), and hafnium/zirconium separation factor ( $\beta_{\text{Hf/Zr}}$ ) are shown in equations 2-4.

$$C_{e(o)} = \frac{(C_{i(a)} - C_{e(a)})V_a}{V_o} = (C_{i(a)} - C_{e(a)}) \times \frac{A}{O} \quad (1)$$

$$E (\%) = \frac{C_{e(o)}}{C_{i(a)}} \times \frac{O}{A} \times 100 \quad (2)$$

$$D = \frac{C_{e(o)}}{C_{e(a)}} \quad (3)$$

$$\beta_{\text{Hf/Zr}} = \frac{D_{\text{Hf}}}{D_{\text{Zr}}} \quad (4)$$

where  $C_{e(o)}$  stands for the zirconium/hafnium concentration in the organic phase after extraction;  $C_{i(a)}$  and  $C_{e(a)}$  represent the zirconium/hafnium concentrations in the aqueous phase before and after extraction, respectively;  $V_a$  and  $V_o$  denote the volumes of the aqueous and organic phases, respectively; A/O is the phase ratio, namely the volume ratio of aqueous phase to organic phase ( $V_a/V_o$ );  $D_{\text{Hf}}$  and  $D_{\text{Zr}}$

stand for the distribution ratios of hafnium and zirconium, respectively.

All the extraction experiments were carried out at room temperature.

## Results and Discussion

### $\beta$ -Substituent effect on the extraction ability for zirconium and hafnium

To discuss conveniently, the dialkylphosphinic acids were classified into two groups. As P208, INET-1, P218, USTB-1 and P227 have different substituents at the  $\beta$ -C, they were discussed together to reveal the  $\beta$ -substituent effect on the extraction ability of dialkylphosphinic acids for zirconium and hafnium. P218, P2132 and Cyanex 272 all have methyl at the  $\beta$ -C, while different substituents at the  $\gamma$ -C or  $\delta$ -C. Hence, they were compared to investigate the  $\gamma$ -,  $\delta$ -substituent effect on the extraction ability of dialkylphosphinic acids for zirconium and hafnium.

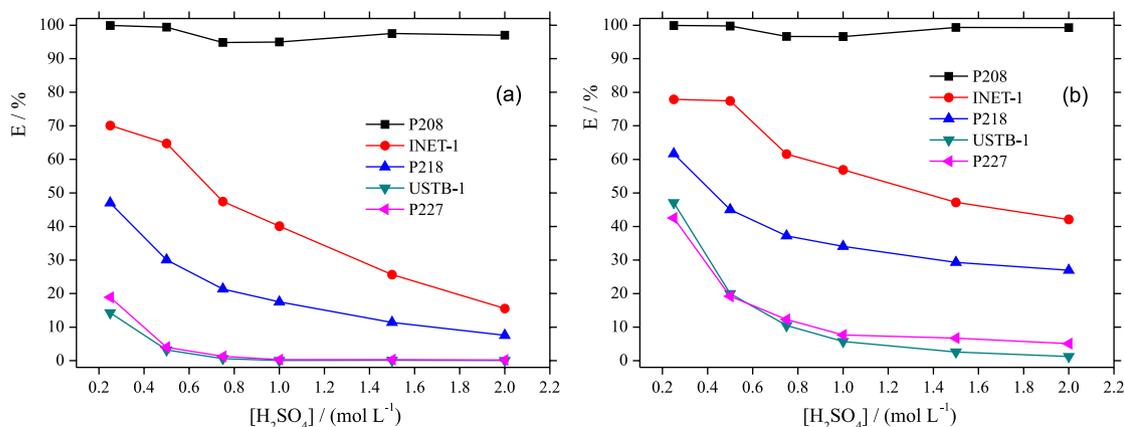
The feed solutions were zirconium-hafnium mixed solutions with different  $\text{H}_2\text{SO}_4$  concentrations in the range of 0.25–2.0 mol L<sup>-1</sup>. The phase ratio A/O was first set at 2. The results are shown in Figure 1. P208 has the highest zirconium extraction percentages, followed by INET-1, and then P218. USTB-1 and P227 have almost equivalent zirconium extraction percentages, which are both lower than P218 (Figure 1a). Similar phenomena occur to hafnium extraction (Figure 1b). These indicate that  $\beta$ -substituents reduce the extraction ability of dialkylphosphinic acids for zirconium and hafnium. The larger steric hindrance of the substituents (ethyl > methyl > H), the weaker extraction ability of the dialkylphosphinic acids. USTB-1 has an identical alkyl to P227, while the other alkyl of USTB-1 is a 5-carbon main chain with one methyl at the  $\beta$ -C and two methyls at the  $\delta$ -C. The substituents at the  $\delta$ -C also weaken the

extraction ability of dialkylphosphinic acids for zirconium and hafnium, which will be discussed in the next subsection. This leads to the almost equivalent extraction ability of USTB-1 and P227 for zirconium and hafnium. It has also been reported that USTB-1 and P227 show nearly the same extraction ability for lutetium (Lu).<sup>38</sup>

At the phase ratio A/O of 2, the extraction percentages of zirconium and hafnium by P218, USTB-1 and P227 are relatively low (Figure 1). Therefore, we further investigated the zirconium and hafnium extraction behaviors by these three extractants at A/O of 1. The results are shown in Figure 2. The extraction percentages of zirconium and hafnium by P218 are greatly improved, especially in low acidities (both ca. 30% at 0.25 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ ). In contrast, the extraction percentages of zirconium and hafnium by USTB-1 and P227 are both increased by only ca. 10% at 0.25 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ . This indicates that P227 and USTB-1 have much weaker extraction ability for zirconium and hafnium than P218, especially at the acidities of more than 1.0 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$  (see Figure 2). P227 and USTB-1 also show equivalent extraction ability for zirconium and hafnium at A/O of 1.

### $\gamma$ , $\delta$ -Substituent effect on the extraction ability for zirconium and hafnium

To investigate the  $\gamma$ ,  $\delta$ -substituent effect on the extraction ability of dialkylphosphinic acids for zirconium and hafnium, we also extracted zirconium and hafnium from their mixed solutions with different  $\text{H}_2\text{SO}_4$  concentrations in the range of 0.25–2.0 mol L<sup>-1</sup>. The concentrations of P218, P2132 and Cyanex 272 were also all 10 mmol L<sup>-1</sup>. The phase ratio A/O was first set at 2. The results are shown in Figure 3. For both zirconium and hafnium, P218 shows the strongest extraction ability among these three extractants, followed by P2132, and then Cyanex 272. This indicates that the ethyl at the  $\gamma$ -C



**Figure 1.** (a) Zirconium and (b) hafnium extraction by  $\beta$ -substituent group extractants at A/O of 2.

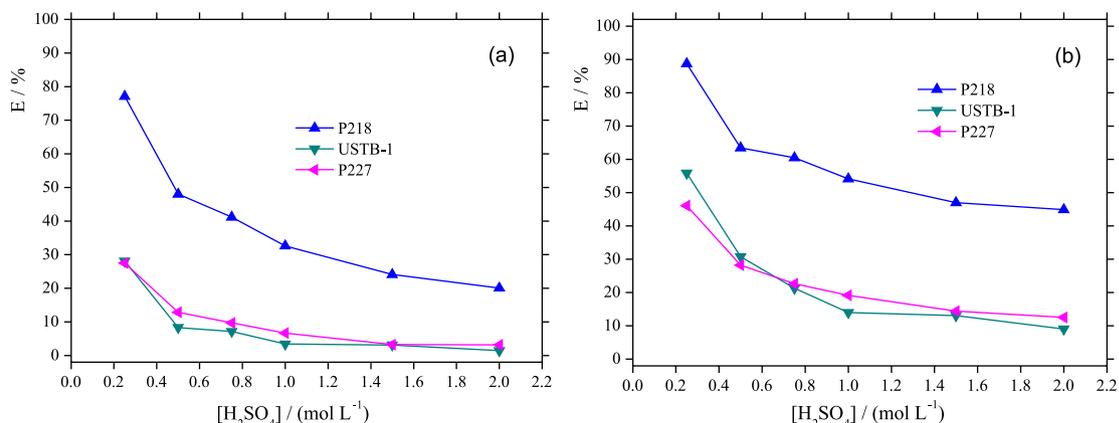


Figure 2. (a) Zirconium and (b) hafnium extraction by  $\beta$ -substituent group extractants at A/O of 1.

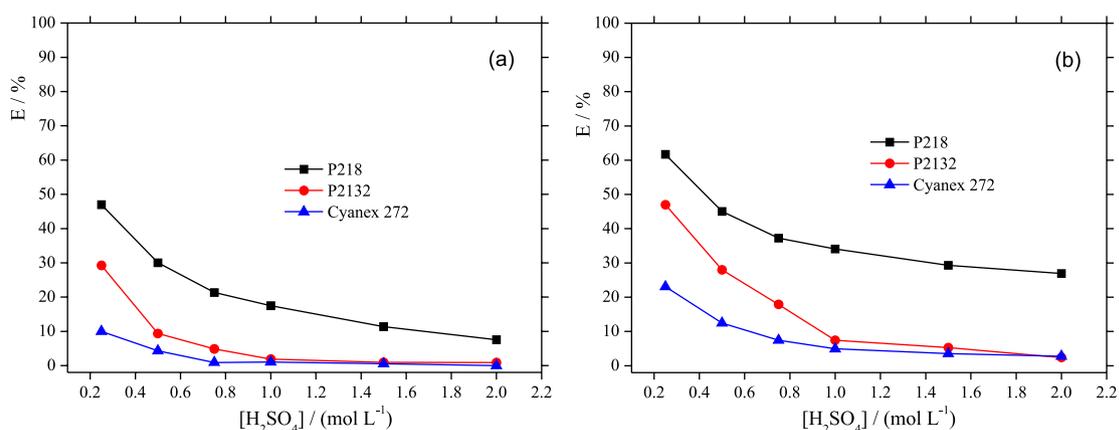


Figure 3. (a) Zirconium and (b) hafnium extraction by  $\gamma$ ,  $\delta$ -substituent group extractants at A/O of 2.

and the two methyls at the  $\delta$ -C both apparently reduce the extraction ability of dialkylphosphinic acids for zirconium and hafnium.

Cyanex 272 has very weak extraction ability for zirconium and hafnium. Its extraction percentages for zirconium and hafnium are apparently lower than those of P227 and USTB-1 (compared Figures 1 and 3). Hence, we also repeated the extraction experiments at A/O of 1. The results are shown in Figure 4. All the extraction

percentages of zirconium and hafnium apparently increased compared to corresponding those A/O of 2, especially at lower acidities ( $< 1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ). Through comparing Figure 3 with Figure 1, and Figure 4 with Figure 2, it can be seen that P2132 has a slightly higher extraction ability for zirconium and hafnium than P227. P227 has an ethyl on its  $\beta$ -C, while P2132 has a methyl on its  $\beta$ -C and an ethyl on its  $\gamma$ -C. This indicates that the extraction ability of dialkylphosphinic acids

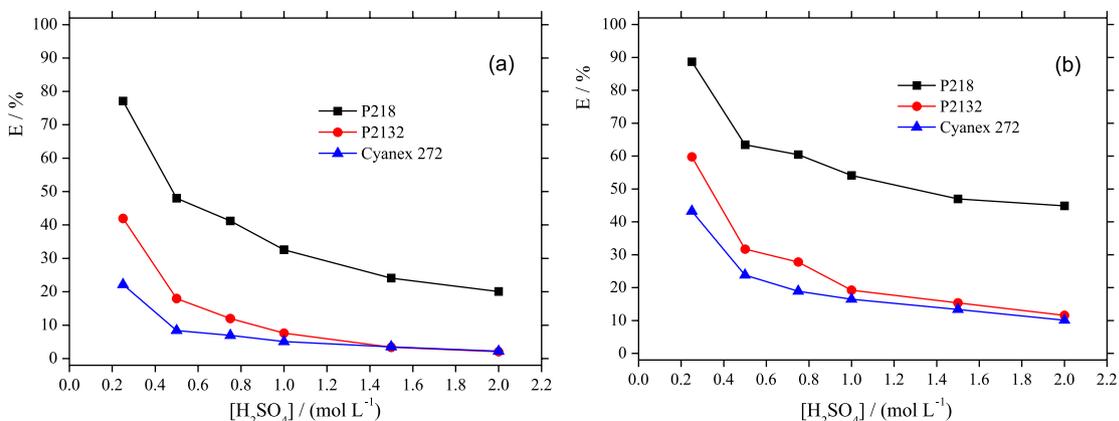
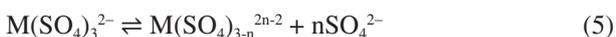


Figure 4. (a) Zirconium and (b) hafnium extraction by  $\gamma$ ,  $\delta$ -substituent group extractants at A/O of 1.

for zirconium and hafnium is more influenced by the substituent at the  $\beta$ -C than that at the  $\gamma$ -C.

Analysis of the zirconium and hafnium extraction by the dialkylphosphinic acids

Tetravalent zirconium ( $Zr^{4+}$ ) and hafnium ( $Hf^{4+}$ ) are hard Lewis acids, while sulfate ion ( $SO_4^{2-}$ ) is hard Lewis base. All of them are high valence ions. Therefore,  $SO_4^{2-}$  has a strong affinity to  $Zr^{4+}$  and  $Hf^{4+}$  to form various complexes. Ma *et al.*<sup>41</sup> predicted the existent forms of zirconium and hafnium at different acidities in  $H_2SO_4$  media using MEDUSA software.<sup>42</sup> According to their results, the prevailing existent forms of zirconium and hafnium are both  $M(SO_4)_3^{2-}$  ( $M = Zr$  or  $Hf$ ) at acidities of  $< 3 \text{ mol L}^{-1} H_2SO_4$ . Organophosphorous acids extract zirconium and hafnium through cation exchange mechanism from low acidic  $H_2SO_4$  solutions, and the extraction reaction can be written as:<sup>15,43-46</sup>



where M represents Zr or Hf,  $n = 2$  or  $3$ ,  $(HL)_2$  denotes dimer form of dialkylphosphinic acid molecule, L represents one dialkylphosphinic acid molecule losing one proton (similarly hereinafter).

$Hf^{4+}$  has a weaker interaction with  $SO_4^{2-}$  than  $Zr^{4+}$ , which leads to selective extraction of hafnium over zirconium by organophosphorous acids from  $H_2SO_4$  media.<sup>45</sup> This is consistent with our results. For all the investigated dialkylphosphinic acids (P208, INET-1, P218, P2132, USTB-1, P227 and Cyanex 272), hafnium has higher extraction percentages than zirconium (see Figures 1-4).

The extraction percentages of zirconium and hafnium all decrease as the  $H_2SO_4$  concentration is increased (see Figures 1-4). This phenomenon is in accordance with the extraction mechanism of cation exchange. According to equation 6, hydrogen ions are released during zirconium and hafnium extraction by organophosphorous acids. Therefore, increasing acidity is against the zirconium and hafnium extraction.

Alkyls are electron-donating groups. Alkyl branches increase the electron cloud density of the oxygen atoms, which leads to weaker acidity of dialkylphosphinic acids and more difficulty in dissociation during extraction. According to equation 6, this is unfavorable for zirconium and hafnium extraction. Ethyl has a stronger electron donor effect, followed by methyl and then H.  $\beta$ -C is nearer to the oxygen atoms of dialkylphosphinic acids

than  $\gamma$ -C. Therefore, electron of the substituents at  $\beta$ -C is easier to transmit to the oxygen atoms of  $-POOH$  group than that of the substituents at  $\gamma$ -C. Therefore, it is easy to understand the effect of  $\beta$ ,  $\gamma$ ,  $\delta$ -substituent effect on zirconium and hafnium extraction from low acidic  $H_2SO_4$  media ( $< 2 \text{ mol L}^{-1}$ ) and the regularities.

Zirconium/hafnium separation performance by dialkylphosphinic acids at A/O of 2

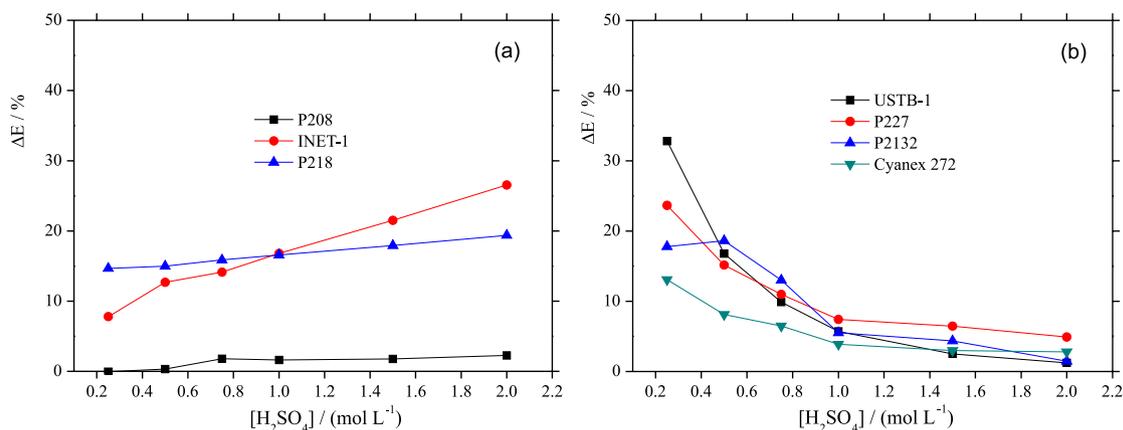
Separation factor ( $\beta$ ) is always used to evaluate the separation performance of two metals. In addition, the corresponding extraction percentages of the two metals and their differences  $\Delta E$  should also be considered, because high separation factors might occur at high extraction percentages of the two metals. For example, one is 99.21%, the other is 99.98%. Despite their separation factor is about 40, the  $\Delta E$  is only 0.77%, which has nonsense in industrial applications. Similarly, high separation factor might also occur at both low extraction percentages of the two metals. Therefore, we not only summarized the hafnium/zirconium separation factors ( $\beta_{Hf/Zr}$ ) in Table 3, but also drew the corresponding differences of their extraction percentages  $\Delta E_{Hf-Zr}$  (namely,  $E_{Hf} - E_{Zr}$ ) for all the dialkylphosphinic acids (see Figure 5). When the  $E_{Hf}$  is  $> 99\%$  or the  $E_{Zr}$  is  $< 1\%$ , the error of  $\beta_{Hf/Zr}$  might be big. Hence, their corresponding  $\beta_{Hf/Zr}$  are not listed in Table 3.

P208, INET-1 and P218 have stronger extraction ability for zirconium and hafnium than USTB-1, P227, P2132 and Cyanex 272 (Figures 1-4). Their  $\Delta E_{Hf-Zr}$  values increase as the acidity increased from 0.25 to  $2 \text{ mol L}^{-1} H_2SO_4$  (Figure 5a). The corresponding  $\beta_{Hf/Zr}$  values basically show the same trend (Table 3). Comparing their maximum  $\beta_{Hf/Zr}$ , it seems that their separation performance for zirconium/hafnium is in the order  $P218 > P208 > INET-1$ . However, the  $\Delta E_{Hf-Zr}$  values of P208 are all  $< 3\%$ , much lower than those of P218 and INET-1 (Figure 5a). This indicates P208 has very poor zirconium/hafnium separation performance at the current conditions. Therefore, among these three extractants, P218 has the best zirconium/hafnium separation performance, followed by INET-1, and then P208.

USTB-1, P227, P2132 and Cyanex 272 have much lower extraction ability for zirconium and hafnium than P208, INET-1 and P218 (Figures 1-4). Their  $\Delta E_{Hf-Zr}$  values basically decrease as the  $H_2SO_4$  concentration increased (Figure 5b). The corresponding  $\beta_{Hf/Zr}$  values show just the opposite trend at acidities of  $< 1.0 \text{ mol L}^{-1} H_2SO_4$  (Table 3). USTB-1 and P227 have their maximum  $\beta_{Hf/Zr}$  of 19.2 and 10.7 respectively, which both occur at  $0.75 \text{ mol L}^{-1} H_2SO_4$ . However, both USTB-1 and P227 have extraction percentages of hafnium as low as ca. 10% at this condition, which means very low zirconium/hafnium separation

**Table 3.** Hafnium/zirconium separation factors ( $\beta_{\text{Hf/Zr}}$ ) at A/O = 2

H <sub>2</sub> SO <sub>4</sub> concentration / (mol L <sup>-1</sup> )	$\beta_{\text{Hf/Zr}}$					
	0.25	0.5	0.75	1.0	1.5	2.0
P208	–	–	1.6	1.5	3.7	4.3
INET-1	1.5	1.9	1.8	2.0	2.6	3.9
P218	1.5	1.9	2.0	2.6	3.2	4.5
USTB-1	5.3	7.6	19.2	–	–	–
P227	3.2	5.7	10.7	–	–	–
P2132	2.1	3.8	4.2	4.1	5.8	2.6
Cyanex 272	2.7	3.1	8.5	–	–	–

**Figure 5.** Difference of (a) zirconium and (b) hafnium extraction percentages  $\Delta E_{\text{Hf-Zr}}$  at A/O of 2.

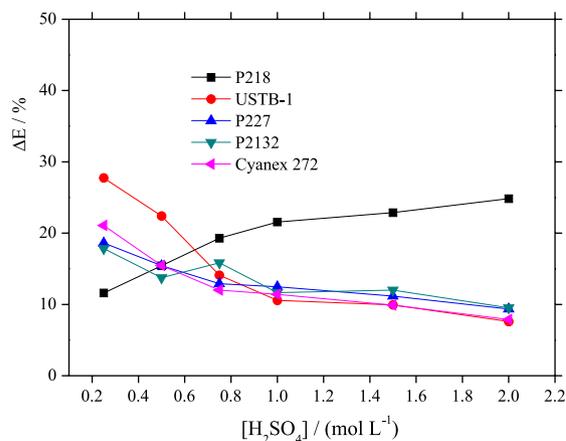
efficiency. Hence, their  $\beta_{\text{Hf/Zr}}$  at 0.75 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> have much less significance than those at 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. As to Cyanex 272, its maximum  $E_{\text{Hf}}$  is still less than 25% (Figure 3b). Besides, it has the smallest  $\Delta E_{\text{Hf-Zr}}$  among these four extractants (Figure 5b). Its zirconium/hafnium separation performance will be discussed in the next subsection. Comparing the  $\beta_{\text{Hf/Zr}}$  of USTB-1, P227 and P2132 at 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, the zirconium/hafnium separation performance is in the sequence USTB-1 > P227 > P2132.

Zirconium/hafnium separation performance by dialkylphosphinic acids at A/O of 1

At the phase ratio A/O of 1, the  $\Delta E_{\text{Hf-Zr}}$  values and the corresponding  $\beta_{\text{Hf/Zr}}$  values by P218, USTB-1, P227, P2132 and Cyanex 272 at the acidities in the range of 0.25–2.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> are summarized in Figure 6 and Table 4, respectively. For P218, its maximum  $\Delta E_{\text{Hf-Zr}}$ , which is 24.8%, also occurs at acidity of 2.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and the corresponding  $\beta_{\text{Hf/Zr}}$  is 3.3.

On the contrary, the maximum  $\Delta E_{\text{Hf-Zr}}$  values of USTB-1, P227, P2132 and Cyanex 272 still occur at low acidity of 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, and the corresponding  $\beta_{\text{Hf/Zr}}$  values are 3.2, 2.3, 2.1 and 2.7, respectively. Among these four extractants, USTB-1 also has the largest  $\Delta E_{\text{Hf-Zr}}$

of 27.7% and  $\beta_{\text{Hf/Zr}}$  of 3.2, indicating USTB-1 has the best zirconium/hafnium separation performance among these four extractants. Cyanex 272 has the second largest  $\Delta E_{\text{Hf-Zr}}$  and  $\beta_{\text{Hf/Zr}}$ . Hence, it has better zirconium/hafnium separation performance than P227 and P2132. P227 has a little bit larger  $\Delta E_{\text{Hf-Zr}}$  and  $\beta_{\text{Hf/Zr}}$  than P2132 at 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. It has better zirconium/hafnium separation performance than P2132. Therefore, the zirconium/hafnium separation performance of these four extractants is in the sequence USTB-1 > Cyanex 272 > P227 > P2132.

**Figure 6.** Difference of zirconium and hafnium extraction percentages  $\Delta E_{\text{Hf-Zr}}$  at A/O of 1.

**Table 4.** Hafnium/zirconium separation factors ( $\beta_{\text{Hf/Zr}}$ ) in  $\text{H}_2\text{SO}_4$  system at A/O of 1

$\text{H}_2\text{SO}_4$ concentration / (mol L <sup>-1</sup> )	$\beta_{\text{Hf/Zr}}$					
	0.25	0.5	0.75	1.0	1.5	2.0
P218	2.3	1.9	2.2	2.4	2.8	3.3
USTB-1	3.2	4.9	3.5	4.6	4.7	6.7
P227	2.3	2.7	2.7	3.3	5.0	4.4
P2132	2.1	2.1	2.8	2.9	5.2	6.2
Cyanex 272	2.7	3.4	3.1	3.7	4.3	5.0

## Conclusions

To reveal the structure-activity of dialkylphosphinic acids, zirconium and hafnium extraction and separation behaviors by seven dialkylphosphinic acids with different substituents at  $\beta$ -C,  $\gamma$ -C or  $\delta$ -C from  $\text{H}_2\text{SO}_4$  media were investigated. The following conclusions are drawn:

(i)  $\beta$ -Substituents reduce the extraction ability of dialkylphosphinic acids for zirconium and hafnium. The larger steric hindrance of the substituents (ethyl > methyl > H), the weaker extraction ability of the dialkylphosphinic acids. The extraction ability of the investigated dialkylphosphinic acids with different  $\beta$ -substituents is in the sequence P208 > INET-1 > P218 > USTB-1 ca. P227. The substituents at the  $\gamma$ -C and  $\delta$ -C also apparently reduce the extraction ability of dialkylphosphinic acids for zirconium and hafnium. The extraction ability of the investigated dialkylphosphinic acids with different  $\gamma$ ,  $\delta$ -substituents is in the order P218 > P2132 > Cyanex 272. The extraction ability of dialkylphosphinic acids for zirconium and hafnium is more influenced by the substituent at the  $\beta$ -C than that at the  $\gamma$ -C.

(ii) As the acidity is increased in  $\text{H}_2\text{SO}_4$  media, the variation trend of  $\Delta E_{\text{Hf-Zr}}$  depends on the extraction ability of dialkylphosphinic acids. Stronger extraction ability leads to an upward trend of  $\Delta E_{\text{Hf-Zr}}$  at acidities in the range of 0.25-2.0 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ , and the corresponding best zirconium/hafnium separation performance occurs at 2.0 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ . On the contrary, weaker extraction ability causes a downward trend of  $\Delta E_{\text{Hf-Zr}}$ , and the corresponding best zirconium/hafnium separation performance occurs at 0.25 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ . For the dialkylphosphinic acids with stronger extraction ability, their zirconium/hafnium separation performance is in the order P218 > INET-1 > P208. For the dialkylphosphinic acids with weaker extraction ability, their zirconium/hafnium separation performance is in the sequence USTB-1 > Cyanex 272 > P227 > P2132.

(iii) USTB-1 has stronger extraction ability and better zirconium/hafnium separation performance than the

commercialized Cyanex 272. The highest  $\beta_{\text{Hf/Zr}}$  in the current study occurs to USTB-1, which reaches 19.2.

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## Author Contributions

Junlian Wang was responsible for methodology, writing original draft, review and editing, supervision and funding acquisition; Hui Liu for investigation, formal analysis, data curation and writing original draft; Wen Xu for methodology and resources; Ziyong Chang for resources and data curation; Peilong Wang for formal analysis; Wang Huajun for supervision and project administration.

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