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Extraction of Zirconium and Hafnium in Polyethylene Glycol-Based Aqueous Biphasic System

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Abstract: The behavior of zirconium and hafnium in PEG 2000- Na_2SO_4 -HCl aqueous biphasic system has been investigated. The dependences of HCl concentration (0.185–0.55 M), extraction temperature (298–318 K), and extraction time (5–120 min) on distribution ratios have been determined. Extraction of these metals in PEG 2000- Na_2SO_4 - H_2SO_4 and PEG 2000- Na_3Cit -HCl systems has been also studied. The sulfate and citrate complexes of Zr and Hf prefer salt-rich phase in contrast to chloride complexes which pass into PEG rich phase in about 50% (w/w) to the greatest degree in room temperature and at short extraction time. The increase of distribution ratios ($D_{\text{Zr}}^* = 3.75$, $D_{\text{Hf}}^* = 4.31$) was observed after addition of water soluble organic ligand - tiron (4,5-dihydroxy-m benzenedisulfonic acid disodium salt). The results obtained in studied conditions are not very useful for the separation of zirconium and hafnium.

Keywords: Aqueous biphasic system, liquid extraction, separation of hafnium and zirconium

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INTRODUCTION

Hafnium commonly occurs in all zirconium minerals in the range of 2–3%. These two metals are the pair of the most similar elements in the periodic table. Their chemical similarity is caused by almost identical atomic and ionic radii. Both of them are used in nuclear industry, what requires their separation. Of the variety of processes proposed for their separation the most promising for industrial use are: solvent extraction (1–4), ionic exchange (5, 6), distillation of fused salts (7, 8).

In recent years an increase in interest in partitioning of metal ions in aqueous biphasic system is observed (9–13). ABS (aqueous biphasic system) is an environmentally friendly extractive system consisting of two dissimilar water soluble polymers or of a water soluble polymer (e.g., polyethylene glycol) and inorganic salt (e.g., sodium sulfate) (9). The process can be considered similar to conventional solvent extraction except of organic diluents which are usually toxic, flammable, volatile, and expensive, and are not used.

For the first time the aqueous biphasic system was utilized for metal ions partition by Shkinev et al. (14). Rogers et al. (10) classified this specific distribution into three categories: 1. partitioning to the PEG-rich phase without an extractant (e.g., TcO_4^- (10)), 2. extraction of negatively charged metal complexes of inorganic ions (anionic halide complexes of Cd and Pb (10)), 3. extraction using a water-soluble complexant (e.g., Alizarin complexes of Th and Pu (12), Arsenazo III complexes of some lanthanides and actinides (14)). There is little knowledge about extractive behavior of hafnium and zirconium in ABS system. Distribution ratios of studied metals in PEG 2000-KSCN-HCl system are reported by Nifant'eva et al. (15), but in spite of promising results, the continuation of this investigation was not found.

In this paper the partitioning of hafnium and zirconium ions has been examined in the aqueous biphasic systems to appraise the chances of separation of these two similar elements in ABS system.

EXPERIMENTAL

Reagents and Solutions

Polyethylene glycol 2000 (PEG 2000) was purchased from Fluka and used without further purification. Reagent grade anhydrous sodium sulfate, trisodium citrate dihydrate, sodium ethylenediaminetetraacetic acid disodium salt (EDTA), 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt (tiron), hydrochloric acid, sulfuric acid, eriochrome black T and “pure” zirconium dichloride oxide octahydrate ($\sim 2\%$ Hf), and zirconium sulfate tetrahydrate ($\sim 2\%$ Hf) all from POCh (Gliwice, Poland) were used as received.

Zirconium dichloride oxide octahydrate 99.9% metal basis (<100 ppm Hf), hafnium dichloride oxide octahydrate 98+% were obtained from Alfa Aesar and used as received. Water was distilled and purified using a Millipore Elix 10 system.

Stock solutions of PEG were prepared by dissolving PEG 2000 in water to give a concentration of 35% (w/w). Salt phases (stock solution) were prepared by weighing out 3 g of sodium sulfate or 11 g of sodium citrate and adding 15 ml solution containing various concentration of acids (HCl, H_2SO_4) to give an initial salt concentrations in salt-rich phase of 16.7, 39.7% (w/w), respectively. Concentrated solutions of studied metals (~ 0.15 g of metal/ml) were prepared and stored in 2 M HCl (except of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in 0.5M H_2SO_4). The solutions were standardized by gravimetric procedure utilizing mandelic acid (16). Tiron (if used) was added in solid state (0.20 or 0.23 g).

Apparatus

IRIS II ADVANTAGE RAD HR (serial no 7063) Thermo Jarrell Ash (USA) inductively coupled plasma emission spectrometer was used. The conditions for determination of Zr and Hf by ICP-AES are presented in Table 1.

Table 1. Operation conditions for determination of Zr and Hf by ICP-AES

	Zr	Hf
Rf [MHz]		27.12
RF power [W]		1150
Argon coolant flow rate [l/min]		14
Argon carrier pressure [PSI]		32
Integration time [s]		
Low WL	20	10
High WL	10	10
Resolution [nm]		
		<0.005 at 200 nm
		<0.01 at 400 nm
		<0.02 at 600 nm
Peristaltic pump flow rate [ml/min]		1.85
Wavelength [nm]	257.1; 316.5; 327.3; 327.9;	196.4; 227.7; 232.2; 235.1
Low WL range [nm]		175–275
High WL range [nm]		210–800

Procedure

To determine the distribution ratios of the metal ions, 15 ml of PEG 2000 stock solution (35%) was mixed with salt stock solution (phase) and 0.5 ml of concentrated solution of Zr, Hf or Zr + Hf and the aqueous biphasic system was vortex-mixed (500 rpm) in a thermostated water bath for 5, 10, 30, or 120 minutes.

After phase separation (about 10 minutes) each phase was placed in a volumetric flask and diluted to 50 ml with 2 M HCl. The content of the macro-component (zirconium or hafnium if extracted individually) was determined in both phases by a volumetric method employing EDTA and eriochrome black T (17). The results were confirmed by ICP-AES after proper dilution. ICP-AES was also used for the determination of microcomponent (hafnium) in zirconium matrix (also in both phases) in the case of simultaneous extraction of examined metals utilizing zirconium compounds containing a natural amount of hafnium (~2% Hf in Zr).

The distribution ratios (D_{Zr} , D_{Hf}) were calculated in the following way:

$$D_M = \frac{[m_{Zr(Hf)}]_{PEG}}{[m_{Zr(Hf)}]_{salt}} \quad (1)$$

where: $[m_{Zr(Hf)}]_{PEG}$ – total zirconium (hafnium) mass content in the PEG-rich phase [g] in applied conditions; $[m_{Zr(Hf)}]_{salt}$ – total zirconium (hafnium) mass content in the salt-rich phase [g] in applied conditions.

The separation factor (SF) was calculated to estimate the possibility of hafnium and zirconium separation.

$$SF = \frac{D_{Zr}}{D_{Hf}} \quad (2)$$

All experiments described above were performed at least in duplicate.

RESULTS AND DISCUSSION

A strong acidic medium is required to avoid zirconium and hafnium hydrolysis and further polymerization of their hydroxo compounds. For this reason all our experiments were performed in the presence of acids (HCl or H_2SO_4). However, sulfate and chloride anions show an opposite influence on distribution ratios of various metals in ABS systems: the presence of chloride ions induces the transfer of metals into the PEG-rich phase (9), and sulfate ions strongly decrease the extraction (e.g., zirconium and hafnium were not extracted into PEG-rich phase in PEG 2000-KSCN- SO_4^{2-} system as opposed to PEG 2000-KSCN-HCl system where distribution ratios of metals were quite high ($D > 10$ for $C_{HCl} > 0.01$) (15). On the other side addition of acids affect the aqueous biphasic system (14).

Therefore, primarily some phase diagrams of the PEG 2000- Na_2SO_4 system for 0, 125 M and 0, 55 M HCl were obtained (in the case of higher HCl concentration, higher concentration of PEG 2000 as well as Na_2SO_4 are necessary to provide heterogeneity of the system, but the increase of these concentrations causes a decrease of the phase separation rate (14). The systems chosen for investigation of Zr (Hf) extraction contained 35% of PEG-2000, 16.7% of Na_2SO_4 and 0.185–0.55 M HCl (taking into account the amount of HCl introduced with Zr (Hf) stock solution) in the initial PEG 2000- Na_2SO_4 -HCl systems (point X). The results are presented in Fig. 1.

The effect of HCl concentration on distribution ratios of Zr and Hf in PEG 2000- Na_2SO_4 -HCl in the HCl concentration range 0.185 – 0.55 M are presented in Fig. 2.

The rise of distribution ratios and some differences in behavior of examined metals can be observed with increasing HCl concentration. For the highest used acid concentration ($C_{\text{HCl}} = 0.55$ M) distribution ratios for studied metals are equal to $D_{\text{Zr}} = 0.96$ and $D_{\text{Hf}} = 0.72$, which means that almost 50% (w/w) of zirconium and about 40% (w/w) of hafnium transfer into the PEG-rich phase. Taking into consideration the “synergistic effect” reported by Peralta-Zamora (18), the extraction of hafnium in presence of zirconium ($\sim 2\%$ Hf in Zr) in the examined system was performed. Unfortunately the existence of this phenomenon was confirmed as well in the studied system: the separation factor for Zr and Hf extracted separately ($C_{\text{HCl}} = 0.55$ M) is equal to $\text{SF} = 1.33$ and lowers to $\text{SF} = 1$ when they are extracted simultaneously. Because of significant differences between the

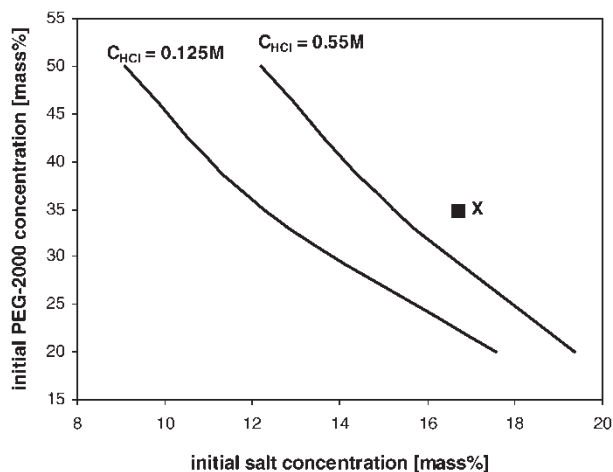


Figure 1. Phase diagrams of PEG 2000- Na_2SO_4 - H_2O -HCl systems for various HCl concentrations.

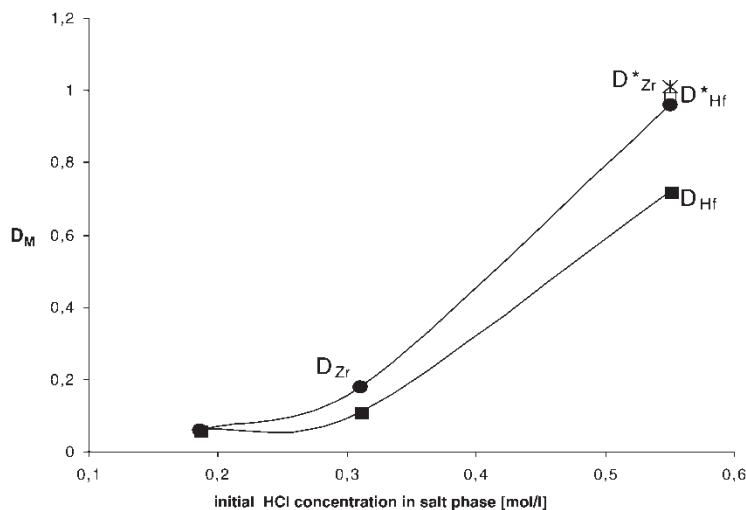


Figure 2. Effect of HCl concentration on distribution ratios of Zr and Hf in PEG 2000- Na_2SO_4 -HCl; temperature $T = 298 \text{ K}$; extraction time $t = 5 \text{ min}$; D_{Hf} , D_{Zr} -distribution ratios of isolated hafnium and zirconium; D_{Hf}^* , D_{Zr}^* -distribution ratios of hafnium and zirconium in their mixtures.

extractive behavior of the isolated elements related to their mixture, all further experiments were carried out utilizing salts of Zr containing $\sim 2\%$ Hf (as those metals occur in the nature) to estimate the actual chances of separation of hafnium from zirconium.

The distribution ratios in the presence of H_2SO_4 in PEG 2000- Na_2SO_4 - H_2SO_4 system and the absence of chloride ions are very low (< 0.02) which means that sulfate complexes of the examined elements prefer a salt-rich phase. This may be qualitatively explained in terms of hardness of occurrent anions (SO_4^{2-} , Cl^-) from which sulfate ions are stronger hard bases than chloride ones, and have greater affinity to the salt phase containing SO_4^{2-} anions. Less hard Cl^- anions and their Zr (Hf) complexes prefer the PEG rich phase.

Studying the effect of extraction time on distribution ratios of investigated metals (Table 2) some remarkable results can be observed. Initially increasing distribution ratios drop significantly if extraction goes on longer than 10 minutes. This untypical trend was earlier reported (9) when the distribution ratios of Arsenazo III complexes of Am were measured as a function of time in ABS. The highest D_{Am} was reached after 3 minutes of extraction and its decrease in another 17 minutes was observed. There was no proposition of explanation of this effect in the mentioned publication. In our opinion this non-specific behavior may be caused by further polymerization of the PEG which was observed by Rogers et al. (9) in the presence of HCl, as well as by forming hydrolyzed and polymerized ions, such as

Table 2. Effect of extraction time on distribution ratios of Zr and Hf in PEG 2000- Na_2SO_4 -HCl; temperature $T = 298 \text{ K}$; initial HCl concentration in salt phase $C_{\text{HCl}} = 0.55 \text{ M}$, D_{Hf}^* , D_{Zr}^* -distribution ratios of hafnium and zirconium extracted in their mixtures

Extraction time [min]	D_{Zr}^*	D_{Hf}^*	SF
5	1.01	0.98	1.03
10	1.28	1.11	1.15
30	0.64	0.58	1.10
120	0.37	0.33	1.12

$[\text{Zr}(\text{Hf})_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ having a greater affinity to the salt phase. The effect of time on the extraction of both elements is similar and the separation factor (SF) remains approximately on the same level.

Table 3 presents the influence of extraction temperature on distribution ratios of studied metals in the range of 298 to 318 K. The reduction of temperature to 288 K caused the crystallization of sodium sulfate and D_{M} could not be determined in such conditions. In the range of 298 to 308 K no significant differences in the partition of investigated elements are observed. The increase of temperature to 318 K results in lowering of D_{M} in the examined system. The volumes of obtained phases in 318 K were different from those observed in 298 and 308 K. They increase in the case of salt phase and decrease in the case of the PEG phase. This fact may partially explain the drop of the distribution ratios of studied metals by existence of some differences in phases composition which has a great influence on the distribution ratios in the ABS system (10, 19). Moreover, the significant increase of Zr and Hf contents in the salt phase in 318 K may be caused by a greater degree of hydrolysis and polymerization of zirconium (hafnium) chloride complexes in higher temperature with forming species of less affinity to the PEG rich phase.

It is advantageous in the ABS system if salt producing second phase forms complexes with metal ions which prefer PEG-rich phase (e.g., KSCN complexes of Sc, Co, Fe (15)). For this purpose we used sodium citrate (Na_3Cit) whose complexes with zirconium and hafnium relatively significantly differ in the stability constant ($K_{\text{IZr}}/K_{\text{IHf}} = 7.5$) (20), which looked very promising regarding their separation. The replacement of sodium sulfate with a proper concentration of sodium citrate to 39.7% (w/w) without changing other parameters (extraction time $t = 5 \text{ min}$; initial HCl concentration in salt phase $C_{\text{HCl}} = 0.55 \text{ M}$; temperature $T = 298 \text{ K}$) results in a two-phase formation. Unfortunately, distribution ratios D_{Zr}^* , D_{Hf}^* were lower than 0.03 which means that both complexes prefer the salt-rich phase.

Table 3. Effect of extraction temperature on distribution ratios of Zr and Hf in PEG 2000- Na_2SO_4 -HCl; extraction time $t = 30$ min; initial HCl concentration in salt phase $C_{\text{HCl}} = 0.55\text{M}$, D_{Hf}^* , D_{Zr}^* -distribution ratios of hafnium and zirconium extracted in their mixture; added amounts: Zr-62.0 mg, Hf 1.30 mg

Extraction temperature [K]	Volume of the phase [ml]		Determined [mg]									SF	
			Zr			Hf							
	Salt	PEG	Salt	PEG	Σ	Salt	PEG	Σ	D _{Zr} [*]	D _{Zr} ^{*av}	D _{Hf} [*]		D _{Hf} ^{*av}
298	7.0	23.0	37.7	24.5	62.2	0.80	0.48	1.28	0.65	0.64	0.60	0.58	1.10
	6.6	24.3	38.7	24.3	63.0	0.82	0.46	1.28	0.63		0.56		
308	7.1	23.8	39.7	22.2	61.9	0.83	0.47	1.30	0.58	0.59	0.57	0.59	1.00
	7.0	24.0	39.7	24.5	64.2	0.80	0.49	1.29	0.62		0.61		
318	10.8	20.0	51.2	10.8	62.0	1.08	0.21	1.29	0.21	0.20	0.19	0.18	1.11
	11.0	19.8	52.0	10.2	62.2	1.09	0.19	1.28	0.20		0.17		

The third category of metal ion extraction in aqueous biphasic systems is extraction using a water-soluble complexant. In this study 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt (tiron) was used because of differences in the stability constants of its complexes with zirconium and hafnium (21, 22).

The addition of the complexing agent to PEG 2000- Na_2SO_4 -HCl system results in significant increase of distribution ratios of studied elements to $D_{\text{Zr}}^* = 3.75$ and $D_{\text{Hf}}^* = 4.31$, what means that about 80% (w/w) of the metals transfer into PEG-rich phase. Calculated separation factor is close to 1, hence the investigated complexant is not very useful for zirconium and hafnium separation in the ABS system. The increase of D_{Zr}^* and D_{Hf}^* is also observed in PEG 2000- Na_2SO_4 - H_2SO_4 system containing tiron. The much lower distribution ratios compared to those obtained in PEG 2000- Na_2SO_4 -HCl system may be caused by partial masking of Zr and Hf by sulfate ions. The citrate complexes of discussed metals are distinctly stronger than tiron complexes and investigated elements almost completely remain in the salt-rich phase (Table 4).

Table 5 shows that distribution ratios of studied metals decrease significantly with increase of pH value and separation factors approach 1. The greater extraction of Zr and Hf as well as SF most different from 1 is observed in more acidic solution. Probably at elevated pH values the solution may contain tiron complexes with partially hydrolyzed and polymerized forms of studied metals which have a higher affinity to the salt-rich phase (D_{Zr}^* and D_{Hf}^* decrease). In such conditions when zirconium (IV) and hafnium (IV) may occur as mixed complex $[\text{Zr}_{(4-x)}\text{Hf}_x(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, tiron shows poor selectivity as it does in more acidic solutions (SF approaches 1).

However, taking into consideration little knowledge about water soluble extractants of studied metals there is still a great potential in the aqueous biphasic system for zirconium and hafnium separation. These ligands are not extensively studied because of their uselessness in traditional oil/water systems.

Table 4. Effect of addition of tiron on distribution ratios of Zr and Hf in ABS systems; extraction time $t = 5$ min; temperature $T = 298$ K; initial HCl concentration in salt phase $C_{\text{HCl}} = 0.55$ M; initial H_2SO_4 concentration in salt phase 2 M; D_{Hf}^* , D_{Zr}^* -distribution ratios of hafnium and zirconium extracted in their mixture; molar ratio Zr/tiron: 1/2.6

Tiron	D_{Zr}^*		D_{Hf}^*		SF	
	With	Without	With	Without	With	Without
PEG 2000- Na_2SO_4 -HCl	3.75	1.01	4.31	0.98	0.87	1.03
PEG 2000- Na_2SO_4 - H_2SO_4	0.19	<0.02	0.23	<0.02	0.83	
PEG 2000- Na_3Cit -HCl	<0.03	<0.03	<0.03	<0.03		

Table 5. Effect of pH value (of initial salt phase) on distribution ratios of Zr and Hf in PEG 2000- Na_2SO_4 -tiron system; extraction time $t = 5$ min; temperature $T = 298$ K; D_{Hf}^* , D_{Zr}^* -distribution ratios of hafnium and zirconium extracted in their mixture; molar ratio Zr/tiron: $^*1/2.6$, $^{**}1/3$

	pH	D_{Zr}^*	D_{Hf}^*	SF
1 [*]	0.3	3.75	4.31	0.87
2 ^{**}	5.0	0.41	0.42	0.98
3 ^{**}	12.0	0.25	0.26	0.96

CONCLUSIONS

The little known extractive behavior of zirconium and hafnium in ABS system has been investigated. Effects of various extraction parameters on distribution ratios of these metals have been determined. The highest values of examined coefficients were obtained at room temperature and at short extraction time (5–10 min). The compounds of zirconium and hafnium with sulfate and citrate ligands prefer the salt-rich phase as opposed to anionic chloride complexes of Zr and Hf which partially pass into PEG-rich phase (extraction above 50%). The addition of a water soluble organic complexing agent (tiron) enhances significantly the extraction of Zr and Hf in PEG 2000- Na_2SO_4 -HCl system (extraction $\sim 80\%$). Unfortunately, with the change of distribution ratios in various conditions no change of the separation factor was observed. Although ABS system in studied conditions proved not very useful for separation of examined elements, numerous advantages of using the aqueous biphasic system in comparison with traditional oil/water extraction incline to look for new selective water soluble complexing agents and continue the investigation of hafnium from zirconium separation in the ABS system.

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