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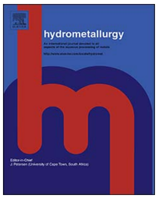

Separation of zirconium from hafnium in sulfate medium using solvent extraction with a new reagent BEAP

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ABSTRACT

A new extractant, bis(2-ethylhexyl)-1-(2-ethylhexylamino)propylphosphonate (BEAP or B) was synthesized to extract and separate zirconium and hafnium from sulfate medium. Under optimum conditions, the separation factor of Zr over Hf was found to be 6.8. The extracted complexes were determined to be $ZrO(HSO_4)_2 \cdot 3B$ and $HfO(HSO_4)_2 \cdot 2B$. The extractions of zirconium and hafnium are both exothermic. A counter-current operation was conducted, in which the content of HfO_2 was decreased from 3% to 0.6% in the ZrO_2 product. It is suggested that much more extraction and scrubbing stages are needed to reach the goal of 0.01% HfO_2 in ZrO_2 product.

1. Introduction

Zirconium and hafnium usually co-exist in nature. Zirconium is widely used as the container and structural material of nuclear reactor due to its low thermal neutron capture cross-section. Differently, hafnium is an important control material for thermonuclear reaction because of its high neutron capture cross-section. Due to their diverse neutron capture properties, it is crucial to separate them before they are used in nuclear energy. For example, the content of hafnium in nuclear zirconium should be $<$ 0.01%. Due to their similar chemical properties, the separation of zirconium and hafnium is still a challenge (Mukherji, 1970; Marczenko and Balcerzak, 2002; Xu et al., 2010; Xu et al., 2015a; Zhang, 2004, 2007).

Many methods such as fractional crystallization (Niemand and Crouse, 2015), fractional precipitation (Schumb and Pittman, 2002), ion exchange (Huffman and Lilly, 1951; Benedict et al., 1954), silica gel adsorption (Hansen and Gunnar, 1949), molten salt distillation (Spink, 1980) and solvent extraction (Fischer and Chalybaeus, 1947; Cox et al., 1958) have been studied for the separation of zirconium and hafnium. Furthermore, only solvent extraction is used in industry with MIBK and TBP as the extractants (Fischer and Chalybaeus, 1947; Fischer et al., 1948; Sommers and Perrine, 2002). However, there are some disadvantages concerned the extraction systems of these two extractants. The MIBK system leads to solvent loss, atmospheric pollution and poor working environment due to the defects that the waste stream contains high concentrations of ammonium, cyanides and organic by-products with low flash point, high vapour pressure and solubility in the aqueous phase (Snyder and Lee, 1992; Taghizadeh et al., 2008; Xu et al., 2010; Banda and Man, 2015). For the TBP system, the extractant has a high aqueous solubility and is not stable for long time operation, the equipments are seriously corroded, and the emulsified phenomenon is found in continuous production (Levitt and Freund, 2002). So other extractants such as Cyanex 923 were studied. Gupta et al. (2005) extracted zirconium from zircon leaching solution using 0.1 mol/L Cyanex 923 solution in toluene and recovered around 98% Zr with the purity of 98%. Nayl et al. (2009) studied the extraction and separation of Zr and Hf from nitrate medium by some Cyanex extractants and found that Cyanex 925 is more efficient than Cyanex 921 and Cyanex 923. Lee and Wang (Lee et al., 2015; Wang and Lee, 2016a) studied the extraction and separation of Zr and Hf using di-2-ethylhexylphosphoric acid (D2EHPA) from sulfate solutions and found that the loading capacity of D2EHPA is low (only 10 g/L Zr and 0.2 g/L Hf with 0.05 mol/L D2EHPA) and the efficient stripping needs strong acidic solutions (4 mol/L H_2SO_4). Synergistic extraction was also applied for the separation of zirconium and hafnium (Rezaee et al., 2011; Banda et al., 2012; Xu et al., 2015b; Xu et al., 2016; Wang and Lee, 2016b). Although, synergistic extraction can overcome some shortcomings of the sole extractant, the fatal problem is that it's so hard to maintain a ratio of multiple extractants for long time operations.

In the present work, a new neutral extractant bis(2-ethylhexyl)-1-(2-ethylhexylamino)propylphosphonate (BEAP) was synthesized and applied for the extraction and separation of zirconium and hafnium from sulfate medium. The extraction stoichiometry was deduced and thermal parameters were calculated.

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2. Experimental

2.1. Chemicals and materials

Bis(2-ethylhexyl)phosphite (Shanghai Rare-earth Chemical Co., Ltd.), 2-ethylhexylamine (Shanghai Aladdin Industrial Co.) and propanal (Beijing Chemical Co., Ltd) were used as raw materials for the synthesis of BEAP without further purification. The extractant was dissolved in *n*-heptane to the required concentrations. The stock solutions of Zr and Hf were prepared by dissolving the corresponding salts in the corresponding mineral acid solutions. All work solutions were obtained by diluting the stock solutions. The initial concentrations of Zr and Hf were fixed to 1.0×10^{-2} mol/L (unless otherwise stated). All other reagents were of analytical reagent grade.

2.2. Apparatus

Nuclear magnetic resonance spectra were determined using a Bruker AV 600 M for ^{1}H NMR (600 MHz) and FT-IR spectra (KBr pellets) using a Bruker Vertex 70 Spectrometer. The metal concentrations were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000).

2.3. Synthesis of bis(2-ethylhexyl)-1-(2-ethylhexylamino) propylphosphonate (BEAP)

BEAP (Fig. 1) was synthesized according to the method in the literature (Stoikov et al., 2000; Kuang et al., 2017; Lu et al., 2017). A mixture of 30.6 g (0.1 mol) bis(2-ethylhexyl)phosphite, 14.2 g (0.11 mol) 2-ethylhexylamine, 6.4 g (0.11 mol) propanal, 80 mL anhydrous toluene and 0.2 g *p*-toluenesulfonic acid were placed in a single-neck round-bottom flask (250 mL) equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser. The mixture was heated with stirring for 6 h in an oil bath at 130 °C. At the end of the reaction 0.1 g of K_2CO_3 was added into the solution, and the mixture was refluxed for 15 min for the removal of the catalyst. The mixture was then cooled, washed with water (3 × 100 mL) and dried. The organic solution was evaporated in a vacuum on the rotary evaporator to remove the excess reagents and solvent until no fraction was steamed out. The obtained product was an oily compound with a yield of 90% (42.80 g) and a purity of 97.80%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 4.01 (m, 4H, CH_2), 2.61 (m, 1H, CH), 2.36 (d, 2H, CH_2), 2.0 (s, 1H, NH), 1.56–1.71 (m, 3H,CH), 1.48 (m, 2H, CH_2), 1.25–1.35 (m, 24H, CH_2), 0.89 (t, 21H, CH_3).

2.4. Experimental procedures

The aqueous and organic phases, 5 mL, each were mixed and shaken using oscillator for 20 min to reach equilibrium at 298 ± 1 K (except the temperature experiment). The phases were then separated by gravity. The metal concentrations in the aqueous phase were determined by ICP-OES. The metal concentrations in the organic phases were obtained by mass balance. Distribution ratios (*D*) were calculated by $D = [M]_{(o)} / [M]_{(a)}$, where $[M]_{(o)}$ and $[M]_{(a)}$ represent the concentrations of the metal ions in the organic and aqueous phases at equilibrium, respectively.

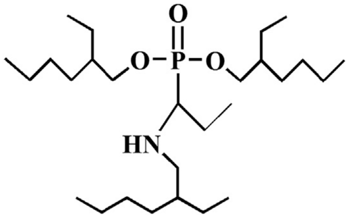

Fig. 1. Molecular structure of bis(2-ethylhexyl)-1-(2-ethylhexylamino)propylphosphonate (BEAP).

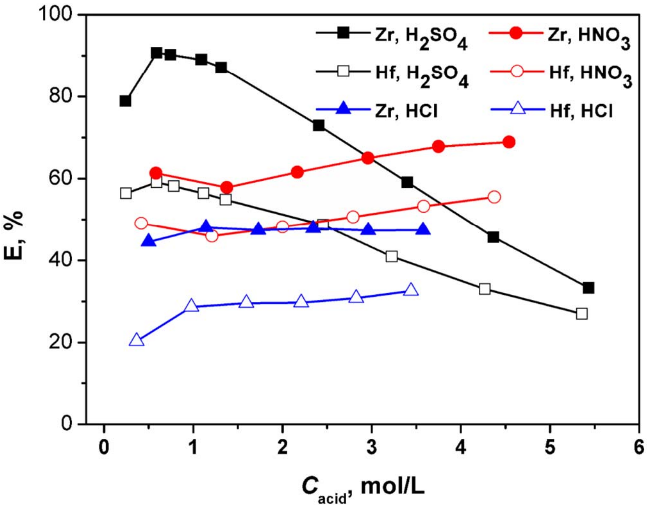

Fig. 2. Effect of acid concentration on the extraction of metal ions.$[Zr^{4+}] = [Hf^{4+}] = 1.0 \times 10^{-2}$ mol/L, [BEAP] $= 5.0 \times 10^{-2}$ mol/L.

3. Results and discussion

3.1. Extraction of Zr and Hf from different acidic media

The extraction of Zr and Hf using BEAP dissolved in *n*-heptane was investigated from various acidic media including H_2SO_4, HCl and HNO_3 solutions. In the experiments, the initial concentrations of Zr and Hf in the aqueous solutions were both kept at 0.01 mol/L, and the concentration of BEAP was maintained at 0.05 mol/L. The ranges of acid concentration were 0.05–6 mol/L for H_2SO_4, 0.05–5 mol/L for HCl, and 0.05–4 mol/L for HNO_3. The phase ratio (O/A) was fixed at 1:1 with a constant total volume.

As shown in Fig. 2, the extractant demonstrated higher extraction ability toward Zr than Hf in all three studied acid systems. Furthermore, the extraction of Zr and Hf by BEAP from different acidic media increased in the order of HCl < HNO_3 < H_2SO_4. In the studied acidic range, the maximum of the extraction percentage of Zr reached 48.0% for the HCl system, 68.9% for the HNO_3 system and 90.7% for the H_2SO_4 system, while that of Hf was 32.5% for the HCl system, 55.5% for the HNO_3 system and 59.1% for the H_2SO_4 system. In the H_2SO_4 medium, the extraction of Zr first increased with the increasing H_2SO_4 concentration when CH_2SO_4 was lower than 0.59 mol/L. Then it decreased with the further increasing acid concentration. Similar trend was also observed for the extraction of Hf. Differently, in the HCl and HNO_3 media, the extraction of Zr and Hf changes slightly with the increasing acid concentration. The separation factor (Table 1) of Zr over Hf reached a maximum of 6.77 at the H_2SO_4 concentration of 0.59 mol/L while that was kept < 2 for the HNO_3 system and < 3.2 for the HCl system. It seems that better separation of Zr from Hf can be obtained with sulfate medium. However, when the H_2SO_4 concentration is > 1.0 mol/L, the extraction of both Zr and Hf decreased rapidly with the

Table 1
Separation factors ($\beta_{Zr/Hf}$) at different acid concentrations.

β					
CH_2SO_4(mol/L)	$\beta_{Zr/Hf}$	CHCl(mol/L)	$\beta_{Zr/Hf}$	$CHNO_3$(mol/L)	$\beta_{Zr/Hf}$
0.24	2.88	0.50	3.14	0.58	1.65
0.59	6.77	1.14	2.30	1.38	1.61
1.09	6.27	1.73	2.14	2.17	1.72
1.32	5.55	2.34	2.17	2.99	1.81
2.41	2.84	2.96	2.02	3.75	1.85
3.40	2.09	3.58	1.87	4.54	1.77