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Liquid-liquid extraction of zirconium(IV) from sulphuric acid medium using a binary mixture of tri-*n*-octylamine and Cyanex923 in kerosene

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ABSTRACT

The extraction behaviour of zirconium(IV) from sulfuric acid medium has been studied with a binary mixture of tri-*n*-octyl amine (TOA) and Cyanex923 (a mixture of four trialkyl phosphine oxides) in kerosene using a novel liquid-liquid extraction method. Quantitative extraction of zirconium(IV) with binary mixture of Cyanex923 and TOA in kerosene was studied by changing different parameters such as acid variation, extractant variation, effect of chloride ion concentration, effect of temperature, metal concentration variation, diluent effect, and pH effect. The percentage of extraction of zirconium(IV) decreased when the concentration of Cyanex923 and TOA increased. The percentage of zirconium(IV) was observed as 97.56% in a binary mixture of 0.007 M Cyanex923 and 0.06 M TOA. Kerosene was found to be an effective diluent for the extraction of zirconium(IV) with 97.56% extraction using a binary mixture of Cyanex923 and TOA. In addition, the stripping of the zirconium(IV) metal ion in the organic phase was also examined.

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1. Introduction

Zirconium (Zr) is a soft, lustrous, ductile, grayish-white, malleable transition metal that is solid at room temperature and at low purities becomes hard and brittle [1]. Zirconium is an extremely corrosion-resistant metal by alkali, saltwater, acids, and other agents [2]. Even though zirconium and hafnium have similar chemical properties, they differ in neutron-absorbing properties that lead to the separation of hafnium from zirconium for nuclear reactor applications [3]. Zirconium is also used as the cladding material for nuclear reactor fuels [4]. Zirconium is a heat-resistant metal. In space vehicle parts, materials fabricated from zirconium metal and its oxide (ZrO₂) are used [3]. The compounds inhold zirconium metal are used in several biomedical applications, such as dental implants and other restorative practices, middle ear ossicular chain reconstruction, knee and hip replacements, *etc.* [5]. Solvent extraction of Zr(IV) from acid chloride medium by using a commercial extractant LIX84-IC was studied by Reddy *et al.* [6]. Using HCl and high concentrations of green amic acid, *N,N*-di-2-ethylhexyl diglycolamic acid (D2EHDGAA), Ma *et al.* developed a novel strategy for separating Zr ions and Hf ions. Based on these results, it was concluded that D2EHDGAA in HCl solution performed well at separating Zr ions and Hf ions. Using 2.5

mol/L HCl, the zirconium oxychloride hydrolysate and simulation liquid had separation factors of 11.4 and 34.5, respectively [7]. Co-extraction and separation of Zr and Hf using primene JM-T extractant as long-chain primary amine from the sulfuric acid medium were carried out by El-Yamani *et al.* [8]. The extraction of Zr from the sulfuric acid medium by using long-chain aliphatic amines was studied by Sato *et al.* [9]. Secondary amines are more effective extractants than tertiary amines for Zr was observed by Sato *et al.* [9]. Using Aliquate-336 as an organic solvent, Zr(IV) extraction through the sulfuric acid medium was carried out by Sato *et al.* [10]. Through solvent extraction technique, by utilizing a new extractant, bis(2-ethylhexyl)-1-(2-ethylhexylamino)propylphosphonate (BEAP or B) the separation of zirconium from hafnium from sulfate medium was completed by Chen *et al.* [11]. They reported that the extraction of both zirconium and hafnium are exothermic processes and the separation factor of Zr over Hf was 6.8 at 25 °C. The equilibrium studies in the extraction of Zr(IV) through sulfate medium using di(2-ethylhexyl)phosphoric acid (D2EHPPA, HR) acid in kerosene were carried out by Juang *et al.* [12]. They reported that at higher loading ratios of D2EHPPA (0.10 < α < 0.32) and at low loading ratios of D2EHPPA (α < 0.09) the extracted species were found to be ZrR₄, ZrR₄(HR)₃ and ZrR₄, ZrR₄(HR), respectively. With Alamine 336 (10%) in kero-

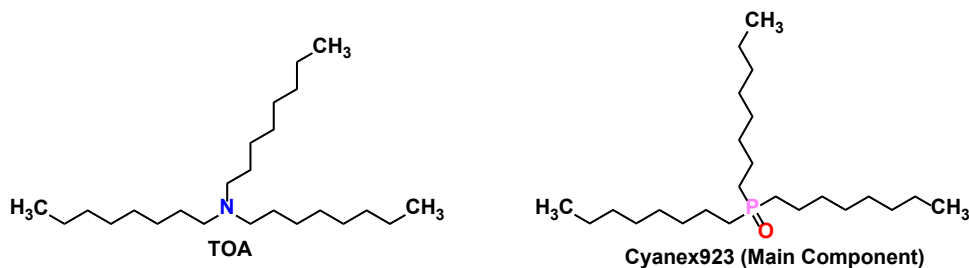


Figure 1. The structure of TOA and Cyanex923 (main component).

sene, Junior *et al.* processed the Brazilian bauxite residue to separate scandium and zirconium. According to them, the D2EHPA and TBP mixture had the same scandium separation factor as Cyanex923 [13]. By varying the concentrations of acid, solvent, and aqueous Zr(IV), the extraction of Zr(IV) using high molecular amines from a sulfuric acid medium was carried out by Schrotterova *et al.* [14]. Using amine-based extractants such as Aliquat336, Alamine300, Alamine308, TEHA, and Alamine-336, Wang and Lee studied the extraction and separation of Zr and Hf from the sulfate medium [15] and Alamine308 got the highest separation factor of 12.4 at 0.5 M sulfuric acid medium. The solvent extraction of trace level Zr and Hf from HCl, HF, HNO₃, and H₂SO₄ media by using trioctylamine (TOA) was demonstrated by Das and Lahiri [16]. They reported that for quantitative extraction of the individual elements at their trace level, TOA was a very effective extractant. Onishi *et al.* [17] studied the spectrophotometric determination of microgram amounts of zirconium, thorium, uranium, and rare earths with arsenazoIII by using theryltrifluoroacetone (TTA) and tri-*n*-octylamine in xylene from HCl medium. Wu *et al.* proposed a pathway for synergistic extraction of Hf over Zr using a binary mixture extractant, *i.e.*, TOPO and N1923 from thiocyanic acid. The efficiency of their process was found to be 86.3% [18]. Solvent extraction behavior of trace level tantalum and niobium by using trioctylamine from sulphuric acid and hydrofluoric acid media that have greater affinities towards niobium and tantalum with TOA was studied by Das *et al.* [19]. Using a binary mixture of *N,N*-octylaniline, and trioctylamine in xylene, Petkar *et al.* [20] investigated the liquid-liquid extraction of Bi(III) from thiocyanate and sulfuric acid medium. By using 4-(5-nonyl)pyridine oxide and trioctylamine oxide in nitric acid and sulphuric acid medium, the extraction of zirconium was investigated by Ejaz [21]. Through solvent extraction techniques, the extraction and separation of Zr and Hf from the nitric acid medium with some phosphine oxide extractants such as Cyanex923, Cyanex921, and Cyanex925 in kerosene were reported by Nayl *et al.* [22]. They reported that, in Cyanex921, Cyanex925, and Cyanex923, the extraction rate of Zr (IV) and Hf(IV) is fast and also suggested that the extraction increases with increasing temperature, implying that the reaction is endothermic. An evaluation of the inertness and performance of organophosphorus-based extraction agents DiOPA, Ionquest 801, and D2EHPA was conducted using both dispersive extraction and per traction solvent extraction (SX) to achieve selective extraction of Zr and Hf from an acid solution of (NH₄)₃Zr(Hf)F₇ [23]. The separation of Zr and Hf with a mixture of Cyanex923 and TBP extractants in the organic phase by using the solvent extraction technique was proposed by Taghizadeh *et al.* [24]. Using the solvent extraction process, Gupta *et al.* [25] investigated the extraction and recovery of Zr from zircon using Cyanex923 extractant in toluene.

Zirconium metal extraction in greater quantities is essential than in trace levels. To determine the amounts of metal in aqueous and organic solutions, the solvent extraction method is a prominent effective method. The important aim of solvent extraction is to recover the metal from its solution using a

suitable extractant. In this work, the quantitative extraction of Zr(IV) by the solvent extraction method operating various parameters such as the acidity of the aqueous phase, the molarity of the extractant, the concentration of chloride ions, the diluents, the temperature and the concentration of the metal of the aqueous phase, the pH has been investigated from the sulphuric acid medium using the binary mixture of Cyanex923 and TOA (Figure 1). The loaded organic phase containing metal has been stripped with TOA and Cyanex923 extractants to find the best strippant for the extraction system.

2. Experimental

2.1. Reagents

A 0.01 M ZrOCl₂·8H₂O (Merck) stock solution was prepared by dissolving in double-distilled water. To restrict further hydrolysis, one mL of concentrated HCl was added to the metal stock solution. Distilled kerosene was used as an organic diluent. TOA (tri-octylamine) (Merck) and a mixture of four trialkyl phosphine oxides, *i.e.*, Cyanex923 (Merck) were used as a commercial extractant without further purification. All other reagents used were of analytical reagent grade.

2.2. Process

10 mL of solutions containing Zr(IV) (0.001 M) in H₂SO₄ and the organic phase containing Cyanex923 and TOA in kerosene were shaken in a separating funnel. In twenty minutes, complete equilibrium was achieved. After five minutes, the phases were settled, and then they were disengaged. The concentration of Zr(IV) in the aqueous phase before and after extraction was determined using the Arsenazo (III) method [18] using a PerkinElmer UV-visible spectrophotometer. The ratio of the equilibrium concentration of Zr(IV) inorganic phase and that in the aqueous phase was taken in the calculation of the distribution coefficient (D). The concentration of Zr(IV) in the organic phase was calculated by using the mass balance, *i.e.*, the difference in metal concentration in the aqueous phase before and after the extraction.

Spectrophotometrically, the absorbance of the metal was measured [18] before and after extraction, from which the distribution ratio was calculated as follows:

$$D = \frac{\text{Abs}_{\text{B.E.}} - \text{Abs}_{\text{A.E.}}}{\text{Abs}_{\text{A.E.}}} \quad (1)$$

where Abs_{B.E.} = Absorbance before extraction and Abs_{A.E.} = Absorbance after extraction. The distribution ratio was observed as the ratio of the equilibrium concentration of metal in the organic phase to that in the aqueous phase.

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \quad (2)$$

where [M]_{aq} and [M]_{org} are the metal concentrations in the aqueous and organic phase after extraction, respectively.

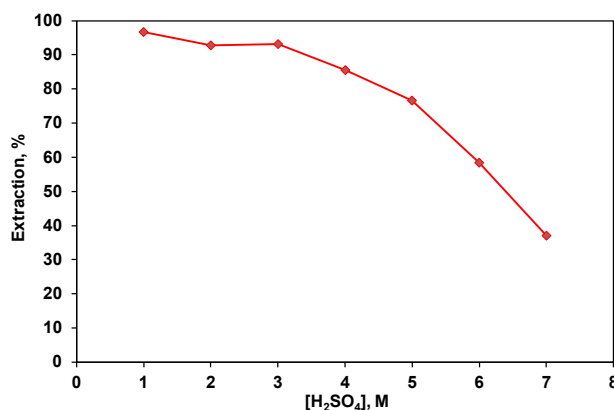


Figure 2. Impact of H₂SO₄ concentration on the extraction percentage of 0.001 M Zr(IV) using the binary mixture of 0.01 M Cyanex923 and 0.1 M TOA in kerosene.

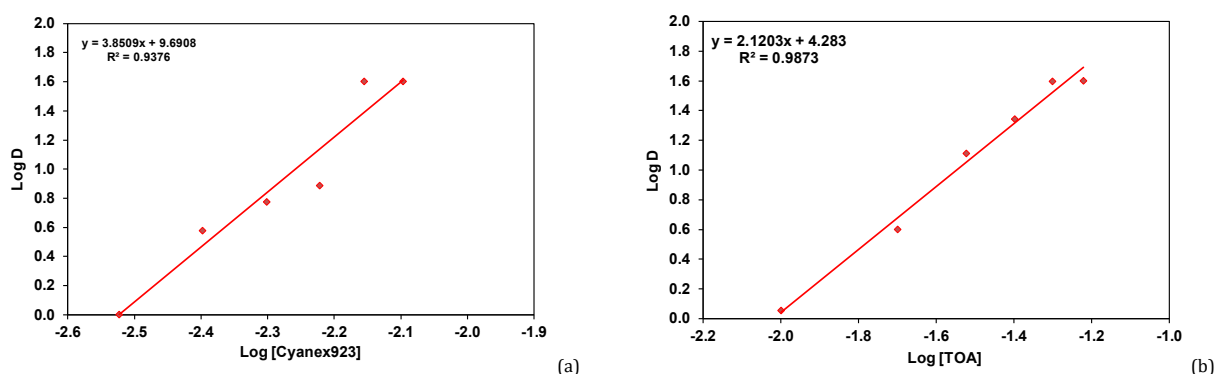


Figure 3. (a) Plot of log D versus log [Cyanex923] in the extraction of 0.001 M Zr(IV) from 1 M H₂SO₄ within the sight of a changing concentration of Cyanex923 at fixed 0.1 M TOA in kerosene and (b) Plot of log D versus log [TOA] in the extraction of 0.001 M Zr(IV) from 1 M H₂SO₄ within the sight of a varying concentration of TOA at fixed 0.007 M Cyanex923 in kerosene.

From the D values, the percentage of extraction (%E) was calculated as

$$\%E = \frac{100 D}{D+1} \quad (3)$$

3. Results and discussion

3.1. Effect of acid concentration

0.001 M Zr(IV) was extracted with 0.01 M Cyanex923 and 0.10 M TOA in kerosene by varying the concentration of H₂SO₄ from 1 to 7 M. The percentage of extraction was 96.61% with 1 M H₂SO₄ and then decreased to 36.98% with 7 M H₂SO₄. Extraction based on aqueous phase acidity was observed due to the more amine salt formation that extracts the metal complex [25]. From the observed data, a continuous decreasing plot is obtained which is shown in Figure 2.

3.2. Effect of extractant concentration

By keeping the concentration of TOA constant (0.1 M), the extraction of 0.001 M Zr(IV) was carried out (1 M H₂SO₄) in the binary mixture of extractant and changing the concentration of Cyanex923 from 0.003 to 0.008 M in kerosene. The percentage of Zr(IV) extraction decreased from 97.56 to 47.69% with a decrease in the concentration of Cyanex923 from 0.008 to 0.003 M in kerosene. The plot of log D versus log [Cyanex923] shows a slope of 3.8509 (Figure 3). At a fixed concentration of Cyanex923 (0.007 M), the effect of TOA on the 0.001 M Zr(IV) extraction was studied by changing the concentration of TOA from 0.01 to 0.06 M. The percentage of extraction increased from 53.16 to 97.56% with the increase in concentration from

0.01 to 0.06 M. The plot of log D versus log[TOA] yields a slope of 2.1203 (Figure 3).

3.3. Effect of chloride ion concentration

On the extraction of 0.001 M Zr (IV), the effect of chloride ion concentration (1 M H₂SO₄) using 0.007 M Cyanex923 and 0.06 M TOA was studied. The percentage of Zr (IV) extraction decreased from 96.26 to 93.87%, from 96.28 to 92.92%, and from 97.12 to 94.79% (Figure 4) within the increase in the concentration of NH₄Cl, KCl, and NaCl, respectively, increasing the chloride ion concentration from 0.001 to 0.080 M.

3.4. Effect of temperature

The effect of temperature on the extraction of 0.001 M Zr(IV) (1 M H₂SO₄) was carried out in the temperature range 318-358 K using a binary mixture of 0.007 M Cyanex923 and 0.06 M TOA in kerosene. The percentage of extraction of Zr(IV) decreased from 91.91 to 87.84% with an increase in temperature. By using Equation (4), the extraction equilibrium constants (K_{eq}) at different temperatures have been calculated. The plot of log K_{eq} versus 1000/T is linear (Figure 5). Enthalpy change (ΔH) and entropy change (ΔS) were calculated to be -10.2 kJ/mol and 10.84 J/K.mol using Van't Hoff equation. It ensures that the extraction process is exothermic, accompanied by an increase in randomness.

$$K_{eq} = \frac{[R_3NHZrOSO_4]_{(org)} \times [R_3PHZrOSO_4]_{(org)}}{[ZrOCl_2]_{(aq)}} \quad (4)$$

$$K_{eq} = \frac{[R_3NHOSO_4]_{(org)} \times [R_3PHSO_4]_{(org)}}{[R_3NHOSO_4]_{(org)} \times [R_3PHSO_4]_{(org)}}$$

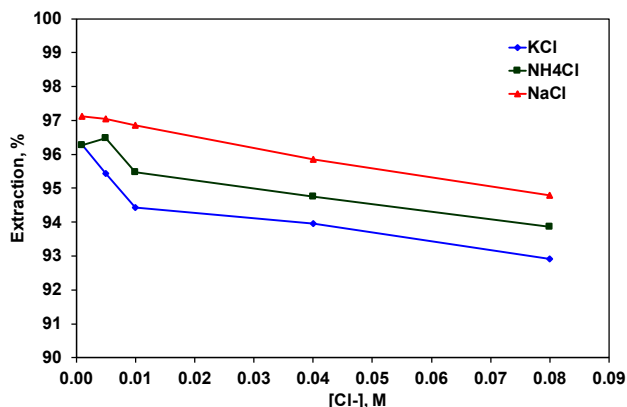


Figure 4. Impact of chloride ion concentration on the extraction of 0.001 M Zr(IV) from 1 M H₂SO₄ using the binary mixture of 0.007 M Cyanex923 and 0.060 M TOA in kerosene.

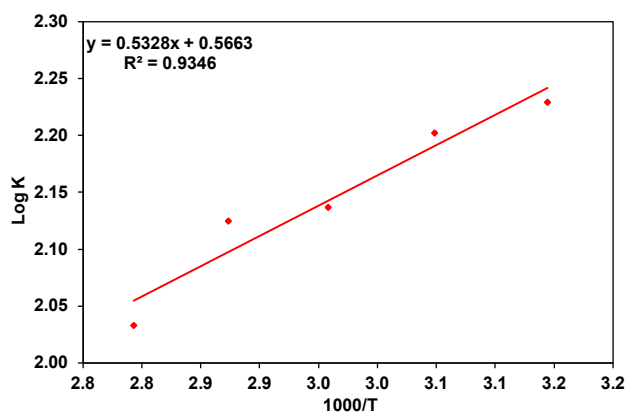


Figure 5. Plot of $\log K_{eq}$ versus $1000/T$ for the extraction of 0.001 M Zr(IV) from 1 M H₂SO₄ using the binary mixture of 0.007 M Cyanex923 and 0.060 M TOA in kerosene.

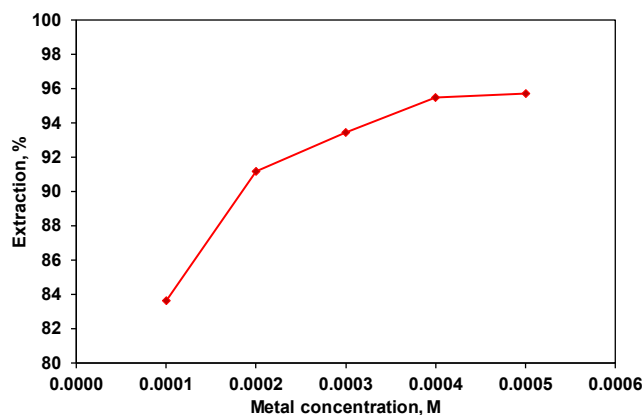


Figure 6. Impact of metal ion concentration on the extraction of 0.001 M Zr(IV) from 1 M H₂SO₄ using the binary mixture of 0.007 M Cyanex923 and 0.060 M TOA in kerosene.

3.5. Effect of metal ion concentration

Using a binary mixture of 0.007 M Cyanex923 and 0.060 M TOA, the extraction of Zr(IV) (1 M H₂SO₄) has been studied by decreasing the concentration of Zr (IV) metal ion from 0.0001 to 0.0005 M (Figure 6). The percentage of extraction was increased from 83.63 to 95.72% with the decrease in metal ion concentration up to 0.0005 M and thereafter remains constant.

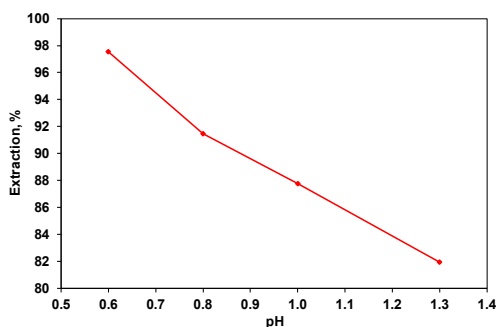
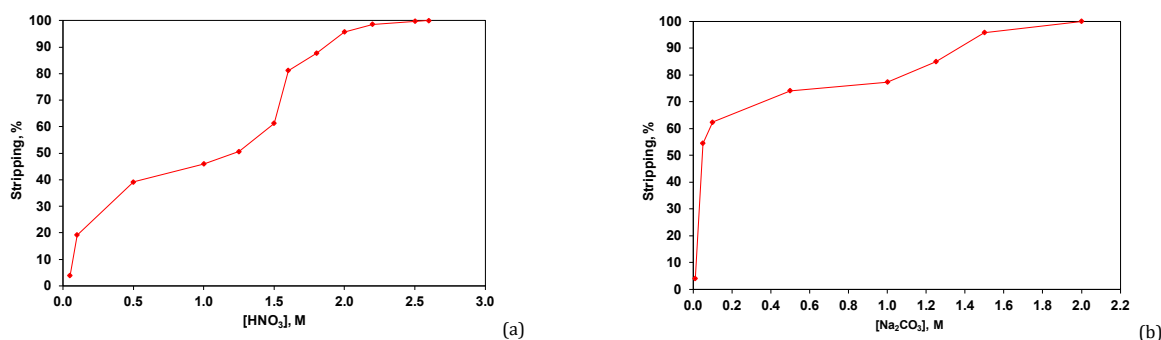
3.6. Effect of diluent

For a successful solvent extraction system, there are two vital aspects, that is, the selection of extractants and diluents

[18]. The influence of diluents on the distribution of metal is correlated with the physicochemical properties of an organic solvent such as dipole moment, dielectric constant, solubility parameter, etc. [18]. Using a binary mixture of 0.007 M Cyanex923 and 0.060 M TOA, the extraction of Zr(IV) has been studied in various organic diluents such as kerosene, benzene, diethyl ether, xylene, carbon tetrachloride, and chloroform. When kerosene was used as a diluent, the percentage of extraction was the maximum as shown in Table 1. Due to easy availability, low cost, and toxicity, kerosene was selected as the diluent for the extraction study.

Table 1. Impact of diluents on the extraction of 0.001 M Zr(IV) using the binary mixture of 0.007 M Cyanex923 and 0.060 M TOA from 1 M H₂SO₄.

Diluents	Distribution ratio	Extraction, %
Kerosene	39.993	97.56
Benzene	28.697	96.63
Diethyl ether	23.973	95.99
Xylene	33.397	97.09
Carbon tetrachloride	10.968	91.64
Chloroform	4.675	82.37

**Figure 7.** Impact of pH on the extraction of Zr(IV) from 1 M H₂SO₄ using the binary mixture of 0.007 M Cyanex923 and 0.060 M TOA in kerosene.**Figure 8.** (a) Plot of % Stripping versus [HNO₃] from the stacked binary organic phase of 0.007 M Cyanex923 and 0.060 M TOA for recuperation of Zr(IV) in kerosene and (b) Plot of % Stripping versus [Na₂CO₃] from the stacked binary organic phase of 0.007 M Cyanex923 and 0.060 M TOA for recovery of Zr(IV) in kerosene.

3.7. Effect of pH

The extraction of 0.001 M Zr (IV) using a binary mixture of 0.060 M TOA and 0.007 M Cyanex923 in kerosene was studied by changing the pH of the aqueous solution from 0.6 to 1.3. The percentage of extraction of Zr(IV) decreased from 97.54 to 81.94% was observed with an increase in pH from 0.6 to 1.3. The detailed data are shown in Figure 7.

3.8. Stripping

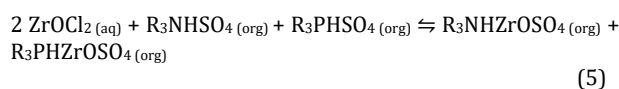
The metal can be extracted back from the loaded organic phase. This extraction process becomes commercially important [18]. The effect of various concentrations of strippants was studied on the stripping of metal ions from the loaded organic solvent at 298 K and a phase ratio of 1:1. Zr (IV) ions were extracted from 1 M H₂SO₄ using a binary mixture of 0.007 M Cyanex923 and 0.060 M TOA. It was observed that the stripping was 100% with 2.6 M HNO₃ and 2 M Na₂CO₃ in one step (Figure 8).

3.9. Extraction equilibrium

The possible extraction mechanism of Zr(IV) from sulphuric acid (H₂SO₄) medium with a binary mixture of Cyanex923 and TOA in distilled kerosene appears to proceed through the protonation of Cyanex923 (R₃P) and TOA (R₃N) forming R₃PHSO₄ and R₃NHSO₄, respectively, followed by

extraction of (R₃NH) ZrOCl₂ and (R₃PH)ZrOSO₄(org) species into the organic phase [25].

Under the experimental conditions studied and from the slope analysis results, the extraction of Zr(IV) from high acid chloride medium with the binary mixture of Cyanex923 and TOA may be described by the following Equations:



The extraction equilibrium constant is given as

$$K_{eq} = \frac{[\text{R}_3\text{NHZrOSO}_{4(\text{org})}] \times [\text{R}_3\text{PHZrOSO}_{4(\text{org})}]}{[\text{ZrOCl}_{2(\text{aq})}] \times [\text{R}_3\text{NHSO}_{4(\text{org})}] \times [\text{R}_3\text{PHSO}_{4(\text{org})}]} \quad (6)$$

$$\Rightarrow K_{eq} = \frac{D}{[\text{R}_3\text{NHSO}_{4(\text{org})}] \times [\text{R}_3\text{PHSO}_{4(\text{org})}]} \quad (7)$$

$$\text{where } D = \frac{[\text{R}_3\text{NHZrOSO}_{4(\text{org})}] \times [\text{R}_3\text{PHZrOSO}_{4(\text{org})}]}{[\text{ZrOCl}_{2(\text{aq})}]} \quad (8)$$

4. Conclusions

This work highlights the extraction of 0.001 M Zr(IV) from 1 M H₂SO₄ using a binary mixture of 0.007 M Cyanex923 and 0.060 M TOA in kerosene is highest *i.e.*, 97.56%. The extraction of Zr(IV) decreases with the increase in acid concentration and pH of the metal solution but increases with the increase in the extractant concentration and the metal ion concentration. The

extraction of Zr(IV) from 1 M H₂SO₄ decreases with an increase in temperature i.e., 318-358 K. The positive influence of temperature shows the extraction to be exothermic. The positive value of change in entropy shows an increase in randomness. The extraction of Zr(IV) from 1 M H₂SO₄ decreases with the increase in chloride ion concentration due to the extraction of chloro complex of zirconium with a binary mixture of TOA and Cyanex923. 100% of Zr(IV) is stripping out from the binary mixture of TOA and Cyanex923 with 2.6 M HNO₃ and 2 M Na₂CO₃. The percentage of Zr(IV) extraction decreases with an increase in the pH of the aqueous solution. Zr(IV) extraction from 1 M H₂SO₄ using a binary mixture of Cyanex923 and TOA has been studied in increasing order in different organic diluents, that is, Kerosene > Xylene > Benzene > Diethyl ether > Carbon tetrachloride > Chloroform. The separation studies of Zr (IV) from Hf (IV) may be undertaken under the condition where the extraction of Zr (IV) is quantitative (> 95%).

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Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.


CRedit authorship contribution statement

Conceptualization, Methodology, Software, Validation, Formal Analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review and Editing, Visualization, Funding acquisition, Supervision, Project Administration: Amit Sahoo, Jaykishon Swain, and Bhikari Charana Bhatta.

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