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Liquid-liquid extraction of Zr(IV) from sulphuric acid medium using tri-*n*-octyl amine in kerosene

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RESEARCH ARTICLE

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ABSTRACT

The extraction behavior of Zr(IV) with tri-*n*-octyl amine (TOA) in kerosene was studied through a new method of solvent extraction. The mechanism of extraction and the species extracted were identified. Quantitative extraction of Zr(IV) with TOA in kerosene was studied by changing different parameters such as acid variation, diluent effect, metal concentration variation, extractant variation, effect of salting out reagent concentration and effect of temperature. It was observed that the percentage of extraction of Zr(IV) increased when the concentration of TOA and the percentage of extraction also increased when the metal ion concentration increased. The percentage of Zr(IV) became 97.4% with 0.1 M TOA from 3.0 M sulphuric acid. Kerosene was found to be effective diluent for the extraction of Zr(IV) with TOA.

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1. Introduction

Zirconium is a corrosion resistance metal by salt water, acids and alkalis [1] which is soluble in sulphuric acid, hydro chloric acid in presence of fluorine [2]. Zirconium is used as the reactor core structural cladding material due to its small capture cross-section [3]. It is a major alloy element, which can improve tensile strength and processing performance. Zirconium dioxide can be used in ceramic industry due to high temperature oxidation resistance [4] and it is also used in enamel, glass industry to increase the elasticity, heat resistance and chemical stability. Zircon ($ZrSiO_4$) has good thermal stability and strong performance on light reflection [5]. Zirconium metal powder is used as evacuating tubes because zirconium can absorb large amount of nitrogen, hydrogen and oxygen. Zirconium is able to form I, II, III, IV oxidation state, but lower than IV oxidation state, it is difficult to extract. Zr(IV) is commonly used in water purification and used in commercial products like deodorant sticks, aerosol antiperspirants [6]. The present work is a systematic study of extraction of Zr(IV) using different parameters.A rapid improved method for solvent extraction and separation of zirconium and hafnium from sulphuric acid system using Primene JMT (a long-chain primary amine) in kerosene was studied by Yamani *et al.* [7]. Sato and Watanabe investigated the extraction of zirconium from sulphuric acid medium by Aliquate-336 through ion exchange mechanism under different conditions [8]. Secondary amines are more effective extractant than tertiary amines for the extraction of zirconium from sulphuric acid was reported by Sato *et al.* [9]. The extraction equilibrium of zirconium in aqueous sulphuric acid using high molecular amines was investigated by Schrotterova *et al.* [10]. Das *et al.* reported that zirconium has been extracted from high concentration of sulphuric acid by using primary, secondary, tertiary amines and a sequential separation of hafnium, zirconium, niobium in acidic medium by using di-(2-ethylhexyl) phosphoric acid [11]. Equilibrium studies of the extraction of zirconium using di-(2-ethylhexyl) phosphoric acid (D2EHPA) from sulphuric acid in kerosene was studied by Juang *et al.* [12]. He reported that the extracted complex species were found to be ZrR_4 and $ZrR_4(HR)$ at low loading ratios of D2EHPA ($\alpha < 0.09$) but became ZrR_4 and $ZrR_4(HR)$ at higher loading ratios of D2EHPA ($0.10 < \alpha < 0.32$). The extraction and separation of zirconium and hafnium from sulphate medium by using *bis*(2-ethylhexyl)-1-(2-ethylhexylamino) propylphosphonate (BEAP) was investigated by Chen *et al.* [13]. He reported that the extractions of both zirconium and hafnium are exothermic and the separation factor of zirconium

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over hafnium was found to be 6.8 under optimum conditions. Wang and Lee investigated that the concentration range of sulphuric acid 0.1-3.0 M using amino based extractants, zirconium was selectively extracted over hafnium [14]. Quantitative stripping of both metals was achieved by using low concentrated sodium carbonate from loaded Alamine 308. Das *et al.* investigated that TOA was very effective extractant for quantitative extraction of zirconium and hafnium at their trace scale concentration in HF, HCl, HNO_3 and H_2SO_4 media [15]. By mixture of TOA and different organophosphorus bases in CCl_4 medium from HCl solutions, the extraction of zirconium was found to be higher than that of single extractant was reported by Biswas *et al.* [16]. He reported that the extraction increases with increase in concentration of amines and neutral donors. In kerosene, using Cyanex-272 as an extractant from acidic chloride solution, the extraction of zirconium was studied and found that addition of sodium salt enhanced the percentage of extraction of zirconium in the order of NaSCN > $NaNO_3$ > Na_2SO_4 > NaCl [17]. Sulphuric acid and hydrofluoric acid media have greater affinities towards niobium and tantalum using TOA as reported by Das *et al.* [18]. Yamani *et al.*investigated that extraction of zirconium depends on acidity, metal and solvent concentration, diluent type and temperature by using tri-caprylmethylammoniumchloride from sulphate media [19]. Cerrai and Testa studied the extraction and separation of Zr and Hf with TOA and Aliquat-336 from hydrochloric acid media [20]. The solvent extraction of zirconium by 4-(5-nonyl)pyridine oxide and trioctylamine oxide from nitric acid and sulphuric acid solution was reported by M. Ejaz [21]. Extraction of cadmium by organophosphorus extractants using sulphate solutions have been investigated by cation exchange mechanism [22]. A synergistic effect for the extraction of Nd^{3+} and Sn^{3+} including stripping and separation from sulphuric acid medium by using mixture of mono-2-ethylhexylester and di-(2-ethylhexyl)phosphoric acid was studied by Huang *et al.* [23].

It is necessary to extract the zirconium metal in greater percentage using different parameters. Liquid-liquid extraction is a prominent effective method for determining the quantities of metal in aqueous and organic solution. The important aim of liquid-liquid extraction is to recover the metal from its solution using a suitable extractant. In the present study, an attempt has been made to investigate the quantitative extraction of zirconium(IV) by liquid-liquid extraction method operating various parameters such as aqueous phase acidity, extractant molarity, chloride ion concentration, diluents, and temperature from sulphuric acid medium using tri-octyl amine (TOA). The quantitative extraction of individual elements was very effective by using TOA at their trace scale concentration reported by Das *et al.* [15]. Stripping of the loaded organic phase containing metal with TOA extractant has been done to find out the best strippant for the extraction system.

2. Experimental

2.1. Reagents

Stock solution of $ZrOCl_2.8H_2O$ (Merck) (0.01M) was prepared by dissolving required amount in double distilled water.1 mL of concentrated HCl was added to the stock solution to avoid further hydrolysis. Distilled kerosene was used as organic phase diluent. The commercial extractant, tri-octyl amine (TOA) (Merck) was used without further purification. All other reagents used were of analytical reagent grade.

2.2. Theory

Equal volumes (10mL) of solutions containing Zr(IV) (0.001M) in H_2SO_4 and the organic phase containing TOA in kerosene were shaken in a separating funnel. Complete equilibrium was achieved in thirty minutes. The phases were allowed to settle for five minutes and then they were disengaged. Arsenazo III was used as a colorimetric reagent. The Zr(IV) concentration in the aqueous phase before and after the extraction was determined by Arsenazo(III) method using a Perkin Elmer UV-Visible spectrophotometer. Spectrophotometric determination of micro gram amounts of zirconium, uranium, thorium with Arsenazo(III) using xylene in HCl medium was studied by Onishi *et al.* [24]. The distribution coefficient (D) was calculated by taking the ratio of equilibrium concentration of Zr (IV) in organic phase and that in the aqueous phase. The concentration of zirconium in the organic phase was calculated by using the mass balance i.e., the difference of metal concentration in the aqueous phase before and after the extraction. Metal ion concentration is directly related to the absorbance of metal [25].

The absorbance of metal was measured spectrophotometrically before and after extraction from which the distribution ratio was calculated as follows:

$$D = \frac{Abs_{B.E.} - Abs_{A.E.}}{Abs_{A.E.}} \tag{1}$$

where $Abs_{B.E.}$ = Absorbance before extraction and $Abs_{A.E.}$ = Absorbance after extraction.

The distribution ratio was obtained as the ratio of equilibrium concentration of metal in the organic phase to that in the aqueous phase

$$D = \frac{[M]_{org}}{[M]_{aq}} \tag{2}$$

where $[M]_{org}$ and $[M]_{aq}$ are the metal concentration in the organic and aqueous phase after the extraction, respectively. From the D values, the percentage of extraction was calculated as

$$\%E = \frac{100\ D}{D+1} \tag{3}$$

3. Results and discussion

3.1. Effect of equilibration time

The effect of equilibration time on the extraction of Zr(IV) from 5.0 M H_2SO_4 with 0.1 M TOA in kerosene at 1:1 phase ratio was studied (Figure 1). When shaking time was increased from five minutes to thirty minutes, the extraction percentage increased from 58.67% in five minutes to 96.49% in thirty minutes and thereafter remained constant. The equilibrium was reached in 30 minutes as shown in figure 1. Therefore, in all experiments 30 minutes shaking time was maintained.

3.2. Effect of acid concentration

The extraction of Zr(IV) was studied with 0.1M TOA in kerosene by varying H_2SO_4 concentration from3.0 to7.0 M. Extraction was 97.4% with 3.0 M H_2SO_4 and then decreased up to 93.51% with 7.0 M H_2SO_4. In the low acid concentration (1.0 to 3.0 M), turbidity appeared and phase separation was not possible. It was observed that extraction depends on aqueous phase acidity due to the formation of more amine salt, which extracts the metal complex. The data are given in Figure 2. Extraction of zirconium decreases by increasing acid concentration was reported by Reddy *et al.* [17].

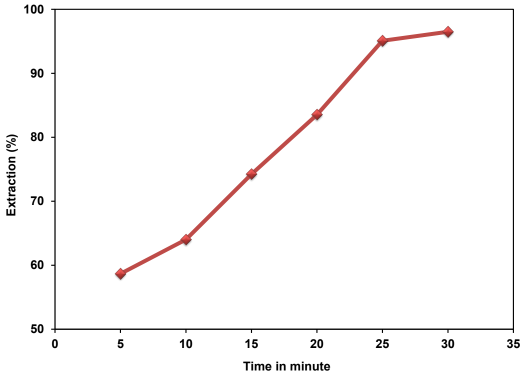

Figure 1. Plot of %Extraction versus equilibration time in the extraction of 0.001 M Zr(IV) from 5.0 M H_2SO_4 using 0.1 M TOA.

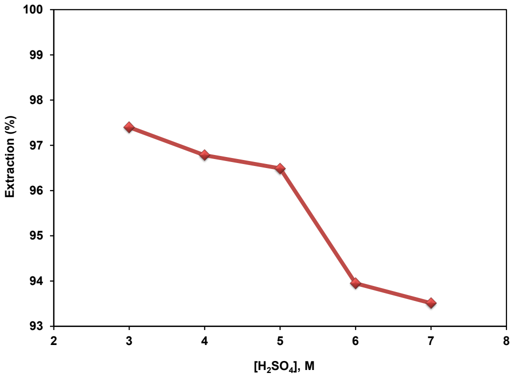

Figure 2. Effect of sulphuric acid concentration on the percentage of extraction of 0.001 M Zr(IV) using 0.1 M TOA.

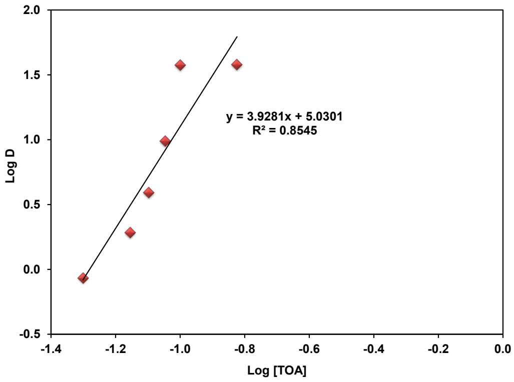

Figure 3. Plot of log D versus log [TOA] in the extraction of 0.001 M Zr(IV) from 3.0 M H_2SO_4.

3.3. *Effect of extractant concentration*

The extraction of 0.001M Zr(IV) with 0.05M to 0.15M TOA in kerosene was carried out from 3.0 M H_2SO_4 solution. The percentage of extraction of zirconium was increased with the increase in amine concentration from 46.23 to 97.43%. The plot of log D versus log [TOA] yields a slope of 3.9281 (Figure 3), which revealed the incorporation of 4 molecules of amine extractant in the extracted zirconium complex. Zirconium has been extracted by all amines at high concentration of sulphuric acid reported by Schrotterova *et al.* [10].

3.4. *Extraction equilibrium*

The possible extraction mechanism of Zr(IV) form H_2SO_4 medium with TOA in kerosene appears to proceed through the protonation of TOA (R_3N) forming R_3NHSO_4 followed by extraction of (R_3NH) $ZrOCl_2$ species into the organic phase. Under the studied experimental conditions and from the slope analysis results, the extraction of Zr(IV) from high acidic chloride medium with TOA may be described in general by the following equation:

$$ZrOCl_{2(aq)} + R_3NHSO_{4\,(org)} \rightleftharpoons R_3NHZrOSO_{4(org)} \qquad (4)$$

The extraction equilibrium constant is given as

$$K_{eq} = \frac{[R_3NHZrOSO_4]_{(org)}}{[ZrOCl_2]_{(aq)}[R_3NHSO_4]_{(org)}} \Rightarrow K_{eq} = \frac{D}{[R_3NHSO_4]_{(org)}} \qquad (5)$$

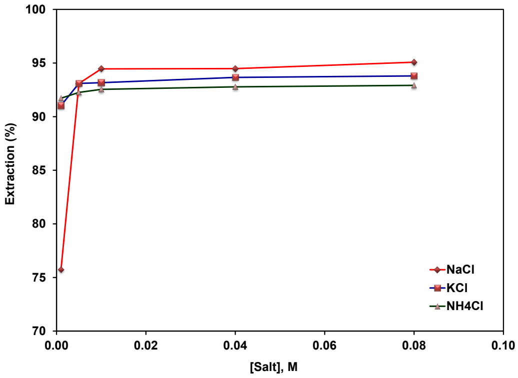

Figure 4. Effect of salting out reagent concentration on extraction of 0.001 M Zr(IV) from 3.0 M H_2SO_4 using 0.1 M TOA in kerosene.

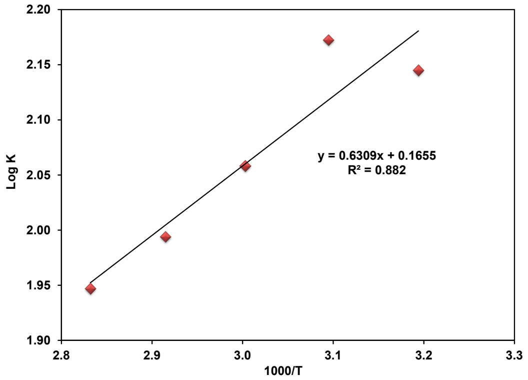

Figure 5. Plot of log K_{eq} *vs* 1000/T for the extraction of 0.001 M Zr(IV) from 3.0 M H_2SO_4 using 0.1 M TOA in kerosene.

where $D = \frac{[R_3NHZrOSO_4]_{(org)}}{[ZrOCl_2]_{(aq)}}$.

3.5. Effect of salting out reagent concentration

The effect of salting out reagent concentration on the extraction of 0.001M Zr(IV) from 3.0 MH_2SO_4 using 0.1M TOA was studied. The percentage of extraction of Zr(IV) increased from 91.72 to 92.92%, from 91.03 to 93.8% and from 75.73 to 95.08% (Figure 4) with increase in concentration of NH_4Cl, KCl and NaCl, respectively, from 0.001to 0.08M.The percentage of extraction increased with increase in salting out reagent concentration due to extraction of chlorocomplex of Zr(IV) with TOA. Reddy *et al.* [26] reported solvent extraction of Zr(IV) from acidic chloride solutions and suggested that the percentage of extraction of Zr(IV) increases with increase in chloride ion concentration at constant H^+ ion concentration.

3.6. Effect of temperature

Experiments were carried out in the temperature range 313-353 K to study the effect of temperature on the extraction of 0.001 M Zr(IV) from 3.0 M H_2SO_4using 0.1 M TOA in kerosene. It was observed that the percentage of extraction of Zr(IV) decreases from 93.8 to 89.84% with increase in temperature. The extraction equilibrium constants (K_{eq}) at different temperature have been calculated using Equation (5). The plot of log K_{eq} *vs* 1000/T is linear (Figure 5). Change in enthalpy (ΔH) and change in entropy (ΔS) were calculated to be -12.07 kJ/mol and 3.16J/mol.K, respectively, using Van't Hoff equation. It ensures the extraction process to be exothermic accompanying with an increase in the randomness. Chen *et al.* investigated that extractions of zirconium and hafnium are both exothermic [13]. The extraction of zirconium from acidic medium using Cyanex 272 (0.005 M) was exothermic reaction as reported by Reddy *et al.* [17].

3.7. Effect of metal ion concentration

The extraction of Zr(IV) from 3.0 M H_2SO_4 using 0.1 M TOA was studied by increasing the concentration of the Zr(IV) from 0.0001 to 0.0006 M. The percentage of extraction increased from 75.5 to 92.1% with the increase in metal ion concentration up to 0.0005 M and thereafter remains constant (Figure 6). Taghizadeh *et al.* [25] reported that at high extractant to metal ratio, with increase in metal ion concentration, the extraction of both Zr(IV) and Hf(IV) increases. This is an agreement with the current observation.

3.8. Effect of diluents

The selection of extractants and diluents are two important aspects of a successful solvent extraction system. The influence of diluents on distribution of metal is correlated with the physic-chemical properties of organic solvent such as solubility parameter, dipole moment, dielectric constant, etc. The extraction of Zr(IV) from 3.0 M H_2SO_4 using 0.1 M TOA was studied in different organic diluents namely kerosene, benzene, diethyl ether, xylene, carbon tetrachloride and chloroform. The percentage of extraction was maximum when kerosene was used as diluent as shown in Table 1. Kerosene was chosen as the diluent for the study due to low toxicity, low cost, easy availability and it gives maximum percentage of extraction. The extent of extraction of metal followed in the order: xylene > toluene >benzene in accordance with decreasing their basicity about aromatic diluents reported by Yamani *et al.* [27].

Table 1. Effect of diluents on the extraction of Zr(IV) from 3.0 M H_2SO_4 using 0.1 M TOA.

Diluents	Distribution ratio	Extraction (%)
Kerosene	37.520	97.40
Benzene	21.449	95.54
Diethyl ether	8.836	89.83
Xylene	25.178	96.17
Carbontetrachloride	6.296	86.29
Chloroform	7.945	88.82

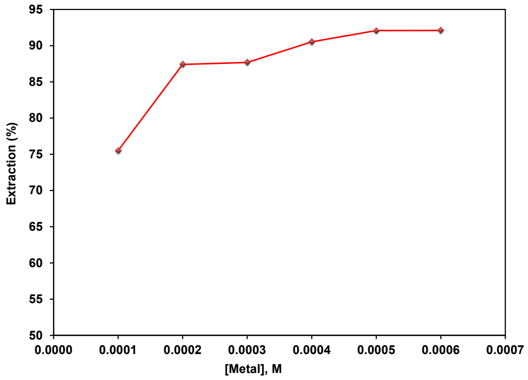

Figure 6. Effect of metal ion concentration for extraction of Zr(IV) from 3.0 M H_2SO_4 using 0.1 M TOA in kerosene.

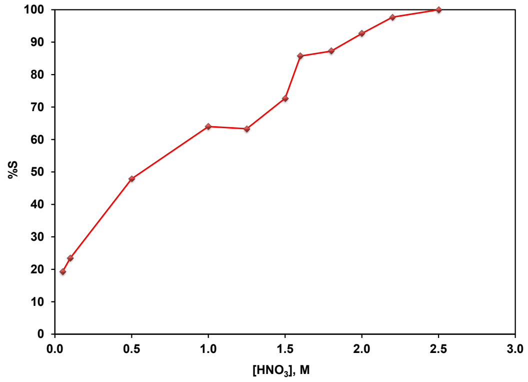

Figure 7. Plot of % stripping *vs* [HNO_3] M for recovery of Zr(IV) from loaded organic phase of 0.1 M TOA in kerosene.

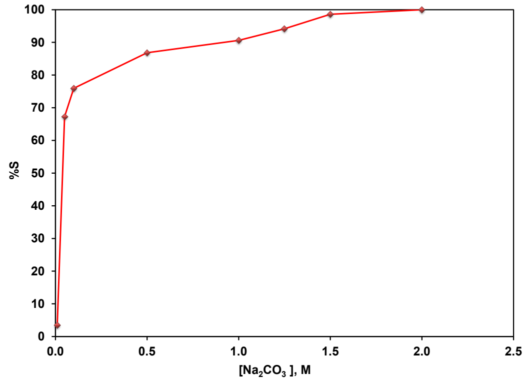

Figure 8. Plot of % stripping versus [Na_2CO_3] M for recovery of Zr(IV) from loaded organic phase of 0.1 M TOA in kerosene.

3.9. Stripping

In aqueous phase, the back extraction of metal takes place from loaded organic phase by stripping. It leads for the reuse of the solvent in another experiment. Extraction process becomes commercially important if the metal can be back extracted from the loaded organic phase. The effect of various concentrations of strippants on the stripping of metal ions from the loaded organic solvent was studied at 298 K and phase ratio 1:1. Zr (IV) is extracted from 3.0 M H_2SO_4 using 0.1 M TOA. From the experimental data, it was found that stripping was 100% with 2.5 M HNO_3 (Figure 7) and 2.0 M Na_2CO_3 (Figure 8) in one step. Quantitative stripping of both zirconium and hafnium has been made at low concentration of Na_2CO_3 solution from the loaded Alamine 308 was reported by Wang *et al.* [14].

4. Conclusions

The extraction of Zr(IV) decreases with increase in acid concentration but increases with concomitant increase in extractant concentration and concentration of metal ion. Under 30 minutes shaking, the percentage of extraction of Zr(IV) reaches 96.49% from 5.0 M H_2SO_4 with 0.1 M TOA. The maximum percentage i.e. 97.4% is obtained from 3.0 M $H_2SO_4$with 0.1 M TOA. The extraction of Zr(IV) from 3.0 M H_2SO_4 decreases with increase in temperature i.e., 313-353 K. The positive influence of temperature shows the extraction to be exothermic. The positive value of change in entropy shows an increase in the randomness.The extraction of Zr(IV) from 3.0 M H_2SO_4 increases with increase in salting out reagent concentration due to the extraction of chloro complex of zirconium with TOA. Kerosene is found to be effective extractant for the extraction of zirconium from 3.0 M H_2SO_4. When kerosene is used as diluent, the percentage of extraction of Zr(IV) from 3.0 M H_2SO_4 with 0.1M TOA reaches 97.4%. Both HNO_3 and Na_2CO_3 are found to be good strippants for the stripping of the metal from the loaded organic phase.

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Disclosure statement

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

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