Liquid-Liquid Extraction of Zr(IV) from Sulphuric Acid Medium using Cyanex 923 in Kerosene

Jaykishon Swain[1], Amit Sahoo[2], Smrutiranjan Jena[3], BhikariCharana Bhatta[4*]
**Corresponding author at: Department of Chemistry, College of Engineering and Technology, Bhubaneswar-751029, Odisha, India.*

Abstract

The extraction behaviour of Zr(IV) from sulphuric acid with cyanex 923 (a mixture of four trialkyl phosphine oxides) in kerosene has been studied through a novel method liquid – liquid extraction. The mechanism of extraction and the species extracted have been identified. Quantitative extraction of Zr(IV) with cyanex 923 in kerosene was studied by changing different parameters such as acid variation, extractant variation, effect of salting out reagent concentration, effect of temperature, metal concentration variation and diluent effect. It was observed that the percentage of extraction of Zr(IV) increased when the concentrations of cyanex 923 and metal ion concentration increased. Kerosene was found to be effective diluent for the extraction of Zr(IV) withcyanex 923.

Keywords - *Zirconium, Sulphuric acid, Cyanex 923, Kerosene, Solvent extraction*

I. INTRODUCTION

Zirconium (with symbol; Zr) is a soft, malleable, lustrous, greyish white and ductile transition metal which becomes brittle, hard at lower purities and solid at room temperature [1][2]. It is a strong transition metal which resembles to Hafnium (Hf) to a greater extent and, to a lesser extent Titanium (Ti). The silicate mineral, zircon ($ZrSiO_4$) is the chief source of zirconium [1]. Zircon has been produced as the by-product from the mining and processing where rutile and ilmenite are being mined [3]. 1% - 3% of Hf contaminant is found to be present in commercial Zr [4] because of similar chemical properties of both the elements. Zirconium and Hafnium differ strongly in neutron absorbing properties and Hafnium has been separated from Zirconium for nuclear reactors applications [5]. Zirconium has a wide range of coordination complexes and inorganic compounds which are colourless and diamagnetic solids [6]. In those complexes, Zr possesses the oxidation state +4. Till today, a fewer compounds are found where Zr has +3 oxidation state and Zr (II) is very rare. Zirconia, also known as Zirconium dioxide (ZrO_2) is the most common oxide which is solid and colourless compound. Zirconia in its cubic form has chemical resistance and exceptional fracture toughness [7] which is also used as the thermal barrier coating [8].

The kinetics of liquid - liquid extraction of Zr (IV) by Di-(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene from chloride media by single drop method was investigated by Biswas *et al* [9]. The extraction and separation of zirconium and hafnium by liquid anion exchange method was reported by Karve*et al* [10]. They reported the extraction of zirconium and hafnium with 0.1 M Aliquat 336S in tolune from 0.005 M of ascorbic acid. Third phase formation in the extraction of zirconium (IV) from nitric acid media by TRPO (trialkyl phosphine oxide) in kerosene was studied by Xu *et al* [11]. Nayl*et al* [12] carried out the solvent extraction to extract and separate zirconium and hafnium from nitric acid solutions using some phosphine oxide extractants such as cyanex 921, cyanex 923, cyanex 925 in kerosene. He reported that the rate of extraction of Zr(IV) and Hf(IV) is fast in cyanex 921, cyanex 923 and cyanex 925 extractants. He also suggested that the extraction increases with increasing temperature and the reaction is endothermic. The extraction of zirconium and hafnium from acidic nitrate solutions with Cyanex 272 was reported by Taghizadeh*et al* [13]. They found that the instability constants for zirconium and hafnium complexes have had a crucial consequence on the extraction effectiveness. The extraction of Zr/Hf using TBP – D2EHPHA mixtures in a solvent extraction system and prediction of Zr/Hf extraction curves was reported by Jirandehi*et al* [14]. The liquid - liquid extraction and recovery of zirconium and hafnium from zircon using cyanex 923 was studied by Gupta *et al* [15]. The extraction of Zr and Hf from acidic chloride solutions with versatic acid-10 was reported by Lee *et al* [16]. Reddy *et al* [17] carried out solvent extraction of Zr(IV) from acidic chloride solution using cyanex 272 as an extractant in dilute kerosene. He reported that the extraction of Zr increased when the extractant concentration increased but decreased when acid concentration increased. Liquid - liquid extraction of Zr(IV) from low acidic chloride solution using LIX 84 – IC was investigated by Reddy *et al* [18]. The percentage of extraction of Zr(IV) was found to be about 97.4% from sulphuric acid medium using tri-n-octyl amine in kerosene as reported by Swain *et al* [19]. The extraction of Zr(IV) from acidic chloride medium by binary mixture Cyanex 923 and TOA using kerosene as diluent was studied by Bhatta *et al*

[20]. They reported that the percentage of extraction of Zr(IV) became 100% with binary mixture of 0.1M TOA and 0.01M cyanex 923 from 7M HCl. Taghizadeh*et al* [21] proposed the separation of Zr and Hf by solvent extraction technique using mixture of TBP and Cyanex 923 in the organic phase. Hefny*et al* [22] studied solvent extraction of Zr(IV) from aqueous nitrate medium using thenoyltrifluoroacetone (HTTA) as extractant in several diluents such as kerosene, chloroform ($CHCl_3$), Carbon tetrachloride (CCl_4), benzene, toluene and nitro benzene. The analysis of high purity Cerium oxide using Cyanex 923 as the extractant was investigating by Duan*et al* [23]. A systematic study of the solvent extraction of U(VI) and Th(VI) from hydrobromic acid medium using the neutral phosphine oxide extractantcyanex 923 was performed by Ghag*et al* [24]. The extraction of Ga (III) by Cyanex 923 and Cyanex 925 in kerosene from hydrochloric acid medium was studied by Ahmed *et al* [25]. The extraction of Uranium (VI) from thiocyanate solutions using Cyanex 923, Cyanex 272 as extractant in xylene was investigated by Reddy *et al* [26].

II. EXPERIMENTAL

A. 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 extractantcyanex 923 (a mixture of four tri-alkyl phosphine oxides) (Merck) was used without further purification. All other reagents used were of analytical reagent grade.

B. Theory

Equal volumes (10 mL) of solutions containing Zr(IV) (0.001 M) in H_2SO_4 and the organic phase containing cyanex 923 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 [10] using a Perkin Elmer UV-Visible spectrophotometer. 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.

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

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

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

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

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

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

III. RESULTS AND DISCUSSIONS

A. Effect of acid concentration

The extraction of0.001M Zr(IV) was studied with 0.01M cyanex 923 in kerosene by varying H_2SO_4 concentration from 2M to 6M. The percentage of extraction was 65.36 with 2M H_2SO_4 and then decreased up to 9.82 % with 6M H_2SO_4. Percentage of extraction decreased increasing the acid concentration as reported by Reddy *et al* [17]. 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 table 3.1 (Fig. 3.1).

$[H_2SO_4]$, M	D	% E
2	1.887	65.36
3	1.858	65.01
4	0.634	38.8
5	0.271	21.32
6	0.109	9.82

Table 3.1.: Effect of H_2SO_4 concentration on extraction of 0.001M Zr (IV) using 0.01M cyanex 923 in kerosene.

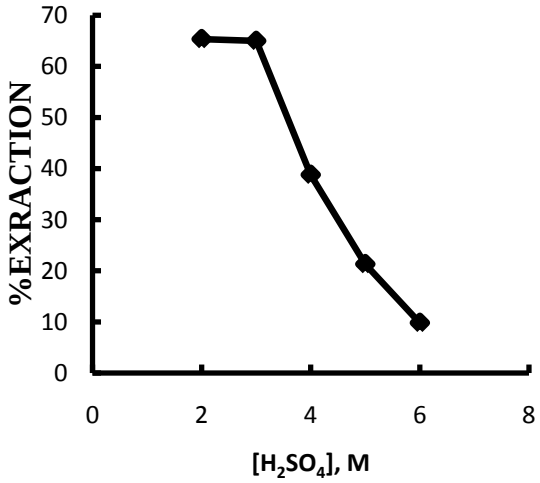

Fig.3.1. Effect of sulphuric acid concentration on the percentage of extraction of 0.001M Zr(IV) using 0.01M cyanex 923 in kerosene.

B. Effect of extractant concentration

The extraction of 0.001M Zr (IV) was carried out from 3M H_2SO_4 solution by changing the concentration of cyanex 923 from 0.006M to 0.01M in kerosene. The percentage of extraction of zirconium increased from 4.67% to 65.01% with the increase in concentration of cyanex 923 from 0.006M to 0.01M in kerosene (Table 3.2.1). Reddy *et al* [17] also investigated that when the concentration of extractant was increased, the percentage of extraction increased accordingly. This is an agreement with the current observation. The plot of log D versus log [cyanex 923] yields a slope of 6.8224 (Fig.3.2.1) which reveals that incorporation of 6 molecules of extractant complex in the extracted species.

Table 3.2.1.: Effect of extractant concentration on extraction of 0.001 M Zr(IV) from 3M H_2SO_4 in kerosene.

[Cyanex 923], M	D	% E
0.006	0.049	4.67
0.007	0.083	7.66
0.008	0.225	18.36
0.009	0.396	28.36
0.01	1.858	65.01

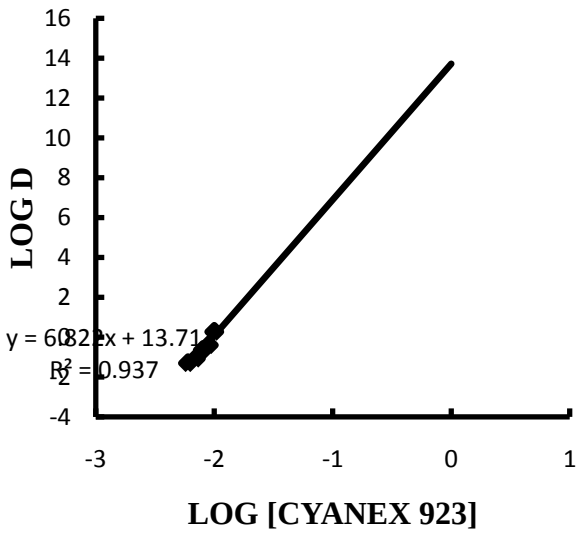

Fig. 3.2.1. Plot of log D versus log [cyanex 923] in the extraction of 0.001 M Zr (IV) from 3M H_2SO_4 in kerosene.

C. Extraction Equilibrium

The possible extraction mechanism of Zr(IV) form H_2SO_4 medium with cyanex 923 in kerosene appears to proceed through the protonation of cyanex 923 (R_3P) forming R_3PHSO_4 respectively followed by extraction of $(R_3PH)ZrOSO_{4(org)}$ species into the organic phase.

Under the studied experimental conditions and from the slope analysis results, the model of the extraction of Zr(IV) from high acidic chloride medium with cyanex 923 may be described by the following equation:

$$ZrOCl_{2(aq)} + R_3PHSO_{4(org)} = R_3PHZrOSO_{4(org)} \quad \textbf{(1)}$$

The extraction equilibrium constant is given as

$$K_{eq} = \frac{[R_3PHZrOSO_4]_{(org)}}{[ZrOCl_2]_{(aq)}[R_3PHSO_4]_{(org)}} \quad \textbf{(2)}$$

$$\Rightarrow K_{eq} = \frac{D}{[R_3PHSO_4]_{(org)}} \quad \textbf{(3)}$$

$$\text{Where } D = \frac{[R_3PHZrOSO_4]_{(org)}}{[ZrOCl_2]_{(aq)}}$$

D. Effect of salting out reagent concentration

The effect of salting out reagent concentration on the extraction of 0.001M Zr (IV) from 3MH_2SO_4using 0.01M cyanex 923 was studied. The percentage of extraction of Zr (IV) decreases from 27.16% to 8.67%, from 17.49% to 2.15% and from 9.9% to 5.3% (Fig. 3.3) with increase in concentration

of NH_4Cl, KCl and NaCl respectively from 0.001M to 0.08M (Table 3.3). The increase in salt concentration decreases the formation of neutral zirconium chlorocomplex in the aqueous phase leading to less extraction.

Table 3.3.: Effect of salting out reagent concentration on extraction of 0.001M Zr (IV) from 3M H_2SO_4using 0.01Mcyanex 923 in kerosene.

[NH_4Cl], [KCl], [NaCl], M	% E		
	NH_4Cl	KCl	NaCl
0.001	27.16	17.49	9.9
0.005	24.35	17.01	8.92
0.01	17.08	7.66	8.75
0.04	9.42	3.47	8.5
0.08	8.67	2.15	5.3

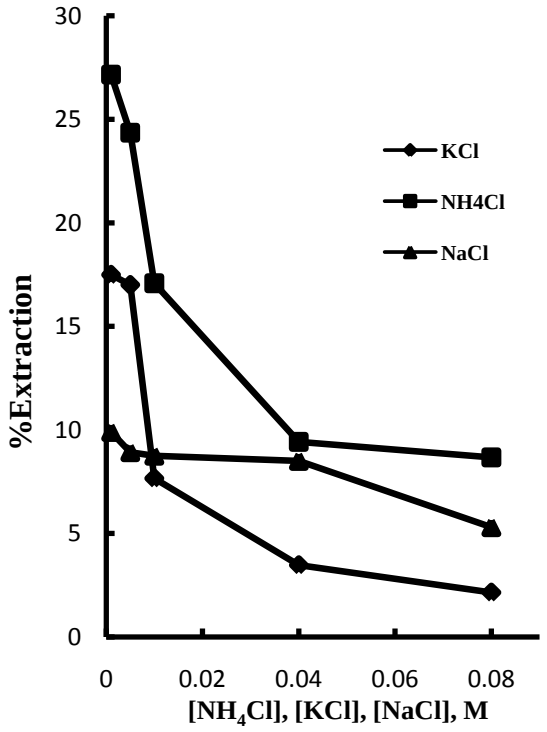

Fig 3.3. Effect of salting out reagent concentration on the extraction of 0.001M Zr (IV) from 3M H_2SO_4using 0.01Mcyanex 923 in kerosene.

E. Effect of Temperature

Experiments were carried out in the temperature range 303k – 343k to study the effect of temperature on the extraction of 0.001M Zr (IV) from 3M H_2SO_4 using 0.01M cyanex 923 in kerosene. It was observed that the percentage of extraction of Zr(IV) decreased from 22.72% to 1.38% (Table 3.4) with increase in temperature. The extraction equilibrium constants (K_{eq}) at different temperature have been calculated using equation (3). The plot of log K_{eq}versus 1000/T is linear (Fig. 3.4). Change in enthalpy (ΔH) and change in entropy (ΔS) were calculated to be -11.25 KJ $mol^{-1}$and $0.6241JK^{-1}mol^{-1}$using Van't Hoff equation. It ensures the extraction process to be exothermic accompanying with an increase in the randomness. Chen *et al* [27] also investigated that the extraction of zirconium and hafnium are both exothermic.

Table 3.4.: Effect of temperature on extraction of 0.001 M Zr (IV) from 3M H_2SO_4using 0.01Mcyanex 923 in kerosene.

Temperature in k	D	% E	K_{eq}
303	0.941	48.48	94.1
313	0.798	44.38	79.8
323	0.701	41.21	70.1
333	0.675	40.29	67.5
343	0.533	34.76	53.3

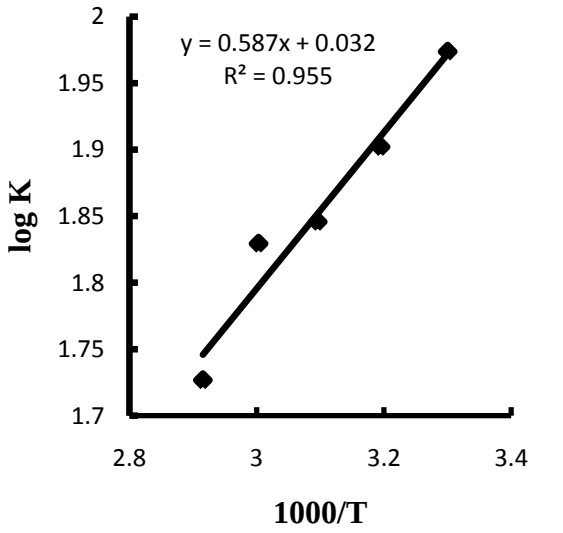

Fig. 3.4. Plot of log K_{eq} versus 1000/T for the extraction of 0.001M Zr (IV) from 3M H_2SO_4using 0.01Mcyanex 923 in kerosene.

F. Effect of metal ion concentration

The extraction of Zr(IV) from 3M H_2SO_4 using 0.01M cyanex 923 was studied by increasing the concentration of the Zr(IV) from 0.0001M to 0.0005M. The percentage of extraction increased from 23.19% to 59.83% with the increase in metal ion concentration up to 0.0005M and thereafter remains constant. The detail data showed in (table 3.5) and (fig. 3.5). Extraction of Zr(IV) from sulphuric acid

using TOA in kerosene was found to be exothermic as reported by Swain *et al* [19].

Table 3.5.: Effect of metal ion concentration on extraction of Zr (IV) from 3M H_2SO_4 using 0.01M cyanex 923 in kerosene.

[Metal], M	D	%E
0.0001	0.302	23.19
0.0002	0.341	25.42
0.0003	0.494	33.06
0.0004	0.754	42.98
0.0005	1.49	59.83

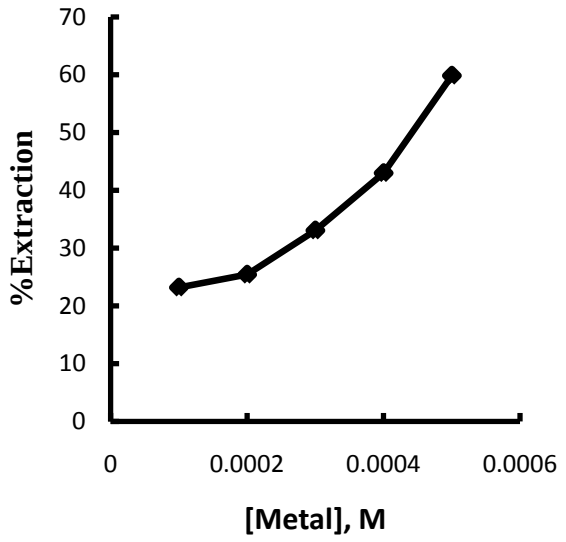

Fig. 3.5. Effect of metal ion concentration for extraction of Zr(IV) from 3M H_2SO_4 using 0.01M cyanex 923 in kerosene.

G. Effect of diluents

The selection of extractants and diluents are two vital 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 3M H_2SO_4 using 0.01M cyanex 923 was studied in different organic diluents namely kerosene, benzene, diethyl ether, xylene, carbon tetrachloride, chloroform. The percentage of extraction was maximum when kerosene was used as diluent as shown in (table 3.6). Kerosene was selected as the diluent for the study due to low toxicity, low cost and easy availability. The percentage of extraction decreased in the order, kerosene > benzene > chloroform > carbon tetrachloride > xylene > diethyl ether.

Table 3.6.: Effect of diluents on the extraction of 0.001M Zr(IV) from 3M H_2SO_4using 0.01M cyanex 923 in kerosene.

Diluents	D	% E
Kerosene	1.858	65.01
Benzene	0.141	12.35
Diethyl ether	0.053	5.03
Xylene	0.079	7.32
Carbon tetrachloride	0.081	7.49
Chloroform	0.12	10.71

IV. CONCLUSION

The extraction of Zr(IV) decreases with increase in acid concentration but increases with increase in concentration of metal ion and extractant concentration. The extraction of Zr(IV) from 3M H_2SO_4 decreases with increase in temperature i.e., 303 K – 343 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 3M H_2SO_4 decreases with increase in salting out concentration.The extraction of Zr(IV) from 3M H_2SO_4 using cyanex 923 has been studied in different diluents and the diluents are arranged in the increasing order prior to extraction in the following manner.

kerosene > benzene > chloroform > carbon tetrachloride > xylene > diethyl ether.

V. ACKNOWLEDGEMENT

The authors express their sincere thanks to authorities of College of Engineering and Technology, Bhubaneswar for their constant encouragement to carry out this research work.

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