Chapter 1

Introduction
Introduction

1.1 Chemistry of Zirconium

Zirconium is the second row transition element with the symbol Zr, atomic number 40 and atomic mass 91.224 a.m.u. It belongs to titanium subgroup, subgroup IVB. The name of zirconium is taken from the mineral zircon, the most important source of zirconium and from Persian word “Zargun-”, which means gold like metal [1]. Zirconium is a grey, lustrous metal, hard and ductile with the appearance of stainless steel available in the form of platelets or flakes. In powder form, zirconium is highly flammable, but the solid form is less prone to ignition and the colour is bluish black. Zirconium is an elastic metal, like other metals with lower melting points. Its mechanical strength decreases with increasing temperature. Zirconium is very abundant – but is typically found in ores combined with other elements. The chemistry of zirconium is well presented by Blumenthal [2]. The metallurgy of zirconium is well presented by Lustman and Kerze in their book [3].

1.2. Sources and Application

1.2.1. Sources

Zirconium is not found in nature as a native metal. It reflects its intrinsic instability with respect to water. The principal commercial source of zirconium is Zircon (ZrSiO₄) [4] which is primarily found in Australia, Brazil, India, Russia, South Africa and united states. About 80% Zircon mining occurs in Australia and South Africa. Zircon resources exceed 60 million tonnes worldwide. Zirconium also occurs in more than 140 other minerals, including commercially useful ores badeleyite and kosnarite. The specific gravity of Zircon (4.7) enables it to be concentrated with other heavy minerals by gravity methods.

The first crude zirconium metal (Zr) was produced in 1824 by Berzelius [5] by heating potassium (K) and potassium herxa-fluorozirconate (K₂ZrF₆) to produce a black powder Zr metal. It was only a century later that the first high purity Zr metal was produced by Van Arkel and de Boer [6]. They vaporized Zirconium tetraiodide (ZrI₄) into a bulb containing a hot tungsten filament which caused the tetraiodide to dissociate, depositing Zr on the filament.
Zirconium forms a wide range of inorganic compounds and co-ordination Complexes [7]. Most of the Zr(IV) metal is produced by the reduction of Zr (IV) chloride with magnesium metal in the Kroll process.

**Zirconia**

The most common oxide is zirconium dioxide ZrO$_2$, also called as zirconia. It is a colourless solid has exceptional fracture toughness and chemical resistance, especially in its cubic form [8]. It is used in laboratory crucibles, metallurgical furnaces as a refractory material. It contains 73% zirconium and 0.4 to 17% hafnium.

**Zircon**

Zircon is widely distributed in earth’s crust as a component of igneous, metamorphic and sedimentary rocks. Due to zircon’s resistance to weathering and attrition, it is found in the heavy residues of various rocks and beach sands—all over the world. In some places beaches developed into many miles of sand dunes. The action of the wind and waves concentrated heavy minerals like zircon, ilmenite rutile up to about 2% [9]. The 2% is further processed to separate the zircon, ilmenite and rutile. It generally contains 49% zirconium.

1.2.2. Applications of Zirconium

Zirconium metal is highly desirable as a cladding material for nuclear fuel rods in nuclear power plants, because of its very low nuclear absorption cross-section for thermal neutron [7]. However, to use this Zr metal it has to be purified from hafnium. For this purpose, it is mainly used in the form of zircaloys. The materials fabricated from zirconium metal and its oxide (ZrO$_2$) are used in space vehicle parts for their resistance to heat [10]. The zircon used to make metal is grounded in a ball mill with calcined petroleum coke to make a feed suitable for carbo-chlorination. In addition to its use, it is used for sand molds and cores, mold washes and mold facings. Zircon and Zirconia are also used in refractory application, principally for brick for lining steel ladles, and for applications such as fused, cast and bonded bricks and shapes.

Advanced technology application of zirconium include stabilized and partially stabilized zirconia (PSZ) used in industrial cutting blades, ceramic engine parts, liners for engine exhaust chambers, thermal barrier coating for jet engine compressor blades and in
rocket nozzles. The high reactivity of zirconium towards oxygen, apparent only at high temperature is the basis of some specialized applications as explosive primers and as getters in vacuum tubes.

1.3. Techniques employed for separation and recovery of Zirconium

The conversion of zirconium content of zircon to zirconium metal is achieved through the following methods [11].

(i) Decomposition of zircon

Zircon is decomposed with strong reagents and at high temperature.

(ii) Separation of hafnium

The separation processes such as solvent extraction, ion exchange, distillation, selective partial reduction, fractional precipitation and caustic leaching and generally used for removing hafnium from zirconium compounds.

(iii) Reduction

Kroll process involves reduction of zirconium tetrachloride vapour by molten magnesium in argon atmosphere. It converts zircon to zirconium metal sponge.

(iv) Refining

Zirconium sponge obtained from Kroll process can be purified by electro refining or by electron beam melting.

1.4. Physical and Chemical Properties of Zirconium

Some of the physical and chemical properties of the zirconium metal are presented in the table 1.1
Table 1.1.: Properties of Zirconium

<table>
<thead>
<tr>
<th>Properties</th>
<th>Zirconium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Zr</td>
</tr>
<tr>
<td>Atomic No.</td>
<td>40</td>
</tr>
<tr>
<td>Standard Atomic Weight</td>
<td>91.224 a.m.u.</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[Kr] 5s² 4d²</td>
</tr>
<tr>
<td>Atomic radius</td>
<td>1.452Å</td>
</tr>
<tr>
<td>Ionic radius</td>
<td>0.74 Å</td>
</tr>
<tr>
<td>Density</td>
<td>6.52 g cm⁻³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1855 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>4377 °C</td>
</tr>
<tr>
<td>Thermal neutron Cross-section</td>
<td>0.18 barn</td>
</tr>
<tr>
<td>Thermal conductivity at 25°C</td>
<td>21.1 Wm⁻¹K⁻¹</td>
</tr>
<tr>
<td>Oxidation states</td>
<td>+4, +3, +2</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.33</td>
</tr>
</tbody>
</table>

1.5 Solution Chemistry of Zirconium

Zirconium, an element of group IVA, contains two electrons in its outermost (n) shells and two electrons in the (n-1) d shells. Therefore, +4 oxidation state is the common in zirconium and important complexes are formed with ions of this valance, although the +2 and +3 oxidation state exist for zirconium in some crystalline compounds. Zirconium is a Pearson hard acid [12], showing a strong affinity for ‘hard’ ligands such as F⁻, SO₄²⁻, OH⁻, NO₃⁻ and borderline ligand such as Cl⁻.

Because of its high charge, the Zr (IV) aqueous ion shows a relatively strong tendency to hydrolyze. The Zr(IV) ion does not exist in solution, but rather, zirconium exists as the Zirconyl (ZrO²⁺). It is therefore, necessary to consider the effect of zirconyl ion on zirconium aqueous chemistry.
The size and the charge of zirconyl ion also have implications when calculating activity co-efficient. The activity co-efficient of an ion in solution is directly proportional to its charge and inversely related to an ion size parameter. Therefore the larger ion size and lower charge of zirconyl ion should both contribute to a lower activity than that of Zr (IV) for solution of identical ionic strength.

1.5.1. Zirconium complexes in Aqueous Solution

Due to its high charge, small radius, and comparatively low ionization potential, it is possible to classify Zr (IV) as a typical complex former. On the other hand, water (H$_2$O), hydroxyl ions (OH$^-$) and chloride ions (Cl$^-$) are classified as hard bases. Thus zirconium has a higher attraction for water than for chloride and therefore has a high degree of hydrolysis in an aqueous chloride solution. The most important inorganic ligands have been listed in order of decreasing stability as follows:

$$\text{OH}^- > \text{F}^- > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$$

Among all acceptors, Zirconium (IV) forms the strongest fluoride complexes because HF presents a higher tendency with Zr to polymerize in aqueous solutions. Veyland et al [10] explained the aqueous chemistry of Zr (IV) by the formation of the soluble species Zr (OH)$^{3+}$, Zr$_2$(OH)$_7^{7+}$ and Zr(OH)$_4$ in KNO$_3$ media. The formation constants of the species Zr (OH)$^{3+}$, Zr$_2$(OH)$_7^{7+}$ and Zr(OH)$_4$ as well as the solubility product of zirconium hydroxide were determined in KNO$_3$ media at four ionic strengths.

The strong affinity to F$^-$ and O$^{2-}$ as donor atoms is typical of acceptors of high charge and small radius, and as Zr$^{4+}$ possesses these two qualities to an unusual degree, strong complex formation is expected with these two ligands.

(i) Fluoride complexes

A comparative study of fluoride complexes of several transition metals (indicated that zirconium forms the most stable fluoride complexes. Eight, seven and five coordinated zirconium in molten fluoride was inferred from frequency shifts accompanying changes in free fluoride ion concentration with the help of Raman spectra [13].

$$\text{Zr}^{4+} + n \text{HF} \rightleftharpoons \text{ZrF}_{n}^{4-n} + n \text{H}^+$$
(ii) **Hydroxide complexes**

Zirconium has a great affinity for OH⁻ ions in solution. It increases with increasing pH. The pH range for these complexes is still very acidic. The chemistry of zirconium (IV) in aqueous media is dominated by the complexation of Zr(IV) with OH⁻. The stoichiometry of soluble species are determined from the initial pH of the zirconium oxychloride solutions. Veyland et al [10] explained that the Zr (IV) form soluble species Zr(OH)³⁺, Zr₂(OH)⁷⁺ and Zr(OH)₄ in KNO₃ media, in the pH range of 1.5 to 3.5.

\[
\text{Zr}^{4+} + n \text{OH}^- \rightleftharpoons \text{Zr(OH)}_{n}^{4-n}
\]

(iii) **Sulphate complexes**

No evidence has yet been adduced for the existence in Zr (SO₄)₂ solutions of a single preferred species stable over a range of conditions [14]. They reported direct spectroscopic evidence in favour of the structure of a strongly coordinated metal species in aqueous solution. In aqueous acid sulphate solutions, the SO₄²⁻ ion can displace hydroxyl groups. Of all acceptors, zirconium forms sulphate complexes that are among the strongest found.

\[
\text{Zr}^{4+} + n \text{HSO}_4^- \rightleftharpoons \text{Zr} (\text{SO}_4)_{n}^{4-2n} + n \text{H}^+
\]

(iv) **Nitrate complexes**

The extraction of Zr (IV) from nitrate solution using n-butylphosphoric acid (HDBP) was studied [15] and found that the distribution coefficient for zirconium is proportional to the first power of nitrate ion and independent towards hydrogen ion concentration. The nitrate ion forms stronger complexes with Zr (IV) when compared with perchlorate which is quite a weak complexing agent. Electromigration studies of the three inorganic ligands NO₃⁻, Cl⁻ and ClO₄⁻ reveal relative stability constants in the following order: NO₃⁻ > Cl⁻ > ClO₄⁻.

(v) **Chloride complexes**

Zirconium exhibits a remarkable tendency to hydrolyze in aqueous solution. When ZrCl₄ dissolved in water, it liberates hydrogen ion. With 9.45 M chloride the hydrolysis or polymerization of the zirconium species occurs [16] and chloride complexation of zirconium is based on the equation

\[
\text{Zr}^{4+} + n\text{Cl}^- \rightleftharpoons \text{ZrCl}_{n}^{4-n}
\]
1.5.2. Hydrolysis and Polymerization of Zirconium

The aqueous chemistry of zirconium (IV) is extremely complex. Various physicochemical methods have been employed to identify a number of zirconium species in solution. Generally, hydrolysis and polymerization of zirconium is represented by

$$n\text{Zr}^{4+}(\text{aq}) + m\text{H}_2\text{O} \rightleftharpoons \text{Zr}_n(\text{OH})_{n-m}^{4n-m} + m\text{H}^+ (\text{aq})$$

Connick and Reas [17] reported that the distribution co-efficient of zirconium depends on the degree of polymerization. Schultz and Larsen (1950) [18] studied zirconium polymerization and determined that

$$n\text{Zr}^{(4-x)}(\text{OH})_x \rightleftharpoons \text{Zr}_n(\text{OH})_{n(4-x)}^{n(4-x)} +$$

1.6. Fundamentals of Solvent extraction

1.6.1. General Introduction

Solvent Extraction (SX) is one of the prominent techniques used for the processing of non-ferrous metals at micro and macro level. The process is used on commercial scale for extraction and separation of zirconium [19] and copper, nickel, cobalt, zinc, tungsten, vanadium, gallium, uranium and other rare earth elements [20]. The principle behind this technique is transfer of a solute across the interface between two immiscible liquid phases when they are brought into contact. Usually one of these is aqueous phase and other is organic. The quantitative extraction of metal depends upon relative solubilities of the solute in the two phases. Applications of phase rule to such system predict a definite relationship between the solute concentrations in the two solvents. This is quantitatively described as the distribution law. According to the law at a given temperature, a solute will distribute itself between two immiscible solvents in such a way that at equilibrium, the ratio of the concentration of the solute in two phases will be constant provided the solute remains in the same molecular form in both the phases. For a solute M distributed between two solvents 1 and 2, the law is expressed as:

$$K = [M]_2 / [M]_1$$  \hspace{1cm} (1.6.1.1)

Where K is distribution constant at [M]_1, [M]_2 are the concentration of similar molecular species in the two liquid phases at a constant temperature. The distribution coefficient is a constant and independent of total concentration of the solute and the phase volume ratio.

Thermodynamically, the law will be represented
\[ K_D = \left( \frac{[M]_2}{[M]_1} \right) \left( \frac{\gamma_2}{\gamma_1} \right) \]  

When \( K_D \) is the distribution coefficient and \( \gamma_1 \) and \( \gamma_2 \) are the activity coefficient of the solute M in phases 1 and 2, respectively. The liquid phases involved have been designated as “extract” or “solvent” and “other phase” or “feed”. Since the “organic phase” is commonly quite a complex solution of one or more organic liquids containing one or more extractants and possibly “modifiers” as well as a “diluent”. To use solvent extraction as the unit operation for the separation, concentration and purification of metals, the overall hydrometallurgical route has to be considered.

1.6.2. Process

Solvent extraction processes are concerned with the removal of one or more components from the aqueous phase into an immiscible organic phase using a suitable extractant by forming a proper metallic species. The entire process of solvent extraction is broadly divided into three stages [21-22].

(i) Extraction

A given volume of metal solution with the same volume of extractant in a given organic solvent is equilibrated (by shaking) and set aside for phase separation. The two phases are then separated. This technique is also employed for the separation of two components. After extraction the solute is recovered from the organic phase by scrubbing followed by stripping.

(ii) Scrubbing

The loaded organic phase is washed with an aqueous solution, which favours the extraction of the metal of interest so as to separate the impurities, which have been extracted along with the metal.

(iii) Stripping

The loaded organic phase is stripped off the metal by back extraction to the aqueous phase. Regeneration of the solvent is achieved by treating the solvent with water, alkali or acid solution. This leads to the reuse of the solvent for another cycle.
1.6.3. Applications

Solvent extraction process is employed on a commercial scale to separate and recover transition metals from secondary resources using organic extractants. This process is used for the extraction and separation of metals from acidic, alkaline (including ammoniacal) and mixed sulphate-chloride leach liquors generated in the treatment of complex or the ores or industrial wastes. Several organic extractants are reported for selective extraction and separation of metals. Using this technique, the recovery of specific metals from acidic or alkaline medium in the presence of complexing agents [20], extraction of zirconium from acidic chloride solutions with LIX 84-IC(2-hydroxy-5-nonylacetophenoneoxime) [23] and extraction separation of zirconium from succinate media with 2-octylaminopyridine have been reported [24]. This process can also be employed for reprocessing of spent nuclear fuels and radioactive wastes.

1.6.4. Objectives

In the current scenario it is necessary to determine extraction of metal in greater quantities than in trace levels. Thus, it is an effective method for determining the quantities of metal in aqueous and organic solution. The objective of liquid-liquid extraction is to recover the metal of interest from its solution using a suitable solvent. The extracted species from the loaded organic phase are re-extracted (stripped) into an aqueous phase by a suitable chemical reagent. A novel solvent extraction process, the Universal Extraction (UNEX) process, has been developed for simultaneous separation of cesium, strontium, and the actinides from radioactive acidic waste solutions [25]. The extraction of zirconium from succinate media with N-n-octylaniline was reported by Rajmane et al [26] under controlled concentration of complexing ligand and pH. Banda et al developed a process for separation of zirconium and hafnium from hydrochloric acid media using TEHA (tri 2-ethyl hexyl amine) [27].

1.6.5. Basic Principle

Solvent extraction studies involve the measurement of equilibrium concentration of metal ion in which it is distributed between the aqueous phase and organic phase. The following terms have been used to describe the process [28].

Feed Solution: The feed to a solvent extraction system is the aqueous solution that contains the metals to be extracted.
Extractant : The extractant is diluted in the solvent for the purpose of extracting the desired metal from the feed solution by complexation mechanism or solvation mechanism.

Solvent : The solvent is the immiscible organic liquid mixture, containing the extractant, diluent, modifier and any other required organic component.

Diluent : The diluent is used to dilute the extractant to an appropriate concentration in the solvent.

Extract : The solvent phase leaving the solvent extraction process, containing the metal.

Raffinate : The raffinate is the aqueous phase left from the feed after being contacted by the solvent.

### 1.6.6. Distribution Ratio (D)

To determine the overall distribution of a component in the two phases, thermodynamic distribution coefficient has been replaced with distribution ratio \( D \). When the solute exists in more than one molecular form, a more useful parameter is the distribution ratio. For the distribution of a metal between aqueous and organic phase \( D \) can be expressed as

\[
D = \frac{\text{Total equilibrium metal ion concentration in organic phase}}{\text{Total equilibrium metal ion concentration in aqueous phase}}
\]

\[ (1.6.6.1) \]

It is a number and has no units and is not a constant. The magnitude depends upon several factors such as the phase volume ratio, extractant concentration, temperature, metal ion concentration in the aqueous phase, pH, and presence of anions in the aqueous phase, nature of diluents, etc. Depending on the system, the distribution ratio can be a function of temperature, the concentration of chemical species in the system, nature of diluents and a large number of other parameters. Distribution ratio is related to the change in free energy for the extraction process.

### 1.6.7. Percentage of Extraction (%E)

The extent of extraction can be expressed as the percentage of extraction \( %E \). Its relationship with distribution ratio \( D \) is given by the following equation

\[
%\ E = 100D/[D + \left(\frac{V_{\text{aq}}}{V_{\text{org}}}\right)]
\]

\[ (1.6.7.1) \]
\[ V = \frac{100D}{D+1} \] Where \( V = \frac{V_{aq}}{V_{org}} \)

\( V_{aq} \) and \( V_{org} \) represent the volumes of the aqueous and the organic phase respectively. When the volumes of aqueous and organic phases are equal, the phase volume ratio becomes unity and the above equation can be written as

\[
% E = \frac{100D}{D+1} \tag{1.6.7.2}
\]

### 1.6.8. Separation Factor (β)

It is a measure of the ability of the system to separate two solutes. Under identical experimental conditions two metal ions can be separated from each other if they possess different distribution ratios. If the two solutes, A and B are present in a definite initial concentration ratio \( C_A/C_B \) and if their distribution ratios are \( D_A \) and \( D_B \), then separation factor ‘β’ is expressed as

\[
\beta = \frac{D_A}{D_B} \tag{1.6.8.1}
\]

For efficient separation \( D_A \) and \( D_B \) should be marked in different and the \( \beta \) value should be greater than one.

### 1.7. Factors affecting extraction

The following factors affect the extraction process.

(i) Effect of acid concentration in aqueous phase (ii) Presence of salting out agent in the aqueous phase (iii) Oxidation state of metal ion (iv) Nature of extractant (v) Nature of diluents (vi) Effect of Temperature.

#### 1.7.1. Effect of acid concentration in aqueous phase

The chelating and acidic extractants produce hydrogen ions during the extraction of a metal. More hydrogen ions are liberated when greater amount of metal is extracted. This leads to decrease in pH of the extraction system and subsequent decrease in the extraction percentage. When equilibrium pH increases further, the availability of \( H^+ \) ions decreases which may lead to the hydrolysis of metal ion resulting in non-extractable metal species [29]. Extraction involving ion-pair formation is influenced by protonation of extractant at a given pH. Therefore, aqueous phase acidity plays an important role in extraction.
1.7.2. Presence of salting out agent in the aqueous phase

The addition of particular electrolytes to an aqueous phase in order to increase the distribution ratio of a particular solute. The addition of an inorganic salt into a mixture of water and water miscible organic solvent causes a separation of the solvent from mixture and the formation of a two phase system. The salting out effect can also be used to enhance extraction into non polar immiscible organic solvent. The high polarity water miscible solvents used as salting out system. Polyvalent cations provide better salting out agents and for a given charge, the small cationic size gives greater effect of extraction. At a given concentration of metal, extractant and acid, the percentage extraction of Zr(IV) increases by the addition of sodium salts and followed in the order: Na$_2$SO$_4$ > NaSCN > NaNO$_3$ > NaCl [23].

1.7.3. Oxidation state of the metal ion

The oxidation state of the metal is an important parameter in determining its complex forming ability. Therefore, it affects the extraction of a metal from aqueous solution. Higher the oxidation number of the metal, more stable will be the extracted complex.

1.7.4. Nature of extractant

A good extractant should satisfy the following conditions:(i) The solubility of extractant in diluents should be very high (ii) It should be easily available at affordable cost (iii) It should have low viscosity (iv) It should be non-toxic, non-volatile and non-inflammable (v) The extractant should have high selectivity for the separation of the desired metal (vi) The metal should have high distribution ratio in the extractant (vii) Stripping of the metal form the organic phase should be easily carried out using such extractant [30].

1.7.5. Nature of diluent

The diluents may be liquid or homogeneous mixture of liquids composed of organic solvents. It acts as a carrier or modifier. The diluents by itself do not extract the main extractable solute but in the presence of extractant, extraction takes place. It should be cheap and readily available. It should be non-toxic.
The formation of acid-amine complex depends upon the nature of diluents, which affect the basicity of amine and stability of the ion-pair association in the extract phase. Polar diluents enhance the extraction ability of amines. Interactions between diluents and complex depend on the nature of the diluent molecules as well as the nature of the complex. Hydrogen bonding > dipole-dipole > dipole-induced dipole > induced dipole-induced dipole. Extraction of zirconium from nitrate medium was studied using thenoyltrifluoroacetone (HTTA) as extractant in different diluents by El-Hefny et al [31]. The dipole moments and dielectric constants of different diluents were investigated. The extraction of zirconium from hydrochloric acid solutions using Cyanex 272 was studied using various diluents by Reddy et al [32].

1.7.6. Effect of Temperature

Usually increase of temperature leads to an increase in the extraction of metal [33]. Thermodynamic parameters are involved for the synergistic extraction, complex formation or expansion of co-ordination number of central metal atom [34]. The values of thermodynamic parameters \( \Delta H \) and \( \Delta S \) in the extraction can be determined from the values of the equilibrium constant using Van’t Hoff’s equation.

\[
\log K_{eq} = -\frac{\Delta H}{2.303 RT} + \frac{\Delta S}{2.303R} \quad (1.7.6.1)
\]

The extraction of zirconium from 2-octylaminopyridine was carried out in the temperature range 229-307 K by Noronha et al [24]. They found negative value of \( \Delta G \) which indicates the reaction as spontaneous. Extraction of zirconium from different acid media using Amberlite LA-2, TBP and HDEHP was studied at various temperatures [35]. The temperature variation studies give information regarding inner-sphere and outer-sphere complexation.
### 1.8. Extractants and their classification

#### 1.8.1. Acidic Extractants

<table>
<thead>
<tr>
<th>Class</th>
<th>Name of the compound</th>
<th>Structure of the compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acids</td>
<td>Mono-2-ethylhexyl phosphoric acid (M2EHPA)</td>
<td>HO - P = O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃(CH₂)$_₂$CH₂O - OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₅</td>
</tr>
<tr>
<td></td>
<td>Di-2-ethylhexyl phosphoric acid (D2EHPA)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphonic acids</td>
<td>2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A)</td>
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</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphinic acids</td>
<td>bis-2,4,4-trimethyl pentyl phosphinic acid (Cyanex 272)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bis (2,4,4-trimethyl pentyl) dithio phosphinic acid (Cyanex 301)</td>
<td></td>
</tr>
</tbody>
</table>
Bis (2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302)

<table>
<thead>
<tr>
<th>Class</th>
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<th>Structure of the compound</th>
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</thead>
<tbody>
<tr>
<td>Carboxylic acids</td>
<td>Neo decanoic acid</td>
<td>[Structure]</td>
</tr>
<tr>
<td></td>
<td>(Versatic acid 10)</td>
<td>Where (R&lt;sub&gt;1&lt;/sub&gt; and R&lt;sub&gt;2&lt;/sub&gt; are alkyl groups)</td>
</tr>
<tr>
<td>Sulphonic acid</td>
<td>(5,8-dinonylnaphthyl sulfonic acid)</td>
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1.8.2. Chelating Extractants

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<th>Class</th>
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<th>Structure of the compound</th>
</tr>
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<tbody>
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<td>Hydroxyoximes</td>
<td>5,8-Diethyl-7-hydroxy-6-dodecanone oxime (LIX 63)</td>
<td>[Structure]</td>
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<tr>
<td>Hydroxybenzophenone oximes</td>
<td>2-Hydroxy-5-dodecylbenzophenone oxime (LIX 64)</td>
<td>[Structure] + LIX63</td>
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<tr>
<td>β-Diketones</td>
<td>(LIX 54) 1-Benzoyl-2-nonanone</td>
<td>[Structure]</td>
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### 1.8.3. Basic Extractants

<table>
<thead>
<tr>
<th>Class</th>
<th>Name of the compound</th>
<th>Structure of the compound</th>
</tr>
</thead>
</table>
| Primary amines     | 1,1,3,3,5,5,7,7,9,9-decamethyl decylamine (Primene JMT) | \[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \left( \text{CH}_2 - \text{C} - \right) \frac{4}{2} \text{NH}_2
\end{align*}
\] |
| Secondary amines   | Amberlite LA-1 (N-5,5,7,7-tetramethylocten-2-yl-1,1,3,3,5,5-hexamethyl hexylamine) | \[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \quad \text{NH} \\
\text{R}_1 & = \quad \text{C}_9\text{H}_{19} \text{CH} = \text{CHCH}_2 - \\
\text{R}_2 & = \quad \text{CH}_3 \quad \left( \text{CH}_2 - \text{C} - \right) \frac{2}{2} \text{CH}_3
\end{align*}
\] |
| Tertiary amines    | Tri-octylamine (Alamine 336)              | \[
\begin{align*}
\text{C}_8\text{H}_{17} \\
\text{C}_8\text{H}_{17} - \text{N} \\
\text{C}_8\text{H}_{17} /\n\end{align*}
\] |
|                    | Tri-n-octylamine (Alamine 300)            | \[
\begin{align*}
\text{C}_8\text{H}_{17} \\
\text{C}_8\text{H}_{17} - \text{N} \\
\text{C}_8\text{H}_{17} /\n\end{align*}
\] |
|                    | Tri-iso-octylamine (Alamine 308)          | \[
\begin{align*}
\left( \text{CH}_2 \right)_5 - \text{CH} \quad \left( \text{CH}_3 \right) & \\
\left( \text{CH}_3 \right) & - \text{CH} \quad \left( \text{CH}_2 \right)_5 - \text{N} - \left( \text{CH}_2 \right)_5 - \text{CH} \quad \left( \text{CH}_3 \right)_2
\end{align*}
\] |
|                    | Tri-isodecylamine (Alamine 310)           | \[
\begin{align*}
\left( \text{CH}_2 \right)_7 - \text{CH} \quad \left( \text{CH}_3 \right) & \\
\left( \text{CH}_3 \right) & - \text{CH} \quad \left( \text{CH}_2 \right)_7 - \text{N} - \left( \text{CH}_2 \right)_7 - \text{CH} \quad \left( \text{CH}_3 \right)_2
\end{align*}
\] |
|                    | Tridodecylamine (Alamine 304)             | \[
\begin{align*}
\text{C}_{12}\text{H}_{25} \\
\text{C}_{12}\text{H}_{25} - \text{N} \\
\text{C}_{12}\text{H}_{25} /\n\end{align*}
\] |
<table>
<thead>
<tr>
<th>Quaternary ammonium salts</th>
<th>Tri-capryl methyl ammonium chloride (Aliquat 336)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tri-alkyl (C₈-C₁₀) methyl ammonium chloride (Adogen 464)</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

### 1.8.4. Solvating Extractants

<table>
<thead>
<tr>
<th>Class</th>
<th>Name of the compound</th>
<th>Structure of the compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric ester</td>
<td>Tri-n-butyl phosphate (TBP)</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Phosphonic ester</td>
<td>Di-butyl butylphosphonate (DBBP)</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Phosphine oxide</td>
<td>Tri-n-octyl phosphine oxide (TOPO) (93%) Cyanex 921</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Cyanex 923</td>
<td>Mixture of main trialkyl phosphine oxides (about 95%) Cyanex 923</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

Where \( R, R' = [\text{CH}_3(\text{CH}_2)_7]- \) Normal octyl

### 1.9. Mechanism of Extraction

The extracting systems may broadly be classified depending upon the nature of the extracted species, solute-solvent interaction etc. The process of extraction takes place in the following three steps. (i) Formation of a metal complex (ii) Distribution of the extractable complex (iii) Interaction in the organic phase.
According to Ritcey and Ashbook [36] all the extractants are divided into three classes.

(i) System involving neutral compound formation
(ii) System involving ion association
(iii) System involving solvation.

1.9.1. System involving neutral compound formation

In solvent extraction system, neutral compound formation occurs with (i) acidic extractant such as organophosphorous acids and carboxylic acids (ii) Chelating extractant such as oximes and derivatives of quinoline.

(i) Acidic Extractants

Acidic extractants also known as cation exchangers are orgnonophosphorous carboxylic acids and sulphonic acids. Both extractants can dimerise or polymerize in organic phase by hydrogen bonding which affects their extraction efficiency. The extraction equilibrium can be represented as follows:

\[ M^{n+}(aq) + n(HA)_{2(org)} \rightleftharpoons [MA_n(HA)_{m-n(org)}] + nH^+(aq) \]  \hspace{1cm} (1.9.1.1)

Where \((HA)_2\) is the dimeric form of extractant, \(m\) is the total no. of extractant molecules, \(n\) is the charge on the metal ion and \(MA_n(HA)_{m-n}\) is the complex. Mostly phosphorous based acidic extractants are powerful extracting agents for trivalent lanthanides and actinides. Mono-2-ethyl hexyl phosphoric acids (MEHPA), Di-2-Ethyl phosphoric acid (D\(_2\)EHPA), 2-Ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester commercially known as (PC 88A) or SME428 or P-507 [37]. Out of these extractants, mono and dialkyl phosphoric acid such as (D\(_2\)PHEA) extract by both chelation and solvation [38] mostly in the presence of strong acid in aqueous media. Extraction of Zr, La, Ac, Hf by these extractants have been reported [39-41]. The dialkyl phosphinic acid, Cyanex 272 has been efficiently used for the extraction of Zr(IV) from acid chloride solution [35]. Unlike organophosphorus acid extractants, the carboxylic and sulphonic acids are generally not employed as commercial extractant in metal extraction because, they tend to have high solubility in aqueous phase.

Carboxylic Acids

The metal extraction by these extractants is too much difficult because they aggregate in organic phase. Some carboxylic acids used as extractants are: highly branched aliphatic monocarboxylic acids such as Versatic-9 [42], cyclic aliphatic mono carboxylic
acids called naphthenic acids [43] are used in metal extraction. Carboxylic acids extract metals either alone or in conjugation with other extractants. The extraction of various metal ions with aliphatic and aromatic carboxylic acids has been reported by West et al [44]. Both alkali and alkaline earth metals can be extracted by carboxylic acids. The stoichiometric relation for the extraction of zirconium and hafnium from acid chloride solutions was investigated with Versatic Acid-10 by Lee et al [45].

(ii) Chelating Extractants

These extractants are used for the effective extraction of metal ions from the aqueous medium into the organic phase in which the charge of the metal ion is neutralized. If charge neutralization and coordination requirements are not simultaneously satisfied, the vacant co-ordination positions are occupied by water making the chelate hydrophilic thereby decreasing its extractability [46-47]. In these cases the coordinated water molecules are replaced by other neutral ligands to give better extraction.

The chelation mechanism is represented by the following equilibrium

\[ M^{n+}(_{\text{aq}}) + n(HA)_{(\text{org})} \leftrightarrow MA_{n(\text{org})} + nH^+(_{\text{aq}}) \]  (1.9.1.2)

The functional groups of the chelates contain usually nitrogen and sulphur. Depending on the charge on chelating reagent the metal chelates may be cationic, anionic or neutral. Extraction of metals by chelating agents depends on the nature of extractant, its structure and process of formation of metal complexes. The well known example of these extractants is dithiozone, oximes, β-diketones and common LIX reagents etc. Extraction of Zr and Hf by 4, 4, 4 trifluoro-1-(2-thienyl) -1,3-butanedione (TTA) was studied by Weginwar et al [48]. Enhanced extraction and separation of zirconium and hafnium by 3-phenyl-4-benzoyl-5-isoxazolone in presence of various neutral organo phosphorus extractants was investigated by Reddy et al [49].

1.9.2. System involving ion association

In such systems the extractable species is formed due to interaction between anionic metal species in the aqueous phase and cation coming from organic phase. In this type, extraction is influenced by size of the ion and its hydrophobicity.

Consider a general anion-exchange reaction.

\[ M^{n+}(_{\text{aq}}) + n(R_3NH^+Cl^-)_{(\text{org})} \leftrightarrow (R_3NH)_n M_{(\text{org})} + nCl^-(_{\text{aq}}) \]  (1.9.2.1)
This system has further subdivided into (a) unsolvated ion pairs (b) halo metallic acid (c) amine-anionic metal complex. Some of unsolvated cations and oxyanions combine to form ion pairs, these ions are unsolvated because of their size and structure. Due to bulkiness they break the hydrogen bonded water structure and entered into the organic phase in ionized form but not completely dissociated. In case of halometallic acids, the metal forms complexes with halides and pseudohalide ions and protons. When both metal ion and a halogen acid are present in the aqueous phase, a halo complex is formed. One or more protons are taken by the halo complex to form halometallic acid, which is solvated and exists as ion pair in organic phase [50-51]. Long chain amines and quaternary alkyl ammonium salts are nitrogen-based extractants which extract by anion exchange mechanism [52-53]. Extraction takes place by anion exchange as shown below and form associated ions neutral species.

\[
\begin{align*}
R\text{NH}_3^+X^{-}_{(\text{org})} + Y^{-}_{(\text{aq})} & \iff R\text{NH}_3^+Y^{-}_{(\text{org})} + X^{-}_{(\text{aq})} \\
R_2\text{NH}_2^+X^{-}_{(\text{org})} + Y^{-}_{(\text{aq})} & \iff R_2\text{NH}_2^+Y^{-}_{(\text{org})} + X^{-}_{(\text{aq})} \\
R_3\text{NH}^+X^{-}_{(\text{org})} + Y^{-}_{(\text{aq})} & \iff R_3\text{NH}^+Y^{-}_{(\text{org})} + X^{-}_{(\text{aq})}
\end{align*}
\]

(1.9.2.2) (1.9.2.3) (1.9.2.4)

In general, the ease of extraction of complex metal anionic species from chloride media by amines follows the order: Quaternary > tertiary > secondary > primary. Generally aliphatic amines are better extractants than aromatic amines because of higher basicity. Quaternary salts can extract metals from acidic and alkaline solutions but stripping is difficult [54]. S Banarjee and S. Basu [55] reported that the presence of organophosphorus oxide along with long chain amines enhances the extraction of Zr(IV) from aqueous hydrochloric acid medium. Trivalent lanthanides and actinides can be separated by quaternary alkyl ammonium salts from thiocyanate media [56]. Tri-alkyl amine (Adogen 364), Methyltri-alkyl ammonium chloride(Adogen 464) and tricaprylmethyl ammonium chloride (Aliquat 336) are important commercial nitrogen based extracting agents. Depending on the nature of the diluents the amines may undergo polymerization. The use of quaternary ammonium halides in commercial solvent extraction processes has not been successful. These reagents behave somewhat differently to amines, and have the capability of extracting metals at pH values higher than the normal amines, that is in neutral or slightly alkaline solutions [36]. Tertiary amines and quaternary alkyl ammonium salts containing a mixture of 8 to 10 carbon chains are good extracting agents [57].
1.9.3. System Involving Solvation

The important group of solvent extraction systems is based on the solvation of neutral inorganic molecules or complexes by electron-donor containing extractants [36]. There are two main groups of extractants in this system, organic reagents containing oxygen bonded to carbon, such as ethers, ester, alcohols and ketenes, and other group containing oxygen or sulphur bonded to phosphorus, in alkyl phosphates or alkyl thiophosphates. The strongly polar organophosphorus compounds compete with water, and can replace water molecules from the primary coordination sphere of metal ions. M. Taghizadeh et al [58] investigated that, the selective extraction and separation of Zr and Hf from acidic nitrate medium using Cyanex 272 in kerosene by solvation mechanism. According to Antony and Antony [59], Taguchi method can be a powerful technique in various industries for better yield and productivity. Zr and Hf separation by using Cyanex 923 was studied by Da Silva et al [60]. The extraction equilibria of Sc(III), Zr(IV), Ti(IV), Th(IV), Fe(III) and Lu(III) from sulphuric or hydrochloric acid media by Cyanex 923 and Cyanex 925 was studied by Li et al [61]. The alkyl groups R in Cyanex 923 have straight chains where as those of Cyanex 925 are branched. Irgolic et al [62] found that the extraction of several metal ions including Zr and Hf from HCl, using tris (n-octyl) arsine oxide (TOCASO) in benzene system. The phosphorous analogue of TOCASO and tri (n-octyl) phosphine (TOPO) were found to be superior to tributyl-phosphate (TBP) for several metal extractions. The extraction of Zr and Hf by TOCASO varies considerably from that by TOPO. There are two main groups of extractants: one of them containing oxygen bonded to carbon such as ethers (C-O-O), esters (COOR) and alcohols (C-OH) and ketones (C=O) and another is oxygen bonded to phosphorous (P=O) such as alkyl phosphate esters. Organophosphorus esters (alkyl phosphates, phosphonates and phosphinates) and phosphine oxides containing polar P=O group with oxygen atom are important extracting agents. Here the extracted species does not contain any water molecule because the stronger polar P=O bonds are displaced by the water molecules. The extraction of metal by organophosphorus compounds includes compound formation or solvation depending upon the metal complex species. The ability of extraction of these phosphorus-based reagents in the order: Phosphine oxides > Phosphinates > Phosphonate > Phosphates due to increasing basicity of P=O group. All pentavalent organophosphorus compounds contain four atoms attached to phosphorous by covalent bonds, which consists of three single bonds to phosphorus and one semipolar bond between phosphorus and oxygen. The nature
of \( R_1 \) bound to the central P atom and electronegativity of \( O \) atom bound to P have profound influence on the extracting properties of the ligand. TBP is found to be an effective extractant for extraction of zirconium (IV) from hydrochloric acid solution reported by Levitt [63]. The extraction of zirconium increases steeply with initial acidity of the aqueous phase above about 6M HCl. This implies that the controlling factor is the total chloride ion concentration. Hence, most metal extraction processes are carried out from acid solution, possibility of co-extraction of the acids is to be considered. It may be concluded that, the extraction mechanism of Zr (IV) involves ion association to produce neutral species by charge-neutralization, followed by solvation mechanism. Most of the major species present in organic phase may be generally represented as:

\[
(ZrL_{n}^{4-x})(R_3P=O)_2
\]

When \( L \) = Anions like Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\) etc.

\( x = \) Charge on anions such as Cl\(^-\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^-\)

\( n = \) Number of anions associated with Zr

\( R_3P=O \) is organophosphorus compound such as TBP or TOPO.

Thus the extraction reaction may be represented as

\[
ZrL_{n}^{4-x} + 2R_3P = O \leftrightarrow (ZrL_{n}^{4-x})(R_3PO)_2
\]

(C.9.3.1)

Cyanex 921 is well known as triocty phosphine oxide (TOPO), is type of one example of this reagent and the first member of the family of extractants developed Cytec. Practically, TOPO is known as one of the most stable members of the group of organophosphorus solvating reagents [64]. The advantages of Cyanex 921 are that its solubility is higher in aromatic diluents than in the aliphatic compounds. It is a better extractant because of its higher stability. In 1980, American Cynamid industry included another organophosphorus extractant. Cyanex 923 which is a mixture of four trialkyl phosphine oxides. It is a liquid phosphine oxide while Cyanex 921 is a solid at room temperature. It has various applications in the solvent extraction recovery of both organic and inorganic solutes from aqueous solution. Cyanex 923, being a liquid can be used to advantage over Cyanex 921 for solvent extraction purpose [64]. The four major compounds of Cyanex 923 are:

(i) Trihexyl phosphine oxide  
(ii) Dihexylmonooctyl phosphine oxide  
(iii) Dioctyl monohexyl phosphine oxide  
(iv) Trioctylphosphine oxide
Triphenyl arsine oxides are better solvating agents reported by Patil et al. [65]. Neutral bifunctional organophosphorus compounds such as di-hexyl-N,N-diethyl carbamyl methyl phosphonate (DMDECMP) and di-hexyl-N,N-diethyl carbamoyl methyl phosphine oxide (DHDECMP) are better extracting agents than TBP or DBBP (di-butyl butyl phosphinate) [66-68]. N,N-diisobutyl carbamoyl methyl phosphine oxide (CMPO) is used more for extraction of lanthanides and actinides [69-70]. Sulphoxides are having semi polar S=O group with lone pair of electron on both sulphur and oxygen atoms can solvate metal ions by co-ordination through either sulphur or oxygen [71]. The third phase formation in the extraction of zirconium (IV) from nitric acid media by TRPO(trialkyl phosphine oxide) in kerosene was studied [72]. The limiting organic concentrations (LOC) of Zr (IV) under various experimental conditions were determined. Extraction of Zr (IV) and Hf (IV) was investigated by Wang et al [73] from hydrochloric acid solution by using acidic organophosphorus extractants and their mixtures with TOPO by solvation reaction. Extraction of Zr (IV) and Hf (IV) was studied by Mishra et al [74] by mixtures of Aliquat 336 with neutral donor tri-n-octyl phosphine oxide (TOPO) from acidic thiocyanate media by solvation mechanism.

1.10. Synergistic Extraction

Synergism is the phenomenon in which, the co-operative effect of two or more extracting agents is greater than the sum of their individual extractive powers. The reverse phenomenon, where the mixture of two agents has less extractive power than one of them is known as Antagonism. In synergistic extraction, one or several new hydrophobic species are formed than with a single extractant. In this system generally a mixture of cation exchange extractants or chelating agents and neutral solvating extractants are participating together. Synergism was first discovered by Blake et al [75]. The distribution ratio of a synergistic extraction system can be represented as.

\[ D_{\text{mix}} = D_A + D_B + \Delta D \]  

(1.10.1)

Where \( D_A \), \( D_B \) and \( D_{\text{mix}} \) are the distribution ratios of metal ion with the extractants A, B and their mixtures, respectively. \( \Delta D \) is the increase in the distribution ratio. If \( \Delta D \) value is positive it shows synergism and if it is negative, antagonism is observed. The synergistic coefficient (S.C.) for the combination of any two extractants is given by

\[ \text{S.C.} = \log \left[ \frac{D_{\text{mix}}}{(D_A+D_B)} \right] \]  

(1.10.2)
If S.C. > 0, synergistic effect and if S.C. < 0 antagonistic effect is observed.

When a neutral solvating agent is added to a chelating extractant, formation of synergistic adduct takes place. The mechanism can be represented as

$$M^{n+}_{(aq.)} + nHA_{(org)} \leftrightarrow MAr_{n(org)} + nH_{(aq)}^+$$  \hspace{1cm} (1.10.3)

Where $M^{n+}$ is the metal ion, HA is the chelating extractant, $MAr_n$ is the neutral chelate.

It further combines with neutral ligand forming the adduct $MA_n.mS$ which is given by

$$MA_n_{(org)} + mS_{(org)} \leftrightarrow MA_n.mS_{(org)}$$  \hspace{1cm} (1.10.4)

The overall synergistic extraction may be represented as

$$M^{n+}_{(aq.)} + nHA_{(org)} + mS_{(org)} \leftrightarrow MA_n.mS_{(org)} + nH^+_{(aq)}$$  \hspace{1cm} (1.10.5)

Synergistic extraction is useful in mutual separation and determination of metals, recovery of metals, determination of stability constants of metal ligand complexes, enhancement in the extraction studies on the co-ordination capability of the metal ion, etc. The mixed extractants (synergistic combination) exhibit the most desirable features of the constituent single extractants. Such characteristics of mixed extractants effectively reduces plant operation costs. Reddy et al studied the synergism for extraction of Zr(IV) using 2-thienoyl trifluoro acetone(TTA) in the presence of di-n-pentyl sulphoxide (DPSO) in carbon tetrachloride [76]. Synergism also studied by Mishra et al for extraction of Zr(IV) and Nb(IV) with a mixture of Aliquat 336 or Alamine 336 and dioctyl sulphoxide(DOSO) in benzene [77]. The synergistic extraction of Zr (IV), Nb(IV) and Hf(IV) with mixture of Aliquat 336 and neutral solvating agents such as TOPO has been studied in thiocyanate media [74]. Synergism is reported by Biswas et al using mixture of TOA and different organophosphorous compounds in carbon tetrachloride [78].Mixture of alkyl salicylic acid and sulphoxides [79] and using mixture of salicylaldoxime and neutral donors in dichloromethane for Zr(IV) have been studied [55].Synergistic extraction of Zr(IV) and Hf(IV) using mixture of 4-Acyl bis(1-phenyl-3-methyl-5-pyrazolones) and neutral organophosphorus extractants was successfully presented by Reddy et al [80].
1.11. Solvent Extraction of Zirconium

**Literature Review**

A review on the solvent extraction of Zr(IV) and other associated elements using amines, organophosphorus extractants and synergistic extraction done by several researchers have been described here in a tabular form.

### 1.11.1. Solvent extraction of zirconium with Amine and nitrogen donor extractants.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Extraction Data</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(IV) and Hf(IV)</td>
<td>Extraction and separation of Zr(IV) and Hf(IV) from hydrochloric acid media using primary, secondary, tertiary amine was studied. The effect of temperature on extraction and separation factor was also investigated. Extraction is lower at lower temperature but the separation factor is higher.</td>
<td>[81]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr (IV) with tri-n-octyl amine was studied. The advantage of the system was, direct non-aqueous determination consists mainly achieving an appreciable increase of concentration of the desired element due to great volume reduction obtained by solvent extraction and avoiding stripping was investigated.</td>
<td>[82]</td>
</tr>
<tr>
<td>Zr-(IV) and Nb(IV)</td>
<td>Extraction of Zr(IV) from hydrochloric acid solution using tribenzyl amine. The extractable species of Zr(IV) was presented and separation of Zr(IV) and Nb(IV) was studied. The extraction process of Zr(IV) is shown: ZrCl₆²⁻ + 2RCl→R₂ZrCl₆ + 2Cl⁻ followed by the reaction of the above species with TBA-Cl in a chloroform solution: R₂ZrCl₆ + 2RCl → R₂ZrCl₆·2RCl.</td>
<td>[16]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from hydrochloric acid solution using high molecular weight amines in benzene was studied. Tertiary amines are more efficient extractants for zirconium than secondary amines. Extraction efficiencies of different amines were compared.</td>
<td>[83]</td>
</tr>
<tr>
<td><strong>Zr(IV)</strong>, <strong>U(VI)</strong>, <strong>Th(IV)</strong>, and rare earth metals</td>
<td>Spectrophotometric determination Zr(IV), U(VI), Th(IV), and rare earth metals from hydrochloric acid media using TTA(thenoyltrifluoroacetone) in xylene was studied. Extraction behaviour of each metal at various pH was investigated. Each metal is back-extracted from the organic phase before determination.</td>
<td>[84]</td>
</tr>
<tr>
<td>---</td>
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</tr>
<tr>
<td><strong>Zr(IV)</strong></td>
<td>Extraction of Zr(IV) using long chain aliphatic amines from sulphuric acid media was studied. Secondary amines are more efficient extractants for zirconium than tertiary amines was investigated. Extracted organic solutions have examined by I.R. and NMR spectroscopy and the mechanism was formulated.</td>
<td>[85]</td>
</tr>
<tr>
<td><strong>Zr(IV)</strong> and <strong>U(VI)</strong></td>
<td>Extraction of Zr(IV) using 4-(5-nonyl)pyridine oxide and tric- octyl amine oxide was studied from nitric acid, hydrochloric acid and sulphuric acid media. The influence of of salting out agents was described. Separation of Zr(IV) from uranium fission product elements was achieved.</td>
<td>[86]</td>
</tr>
<tr>
<td><strong>Zr(IV)</strong> and <strong>Hf(IV)</strong></td>
<td>Extraction of Zr(IV) and Hf(IV) from sulphuric acid media using a long chain primary amine primene JMT in kerosene was studied. A rapid separation method for Hf-Zr was suggested. A nuclear-pure Zr(IV) product in the aqueous phase, with less than 100ppm Hf(IV) and more than 90% recovery was directly obtained in a one-stage operation.</td>
<td>[87]</td>
</tr>
<tr>
<td><strong>Zr(IV)</strong></td>
<td>Extraction of Zr(IV) from 0.01M malonic acid medium using 4% Amberlite LA-1 or LA-2 in xylene was studied at pH 3.0. The metal was stripped with 2M HCl and then spectrophotometrically determined at 665 nm as its complex with Arsenazo III. This method has been applied to the analysis of zircon was reported.</td>
<td>[88]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr (IV) from Monazite sand in hydrochloric acid media using thenoyltrifluoroacetone(TTA)- xylene was reported. Effects of equilibration time, acid concentration and zirconium-Arsenazo (III) complex was studied. Zirconium reacted with Arsenazo (III) to form an emerald green coloured complex having maximum absorbance at 665nm in 9M HCl medium.</td>
<td>[89]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>The extraction of Zr (IV) from sulphuric acid media using tricaprylmethylammonium chloride (Aliquat-336) was studied. The organic solutions were examined by IR and NMR spectroscopies. A mechanism of ion-exchange reactions was formulated.</td>
<td>[90]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction and separation of Zr (IV) from citric acid media using anberlite LA-1 or LA-2 in xylene was done. Complex of Zr (IV) with Arsenazo (III) and various analysis of Zircon was presented. The method has been extended for the analysis of zirconium from zircon.</td>
<td>[91]</td>
</tr>
<tr>
<td>Zr(IV) and Hf(IV)</td>
<td>Extraction of Zr (IV) from various acid media using Adogen 464 was studied. Separation of Hf (IV) from Zr (IV) was investigated with reference to acidity, concentration of solvent and nature of diluents. Extraction was achieved by aqueous solutions containing 0.11M Zr and organic phases of 0.1M Adogen in kerosene. A method of separation of Hf(IV) from Zr(IV) is also suggested.</td>
<td>[92]</td>
</tr>
<tr>
<td>Ti(IV), Zr(IV) and Hf(IV)</td>
<td>Extraction of Ti (IV), Zr(IV) and Hf(IV) from salicylate media using Aliquat 336 and trioctyl amine in xylene was studied. The extraction depends upon pH, salicylate concentration, amine concentration, diluents and period of equilibration was investigated. The results of both separation and analysis were reported.</td>
<td>[93]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr (IV) from sulphuric acid media using high molecular amines such as tri-n-laurylamine, tri-n-octyl amine etc. was studied. Stoichiometric equations and mechanism for the extraction of Zr(IV) by amines at various acid concentrations were formulated. Zr (IV) can be extracted by all amines and by primary amines it can be extracted at high concentrations of sulphuric acid.</td>
<td>[94]</td>
</tr>
<tr>
<td><strong>Zr(IV) and U(VI)</strong></td>
<td>Separation of Zr (IV) and U(VI) from acidic sulphate media using tertiary amines was studied. Nature of extracted complex of metals and formation of pure zirconium salt was investigated. A method of separation of Zr (IV) and U(VI) was proposed. Zr (IV) and U(VI) are effectively extracted by tertiary amines from weak acidic sulphate solutions. Primene JMT enables the extraction of Zr from more acidic solution.</td>
<td>[95]</td>
</tr>
<tr>
<td><strong>Zr(IV) and Hf(IV)</strong></td>
<td>Separation of Zr(IV) and Hf(IV) from ascorbic acid solution at pH 4.0 using Aliquat 336S in toluene was studied. Separation of Zr(IV) from hafnium was achieved by Stripping from 9 M hydrochloric acid followed by stripping zirconium with 2 M hydrochloric acid.</td>
<td>[96]</td>
</tr>
<tr>
<td><strong>Zr(IV) and Hf(IV)</strong></td>
<td>Extraction behaviour of Zr(IV) and Hf(IV) tracers using tri-octyl amine in HF,HCl,HNO₃ and H₂SO₄ media was studied. TOA was found to be very effective extractant for quantitative extraction of metal at their trace scale concentration.TOA was not so effective for mutual separation of elements when they were present as congeneric pairs in the aqueous solution.</td>
<td>[97]</td>
</tr>
<tr>
<td><strong>Zr(IV)</strong></td>
<td>The reaction of Zr(IV) from hydrochloric acid medium using xylene orange and 1-phenyl-3-methyl-4-benzo pyrocolones-5 was studied. The complex formation of Zr (IV) and maximum absorbance reported. Zr(IV) reacts with the above extractants to form a 1:1:1 amaranth complex from 4M HCl medium at 552nm.</td>
<td>[98]</td>
</tr>
<tr>
<td><strong>Zr(IV) and Hf(IV)</strong></td>
<td>Separation of Zr (IV) and HF(IV) from hydrochloric acid medium using Aliquat 336 in organic diluents was systematically studied. Stochiometry of the Zr (IV) and Hf(IV) species from single metal ion was investigated. The extraction depends upon acid concentration, extractant concentration and nature of diluents was reported.</td>
<td>[29]</td>
</tr>
<tr>
<td><strong>Zr(IV) and Hf(IV)</strong></td>
<td>Extraction and separation of Zr(IV) and Hf(IV) using ammonium(Amberjet 4200 Cl), poly(vinyl-pyridine) and pyridinium from hydrochloric acid medium was studied. Highest separation factor at equilibrium condition were obtained by PVP from 9.5M HCl.</td>
<td>[99]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction and separation of Zr(IV) from succinate medium using N-n-octyl amine in xylene was studied. Quantitative extraction of Zr(IV) was effective with pH range 3.7-5.0. Zr(IV) was back extracted with 0.5 M HNO₃ and trace amount of Zr(IV) was separated effectively from higher amounts of other elements. This method was simple, selective, rapid and eco-friendly. [26]</td>
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<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from different acid feed solution using tri-n-octyl amine and di-cyclohexyl in xylene was studied. Influence of various acids and stripping agents on the extraction was investigated. Di-cyclo-hexyl amine was not a suitable carrier to separate Zr(IV) ions using coupled transport system. [100]</td>
<td></td>
</tr>
<tr>
<td>Zr(IV), Hf(IV) and Th(IV)</td>
<td>Extraction of Zr(IV), Hf(IV) and Th(IV) from acetonitrile solution using naphthol- derivative Schiff base (HAPMN) 1-(4-(4-([CE]-1-(2-hydroxy-1- naphthyl) methylidene]- amino) phenoxy) phenyl] imino] methyl)-2-napthol was studied. The stochiometric coefficients were determined by slope analysis method and formation of 1:1 stable complex was proposed. [101]</td>
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</tr>
<tr>
<td>Zr(IV)</td>
<td>Zr (IV) was extracted from acidic surfactant C-TAB(5%) micellar medium using HDMBBBH(4-Hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone). The mechanism of extraction and interference effect of various diverse ions was studied. This method was rapid, simple, sensitive and selective for extraction of Zr(IV) from synthetic alloy samples. [102]</td>
<td></td>
</tr>
<tr>
<td>Zr(IV) and Hf(IV)</td>
<td>Selective extraction and separation of Zr (IV) from Hf(IV) in hydrochloric acid solution using Amine based extractant such as Alamine 336, Alamine 308, Alamine 300 etc. was studied. Alamine 336 exhibited a greater separation factor than Alamine 300. Complete stripping of Zr(IV) was successfully achieved from the loaded organic phase by simple contact with 1M HCl solution. [103]</td>
<td></td>
</tr>
</tbody>
</table>
Separation study of Zr (IV) and Hf(IV) from hydrochloric acid medium using TEHA (tri-2-ethyl hexyl amine) was studied. Highest separation factor between two the two metals was obtained from 8 M HCl solution. The extractability of the constituents by TEHA was investigated in the following order: HCl > Zr(IV) > Hf(IV).

Zr(IV) was extracted from succinate media using 2-octylamino pyridine (2-OAP). Quantitative extraction takes place at pH 3.7 to 5.01. Back extraction takes place with 0.5M HNO3. Nature of extracted species in organic phase was determined. Proposed method was simple, selective, reproducible, accurate and rapid. Low reagent concentration of 2-OAP was required for quantitative recovery of Zr(IV) as compared to other high molecular weight amines.

1.11.2. Solvent Extraction of Zirconium with organophosphorous extractants

<table>
<thead>
<tr>
<th>Metals</th>
<th>Extraction Data</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from nitric acid media using di-n-butylphosphoric acid (HDBP) was studied. The mechanism of extraction of zirconium by HDBP, and of other metals by di-alkylphosphoric, over a wide range of conditions was discussed and compared with the mechanism of extraction Zr(IV) by tributyl phosphate (TBP) and thenoyltrifluoroacetone (HTTA).</td>
<td>[15]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr (IV) from nitric acid media using butyl lauryl phosphoric acid in dodecane was studied. TBP has an antagonistic effect of the Zr(IV) extraction by HBLP was investigated. The threshold HBLP concentration for an enhancement of zirconium extraction is 2x10^-4M.</td>
<td>[104]</td>
</tr>
<tr>
<td>Index</td>
<td>Formula</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
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<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Hf(IV) and Zr(IV)</td>
<td>Extraction and separation of Hf (IV) from different acid medium using 4-methyl-3-pentene-2-one was studied. A new method for the extractive separation of hafnium from zirconium was suggested. Zirconium was extracted with pure mesityl oxide from 4M nitric acid/ sodium nitrate medium, followed by extraction of Hf(IV) from 0.4M hydrochloric acid/2M ammonium thiocyanate medium.</td>
<td>[105]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr (IV) from hydrochloric acid solution using DPSO (diphenyl sulphoxide), dioctyl sulphoxide(DOSO), tributyl phosphate(TBP) and their mixtures in various solvents was studied. Separation of Zr(IV) from other associated metals was achieved by solvent extraction with sulfoxides.</td>
<td>[106]</td>
</tr>
<tr>
<td>Ti(IV),Zr(IV) and Hf(IV)</td>
<td>Extraction of Ti(IV),Zr(IV) and Hf(IV) from salicylic acid medium using Triphenyl arsine oxide was studied. Rapid, accurate and highly reproducible technique for optimum extraction of metal was reported. The probable composition of the extracted species was ascertained from log D-log C plots.</td>
<td>[107]</td>
</tr>
<tr>
<td>U(VI), Zr(IV) and Th(IV)</td>
<td>Extraction of U(VI), Zr(IV) and Th(IV) from perchlorate medium using PC-88A(2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) in toluene was studied. Quantitative extraction and separation takes place at a particular pH for specific metal was formulated. The probable extracted species was ascertained by plotting log D vs. Log [HR]. U(VI) was stripped with 4M HCl, Zr(IV) with 2.5M NaF and Th(IV) with 8M HCl from the metal loaded organic phase containing PC-88A dissolved in kerosene.</td>
<td>[108]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from solution of HCl, HBr or KI using Amberlite LA-2, TBP and HDEHP in toluene or kerosene was studied. Thermodynamic functions and equilibrium constant were determined for this process. HDEHP was the promising extractant for extraction of Zr(IV) from HCl, Amberlite LA-2 exhibits more effective extraction than TBP from HCl and HBr media.</td>
<td>[35]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr (IV) from hydrochloric acid media using D2EHPA in kerosene was studied. Equilibration time, acid concentration variation, effect of chloride ion concentration and effect of temperature were studied. The possible extraction equilibrium reactions have been suggested and supported by the loading tests.</td>
<td>[109]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from acidic chloride solution using Cyanex 272 in kerosene was studied. The extraction of Zr(IV) increases with an increase of the extractant concentration and decreases with an increase of the H⁺ ion concentration. The effect of the Cl⁻ ion concentration at a constant [H⁺] did not show any change in the D values. The addition of sodium salts enhanced the percentage extraction of Zr (IV).</td>
<td>[32]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from acidic chloride solution using 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC-88A) was studied. Quantitative extraction and effect of temperature and regeneration capacity of PC-88A was successfully reported. Higher acid concentration increases the extraction of zirconium and is quantitative around 1 M HCl. An increase of extractant and chloride ion concentration at constant H⁺ ion increases the extraction of Zr (IV).</td>
<td>[110]</td>
</tr>
</tbody>
</table>

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| **Zr(IV)** | Extraction of Zr(IV) from nitric acid solution using Cyanex 923 in toluene was studied. The percentage of extraction depends upon equilibration time, temperature, and concentration of mineral acid, extractant and metal ion. The separation of Zr(IV) from other associated metal ions were also investigated. The distribution increases with increasing temperature, suggested that the reaction is endothermic. | [111] |
| **Zr(IV) and Hf(IV)** | Extraction and separation of Zr(IV) and Hf(IV) from acidic medium using TBP, D2EHPA or Cyanex 272 was studied. The optimum extraction of Zr(IV) was 71% from 2M nitric acid using Cyanex 272 was achieved. | [112] |
| **Zr(IV) and Hf(IV)** | Extraction of Zr(IV) and Hf(IV) from acidic nitrate medium using Cyanex 272 was studied. The mechanism of the extraction of zirconium and Hafnium and stoichiometric relation was presented. The results showed that zirconium and hafnium were extracted in the form of neutral complexes through solvation mechanism. | [58] |
| **Zr(IV)** | Extraction of Zr(IV) from hydrochloric acid media using TOPO(tri-octyl phosphine oxide) was studied. The complex formation of Zr(IV) and stoichiometric composition of chelate was formulated and a colour was developed in the organic phase by addition of eriochrome Cyanine R reagent(ECR). This method was characterized by simplicity and the wide range of applications. | [113] |
| **Zr(IV)** | Extraction of Zr(IV) from nitric- hydrochloric acid media using tri butyl phosphate(TBP) in kerosene was studied. Effect of extractant, acids, metal ion concentration on the extraction was reported. Higher separation level was obtained when using mixture of acids, especially nitric-hydrochloric acids. | [114] |
| Zr(IV) and Hf(IV) | Extraction of Zr(IV) and Hf(IV) from nitric acid medium using Cyanex extractants such as Cyanex 921, Cyanex 923, Cyanex 925 in kerosene. The effect of various factors like extractant concentration, acid concentration and temperature were investigated. The extraction increases with increasing temperature, suggested that the reaction is endothermic. Under the optimum conditions, the extraction of zirconium was about 90, 87.6, and 91.6% and separation factors equal to 17, 21.4 and 40.7 were obtained from Cyanex 921, Cyanex 923 and Cyanex 925, respectively. | [115] |
| Zr(IV) | Extraction of Zr(IV) from nitric acid media using D2EHPA was studied. The limiting organic concentration of Zr(IV) and effect of diluents on the extraction system was determined. | [116] |
| Zr(IV) and U(VI) | Extraction of Zr(IV) and U(VI) from acidic medium with Arsenazo(III) in mixed aqueous organic medium. Individual and simultaneous determination of Zr(IV) and U(VI) was achieved. This method has advantages of simplicity, accuracy and versatility over other conventional methods. | [117] |
| Zr(IV) | Extraction of Zr(IV) from nitric acid medium using TRPO(trialkyl phosphine oxide) in kerosene was studied. The limiting organic concentrations (LOC) of Zr(IV) under various experimental condition was calculated. Low temperature and high nitric acid concentrations (>3M) were found to facilitate the third phase formation. | [72] |
Zr(IV) and Hf(IV)  
Extraction of Zr(IV) from hydrochloric acid media using acidic organophosphorous extractants and their mixtures with TOPO was studied. Synergistic extraction of Zr(IV) and Hf(IV) was obtained by the mixtures of Cyanex 272 and TOPO. Solvation mechanism was verified for the extraction of Zr(IV) and Hf(IV) by the single extractant.

1.11.3. Solvent extraction of Zirconium (IV) with binary mixture of extractants.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Extraction Data</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from hydrochloric acid media using TTA(2-thenoyl trifluoro acetone) and DPSO(di-n-pentyl sulphoxide) in carbontetrachloride was studied. Effect temperature and synergism adducts was investigated. The extraction of Zr(IV) by DPSO, DOSO decreases with increasing temperature. The conditional equilibrium constant was evaluated.</td>
<td>[76]</td>
</tr>
<tr>
<td>Zr(IV) and Fe(III)</td>
<td>Separation of Fe(III) from Zr(IV) from hydrochloric acid media using D2EHPA, KELEX-100, TBP, Aliquat 336. Separation of Fe(III) from Zr(IV) was studied. Aliquat 336 extracts iron very effectively in concentrated HCl solution and the separation of iron from zirconium is excellent for HCl concentrations between 3 and 4M.</td>
<td>[118]</td>
</tr>
<tr>
<td>Zr(IV) and Nb(IV)</td>
<td>Extraction of Zr(IV) and Nb(IV) from hydrochloric acid solution using Aliquat 336/Alamine 336 and DOSO mixture in benzene was studied. Synergism and quantitative extraction of metals was reported. The extraction behaviour of both metals depends upon extractant and HCl concentration.</td>
<td>[77]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from nitric acid and perchloric acid medium using TBP and its binary mixture with DMSO or pyridine in n-dodecane was studied. Stochiometric calculation was done and a mechanism on the basis of slope analysis was proposed. The decrease in the extraction at higher acid concentrations is because of the loss of free extractant due to formation of [Acid.Extractant] adduct and also due of the partial solubilities of [Metal. Extractant] complexes at higher acidities.</td>
<td>[119]</td>
</tr>
<tr>
<td>Zr(IV), Hf(IV) And Nb(IV)</td>
<td>Extraction of Zr(IV), Hf(IV) and Nb(IV) from acidic thiocyanate medium using Aliquat 336 and mixture with TOPO was studied. It was observed that, the extraction depends upon concentration of HCl, thiocyanate and Aliquat 336. Mixtures of Aliquat 336 and TOPO result synergistic extraction of Zr and Hf from acidic thiocyanate media.</td>
<td>[74]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from hydrochloric acid media using TOA and neutral donors in carbon tetrachloride was studied. Synergism and quantitative extraction of metal was reported. The extraction of Zr(IV) increases with increase in concentration of amines and neutral donors. Synergistic coefficients and apparent formation constants for the complex adducts have also been calculated.</td>
<td>[78]</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>Extraction of Zr(IV) from hydrochloric acid media using salicylaldoxime in dichloromethane and mixture with neutral donors was studied. From the distribution data, adduct formation of both binary species and tertiary species was formulated.</td>
<td>[55]</td>
</tr>
<tr>
<td>Zr(IV) and Hf(IV)</td>
<td>Extraction of Zr(IV) and Hf(IV) from hydrochloric acid medium using 4-Acyl bis(1-phenyl-3-methyl-5-pyrazolones) in the presence of neutral organophosphorous extractants was studied. Synergism was observed. The order of complexation was: TOPO &gt; TRPO &gt; TBP. The equilibrium constants of synergistically extracted complexes have been correlated with neutral organophosphorus extractants.</td>
<td>[80]</td>
</tr>
<tr>
<td>Zr(IV) and Hf(IV)</td>
<td>Separation of Zr(IV) and Hf(IV) from nitric acid solution was studied using mixture of TBP and Cyanex 923. The effect of extractant volume ratio, concentration of extractant in organic phase, nitric acid concentration and NaNO₃ concentration in aqueous phase has been investigated. Lower acid concentration favours more extraction of Zr(IV).</td>
<td>[120]</td>
</tr>
<tr>
<td>Zr(IV) and Hf(IV)</td>
<td>Extraction of Zr(IV) and Hf(IV) from nitric acid solution using TBP-D2EHPA mixtures was studied. Statistical modelling of Zr(IV) and Hf(IV) extraction was stated. Effect of change in the levels of temperature, nitric acid concentration and TBP/D2EHPA ratio the extraction on the extraction/separation of Zr/Hf was studied.</td>
<td>[121]</td>
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</tbody>
</table>
1.12. Aim of the present work

The present work deals with detailed solvent extraction studies of Zr(IV) from hydrochloric acid media using various commercial extractants such as tri-n-octyl amine, Cyanex 921, binary mixture of TOA and Cyanex 921, Cyanex 923 and binary mixture of TOA and Cyanex 921/Cyanex 923 are used in this investigation. The present work has the following objectives.

- To study the extraction of Zr (IV) from hydrochloric acid medium using tri-n-octyl amine, Cyanex 921 and Cyanex 923.
- To understand the extraction behaviour of Zr (IV) under various experimental conditions.
- To study the synergistic aspect of extraction of Zr (IV) using binary mixture of TOA and Cyanex 921/ Cyanex 923.
- To establish optimum conditions for the extraction of Zr (IV) with extractants and their binary mixture.
- To study the separation possibilities of Zr (IV) from Fe (III)/Al (III) from hydrochloric acid media using these extractants.

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