

CS8893

**STUDIES ON LIQUID-LIQUID EXTRACTION SEPARATION OF  
VALUABLE METALS FROM TITANIA WASTES**

---

THESIS SUBMITTED TO COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY IN PARTIAL  
FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

**DOCTOR OF PHILOSOPHY**

IN CHEMISTRY UNDER THE FACULTY OF SCIENCE

BY

**J. SAJI**

UNDER THE SUPERVISION OF  
DR. M. L. P. REDDY



ION-SPECIFIC SEPARATION SCIENCE AND TECHNOLOGY GROUP  
REGIONAL RESEARCH LABORATORY (CSIR)  
THIRUVANANTHAPURAM - 695 019, KERALA, INDIA.

JULY 2002

## DECLARATION

I hereby declare that the matter embodied in the thesis entitled **"Studies on liquid-liquid extraction separation of valuable metals from titania wastes"** is the result of the investigations carried out by me in the Ion-specific Separation Science and Technology Group of Regional Research Laboratory (CSIR), Thiruvananthapuram, under the supervision of Dr. M. L. P. Reddy and the same has not been submitted elsewhere for any other degree.



J. SAJI

Thiruvananthapuram  
July, 2002

---

REGIONAL RESEARCH LABORATORY (CSIR)  
GOVERNMENT OF INDIA  
TRIVANDRUM - 695 019, INDIA

Dr. M. L. P. Reddy  
Scientist EII

---


Tel : 91-471-515 259, Fax : 91-471-491 712

---

### CERTIFICATE

This is to certify that the work embodied in the thesis entitled "**Studies on liquid-liquid extraction separation of valuable metals from titania wastes**" is the result of the investigations carried out by Mr. J. Saji under my supervision in the Ion-specific Separation Science and Technology Group of Regional Research Laboratory (CSIR), Thiruvananthapuram, and the same has not been submitted elsewhere for any other degree.

Thiruvananthapuram  
July, 2002

  
M. L. P. Reddy  
(Thesis Supervisor)

---

Email : mlpreddy@yahoo.co.uk, reddy@csrrltd.ren.nic.in

---

## ACKNOWLEDGEMENTS

It is a great pleasure and privilege to express my deep sense of gratitude to my research supervisor Dr. M. L. P. Reddy for his constant encouragement, intellectual support and scholarly criticism throughout the course of my doctoral studies.

I am grateful to Professor Javed Iqbal, present director and Dr. G. Vijay Nair, former director of Regional Research Laboratory (CSIR), Trivandrum, for providing the necessary facilities to carry out my research work.

My thanks are also due to

- ❖ Dr. G. D. Surender, Head, Process Science and Engineering Division, RRL, for his keen interest and inspiring attitude towards my research work.
- ❖ Dr. T. R. Ramamohan, Deputy Director, RRL, for his help to carry out the mathematical modeling of the experimental data.
- ❖ Dr. T. Prasada Rao, Deputy Director, RRL, for the wholehearted encouragement during the course of my work.
- ❖ Members of Ion-specific Separation Science & Technology Group, RRL, for their invaluable support and co-operation.
- ❖ Ms. S. L. Radhika, Mr. Neil Elijah and Ms. P. N. Remya, who have helped in various stages of the experimental work.
- ❖ Library and other supporting staff of RRL for the help rendered by them.
- ❖ All other friends and colleagues of RRL for their support.

Financial assistance from the Council of Scientific and Industrial Research, New Delhi and the Science, Technology and Environment Committee (STEC), Government of Kerala, in the form of research fellowships is gratefully acknowledged.

Finally, I would like to thank my teachers, friends and relatives for their constant encouragement. Words are inadequate to express my gratitude to my parents, brother and sister who have supported me with affection and encouragement throughout my academic career.

Thiruvananthapuram  
July, 2002

J. Saji

---

## LIST OF PUBLICATIONS

1. Extraction of iron(III) from acidic chloride solutions by Cyanex 923; **J. Saji**, T. P. Rao, C .S. P. Iyer, M. L. P. Reddy; *Hydrometallurgy* **49**, 289 (1998).
2. Solvent extraction of titanium(IV) from acidic chloride solutions by Cyanex 923; K. Saji John, **J. Saji**, M. L. P. Reddy, T. P. Ramamohan, T. P. Rao; *Hydrometallurgy* **51**, 9 (1999).
3. Studies on the liquid-liquid extraction of iron(III) and titanium(IV) with 3-phenyl-4-benzoyl-5-isoxazolone; **J. Saji**, T. P. Rao, T. R. Ramamohan, M. L. P. Reddy; *Talanta* **50**, 1065 (1999).
4. Liquid-liquid extraction of tetravalent titanium from acidic chloride solutions by bis(2,4,4-trimethylpentyl) phosphinic acid; **J. Saji**, K. Saji John, M. L. P. Reddy; *Solvent Extr. Ion. Exch.* **18**, 877 (2000).
5. Liquid-liquid extraction separation of iron(III) chloride from titania wastes using TBP-MIBK mixed solvent system; **J. Saji**, M. L. P. Reddy; *Hydrometallurgy* **61(2)**, 81 (2001).
6. Selective extraction and separation of titanium(IV) from multivalent metal chloride solutions using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester; **J. Saji**, M. L. P. Reddy; *Sep. Sci. Tech.* (2002) (in press).
7. Solvent extraction separation of vanadium(V) from iron(III) and titanium(IV) chloride solutions using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester; **J. Saji** , M. L. P. Reddy; *J. Chem. Tech. & Biotech.* (2002) (in press).

---

# CONTENTS

---

Declaration	i
Certificate	ii
Acknowledgements	iii
List of publications	iv
Preface	viii

## Chapter 1

---

<b>Introduction</b>	<b>1- 32</b>
1.1 Liquid-liquid extraction: General	4
1.2 Liquid-liquid extraction systems	6
1.2.1 Extractants involving compound formation	6
1.2.2 Extractants involving ion association	9
1.2.3 Extractants involving solvation	10
1.3 Liquid-liquid extraction of iron(III), titanium(IV) and vanadium(V) : Literature review	11

## Chapter 2

---

<b>Studies on the extraction and separation of iron(III) from titania waste chloride liquors using neutral solvating extractants</b>	<b>33-54</b>
<b>Part A : Liquid-liquid extraction separation of iron(III) from titania wastes using TBP-MIBK mixed solvent system</b>	<b>33</b>
2.1 Experimental	34
2.2 Results and discussion	36

---

---

2.2.1	Extraction equilibrium	36
2.2.2	Loading capacity of the mixed solvent system	40
2.2.3	Recycling capacity of the mixed solvent system	41
2.2.4	Extraction and Stripping isotherms	41
2.2.5	Extraction of iron(III) from waste chloride liquors of titania industry	43
<b>Part B : Studies on the extraction of iron(III) from acidic chloride solutions using Cyanex 923</b>		<b>46</b>
2.3	Experimental	47
2.4	Results and discussion	47
2.4.1	Extraction equilibrium	47
2.4.2	Dependence of extraction on the nature of diluent	51
2.4.3	Stripping studies	52
2.4.4	Comparison of extraction behaviour of iron(III) with other associated metal ions present in the waste chloride liquors of titanium minerals processing industry	53
 Chapter 3		
<b>Studies on the liquid-liquid extraction of titanium(IV) from acidic chloride solutions using acidic organophosphorus extractants</b>		<b>55-77</b>
3.1	Experimental	56
3.2	Preparation of metal complexes	58
3.3	Results and discussion	58
3.3.1	Effect of phase contact time	58
3.3.2	Extraction of tetravalent titanium from acidic chloride solutions using dialkylphosphonic acid or phosphinic acids	60

---

---

3.3.3	IR spectral studies of the extracted complexes	66
3.3.4	Effect of nature of diluent on the extraction of titanium	69
3.3.5	Loading capacity of the extractants	70
3.3.6	Stripping studies	71
3.3.7	Recycling capacity of EHEHPA or BTMPPA	73
3.3.8	Comparison of extraction behaviour of titanium(IV) with other associated metal ions present in waste chloride liquors of titanium minerals processing industry	74

## Chapter 4

---

<b>Liquid-liquid extraction separation of vanadium(V) from acidic chloride solutions using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester</b>		<b>78-92</b>
4.1	Experimental	79
4.2	Results and discussion	80
4.2.1	Extraction of vanadium(V) from acidic chloride solutions using dialkylphosphonic or phosphinic acids	80
4.2.2	IR spectra of V(V)-EHEHPA complex	83
4.2.3	Effect of the nature of diluent on the extraction of vanadium	84
4.2.4	Loading capacity of EHEHPA by vanadium	85
4.2.5	Extraction and stripping isotherms	86
4.2.6	Recycling capacity of EHEHPA	88
4.2.7	Selective separation of vanadium(V) from multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry	88
Conclusions		93
References		101

---



## PREFACE

The thesis entitled **"STUDIES ON LIQUID-LIQUID EXTRACTION SEPARATION OF VALUABLE METALS FROM TITANIA WASTES"** embodies the results of investigations carried out on the liquid-liquid extraction of iron(III), titanium(IV) and vanadium(V) from acidic chloride solutions using commercially available extractants. The objective of the work is to develop selective liquid-liquid extraction and separation procedures for the recovery of valuable metal species depending upon their value and concentrations in the waste chloride liquors of titanium minerals processing industry. The thesis is comprised of four chapters.

The introductory chapter highlights the significance of waste minimisation through resource recovery (metal values) from the waste chloride liquors of the titanium minerals processing industry with special emphasis on the use of liquid-liquid extraction technique. A general introduction to the extraction chemistry followed by an exhaustive literature review on the recent developments in the extraction studies of iron(III), titanium(IV) and vanadium(V) from acidic aqueous solutions using various extraction systems has also been presented in chapter 1.

The second chapter describes the results on the selective extraction separation of high purity iron(III) chloride from titania waste chloride liquors using a mixed solvent system consisting of tributylphosphate (TBP) and methylisobutyl ketone (MIBK) as an extractant. This chapter also deals with the studies on the extraction behaviour of iron(III) and other associated metal ions from acidic chloride solutions using trialkylphosphine oxide (Cyanex 923) as an extractant.

The third chapter describes the results of the investigations on the extraction behaviour of titanium(IV) and its possible recovery from multivalent metal chloride

---

---

solutions using dialkyl organophosphonic acid such as 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) and organophosphinic acids such as bis(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA) and bis(2,4,4-trimethylpentyl) monothiophosphinic acid (BTMPTPA).

The results of the studies on the extraction behaviour of vanadium(V) from acidic chloride solutions using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) have been incorporated in the fourth chapter. For comparison, studies have also been performed with bis(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA). The potential of EHEHPA as an extractant for the selective recovery of vanadium(V) from the waste chloride liquors of titanium minerals processing industry has also been assessed.

The conclusions and relevant references of the work have been provided towards the end of the thesis.

## ***Chapter 1***

---

### ***Introduction***

The manufacture of the versatile white pigment,  $\text{TiO}_2$  through '*Chloride Process*' generates large amounts of acidic waste chloride liquors containing multivalent metal ions such as magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II), iron(II) and iron(III). The typical composition of the waste chloride liquor from a titanium minerals processing industry is given in Table 1.1. The management of the waste liquors from titanium minerals processing industry represents a major environmental issue, affecting every industrialised country. The iron oxide waste lead to the following negative environmental impact :

1. Occupies premier land area thereby generating solid waste disposal problem.
2. Being acidic in nature, the stored iron oxide tailing ponds pollute the ground water.
3. Due to the presence of toxic metals like chromium and vanadium, these wastes are considered to be hazardous.

Further, many valuable metal species have not been recovered. The more our economy recovers and recycles useful metals from its wastes, the less mining will be needed and less environmental damage will result from waste disposal.

---

**Table 1.1** Typical composition of the waste chloride liquor from titania industry (Kerala Minerals and Metals Ltd., India).

Constituent	g /dm <sup>3</sup>
FeCl <sub>2</sub>	170-210
FeCl <sub>3</sub>	40-60
MgCl <sub>2</sub>	15-16
MnCl <sub>2</sub>	7-8
AlCl <sub>3</sub>	3-6
TiOCl <sub>2</sub>	3-4
CrCl <sub>3</sub>	3-7
VOCl <sub>3</sub>	3-4
HCl	30-40

### *Titania waste disposal in India*

Depending on whether the industry has an acid regeneration plant or not, the iron oxide containing waste from synthetic rutile plants occur either as liquid or solid waste. In order to conform to the minimum environmental regulations, lime neutralisation of acidic chloride waste is adopted leading to enormous quantities of solid wastes. The acid regeneration option overcomes the need for the lime neutralisation since the mineral acid is recovered. However, the iron oxides generated due to the high temperature pyrohydrolysis process are impure, containing several other metallic impurities such that no marketable outlet can be identified and hence resulting as a solid waste. The various industrial units manufacturing synthetic rutile in India along with the process employed are given in Table 1.2.

**Table 1.2** Industrial units manufacturing synthetic rutile in India.

Company	Feed stock	Process
Cochin Minerals and Rutile Ltd.	Ilmenite 'Q' grade	Wah-Chang process, reduction roasting, 2 stage leaching with 30% HCl, Oxidation of 1 <sup>st</sup> leach liquor to FeCl <sub>3</sub> for sale, TiO <sub>2</sub> recovery-88%.
Kerala Minerals and Metals Ltd.	Ilmenite 'Q' grade	Benelite process, reduction roasting, 2 stage leaching with regenerated acid.
Dhrangadra Chemicals Ltd.	Ilmenite 'MK' grade	Wah-Chang process, reduction roasting, 30% HCl leaching, disposal of leach liquor, TiO <sub>2</sub> recovery-90%.
Indian Rare Earths Ltd.	Ilmenite 'OR' grade	Benelite process, reduction roasting, 3 stage leaching with regenerated acid, TiO <sub>2</sub> recovery-<70%.

***International status***

The major strategy for titania waste management abroad is to adopt smelting and other slag based routes so that a pig iron substitute is formed and integrated into the iron and steel industry. In view of the very favorable electric power tariff in Canada and Norway, this approach is essentially region specific and not appropriate for a country such as India with high electric power tariffs.

In order to produce high purity iron oxide suitable for ferrites from ferric chloride waste of the titania industry, International Steel Services, USA (ISSI) has developed a technology based on solvent extraction, in an exclusive joint venture with Kola Science Center, Russia [1]. However, the process details are not available in the open literature.

An innovative region specific approach is required to develop an environmentally and economically viable method to address the iron oxide waste

problem. One such option is to produce high purity metal oxides for use in pigment, electronic and catalyst industries. Nowadays, methods based on liquid-liquid extraction has emerged as a novel and unique technique for the separation and recovery of metal ions from mineral sources as well as from industrial waste streams in place of the traditional pyrometallurgical techniques because of its simplicity, versatility, easy recovery and ready adaptability to scaling up of the process [2-6].

The present work aims to investigate novel solid waste remediation process through resource recovery (metal values) and its reintegration as value added state-of-art products by employing liquid-liquid extraction technique. The metal values proposed to be separated are based on their value, toxicity and concentration in the waste chloride liquors.

1. Iron (concentration and value)
2. Titanium (value)
3. Vanadium (value and toxicity)

### **1.1 Liquid-liquid extraction: General**

Liquid-liquid extraction highlights the usefulness of phase distribution and is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents. For the separation and purification of metal ions, this method is known since 1842, when Peligot [7] discovered the removal of uranium as uranyl nitrate with diethyl ether.

In liquid-liquid extraction, a solute distributes itself between two immiscible liquids. According to Gibbs phase rule,

$$P + V = C + 2 \quad (1)$$

(where P is the number of phases, V, the variance or degrees of freedom and C, the number of components). The distribution of a solute between two immiscible solvents is univariant at constant temperature and pressure. That is, if we choose the concentration of the solute in one phase, its concentration in the other phase is fixed.

The distribution law, stated by Berthelot and Jungfleisch [8] and thermodynamically elaborated by Nernst [9] in 1891, states that at a particular temperature for a solute 'X' distributing between two immiscible solvents 1 and 2, at equilibrium, the ratio of concentrations in the two phases is a constant, provided the nature of the species is the same in both the phases.

$$D = [X]_1/[X]_2 \quad (2)$$

The constant, D, is known as the distribution or extraction coefficient. The chemical potential ( $\mu$ ) of the solute is the same as in each phase at equilibrium provided temperature and pressure are constant, ie;

$$\mu_1 = \mu_2 \quad (3)$$

where the subscripts 1 and 2 refer to the respective solvent phases. Substituting suitable expressions of  $\mu$ ,

$$\mu_1^\circ + RT \ln m_1 + RT \ln \gamma_1 = \mu_2^\circ + RT \ln m_2 + RT \ln \gamma_2. \quad (4)$$

where  $\mu^\circ$ , represents the chemical potential of the solute in a hypothetical ideal 1 molal solution,  $m$ , the solute concentration in molality and  $\gamma$ , the molal activity coefficient.

The molal distribution coefficient,

$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} e^{-(\mu_2^\circ - \mu_1^\circ)/RT} \quad (5)$$

For a system in which the two solvents are completely immiscible under all circumstances the exponential term is a constant, K, so that

---



$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} K \quad (6)$$

Thus,  $D$  depends on the activity coefficients of the solute in each of the phases. When the activity coefficients approach unity, ie. at low concentrations,  $D$  becomes constant. The distribution coefficient is related to the percentage extraction,  $E$ , by the equation

$$E = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \quad (7)$$

where  $V_{aq}$  and  $V_{org}$  are the volumes of the aqueous and organic phases, respectively. The separation factor, S.F., is given by

$$\text{S.F.} = D_1/D_2 \quad (8)$$

where  $D_1$  and  $D_2$  are the distribution coefficients for elements 1 and 2, respectively.

## 1.2 Liquid-liquid extraction systems

The nature of extractable metal species is of fundamental importance in metal extraction systems. Based on this fact, Ritcey and Ashbrook [4] classified the extractants into three classes as indicated below :

- (1) Those which involve compound formation
- (2) Those which involve ion association
- (3) Those which involve solvation of the metal ion

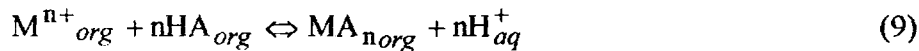
### 1.2.1 Extractants involving compound formation

This class of extractants can be further divided into two sub-classes, namely acidic extractants and chelating extractants. The former are those having reactive groups such as  $-\text{COOH}$ ,  $>\text{P}(\text{O})\text{OH}$ ,  $-\text{SO}_3\text{H}$  while the latter are those which chelate with metal ions.

---

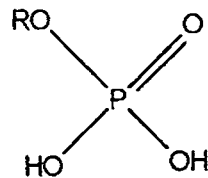
### A. Acidic extractants

Acidic extractants are cationic liquid ion exchangers, extract metal ions by a cation exchange mechanism, in which hydrogens of the extractant are exchanged for metal ions. Basically, the general mechanism is as shown in Eq.(9).

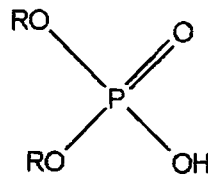


The metal extractants of acidic type used in commercial operations are organic derivatives of phosphorus acids and monocarboxylic acids.

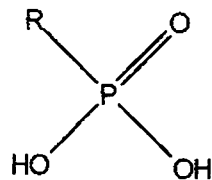
**Acidic organophosphorus extractants** : This type of extractants include the following:



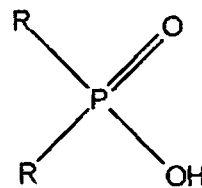
1. Monoalkyl phosphoric acid



2. Dialkylphosphoric acid



3. Monoalkyl phosphonic acid

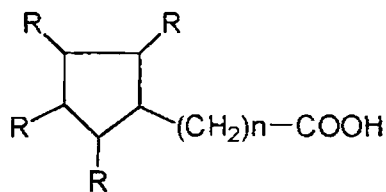


4. Dialkylphosphinic acid

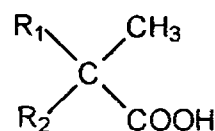
where R can be alkyl or aryl substituent. Of these, alkyl phosphoric acids have proved to be most versatile, especially di-(2-ethylhexyl)phosphoric acid (DEHPA). It has been used commercially for the extraction of many metals including uranium [10], cobalt and nickel [11], rare earths [12] and vanadium [13]. Among the esters of phosphonic acid, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) has been widely used for the extraction and separation of cobalt and nickel [14] and rare earths [15]. Various dialkylphosphinic acid extractants such as bis(2,4,4-

trimethylpentyl)phosphinic acid (Cyanex 272) has been proved to be an important extractant for cobalt/nickel [16] and rare earth separations [17].

**Carboxylic acids:** Carboxylic acids such as naphthenic acid and versatic acids have been well studied for the extraction and separation of metal ions.



Naphthenic acid



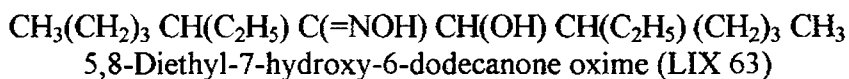
Versatic 911 acid ( $\text{R}_1, \text{R}_2 = \text{C}_4\text{-C}_5$ )

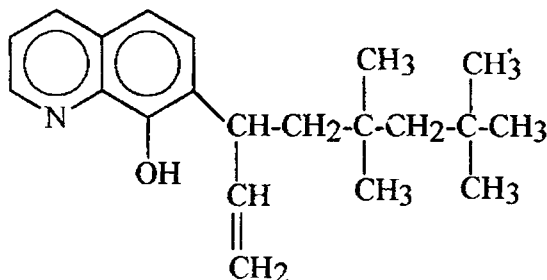
Versatic 10 acid ( $\text{R}_1, \text{R}_2 = \text{C}_6$ )

Commercial solvent extraction processes using carboxylic acids include the extraction of yttrium [18] and separation of cobalt and nickel [19]. Reviews on the use of carboxylic acids in solvent extraction processing of metal ions and their applicability in this field are available in the literature [20, 21].

## B. Chelating extractants

Chelating extractants contain donor atoms such as nitrogen, sulphur or oxygen as the basic atom capable of forming bidentate complexes with metal ions. Examples of some chelating reagents are dithizone, cupferron, acetylacetone, thenoyltrifluoroacetone, 4-acyl-5-pyrazolones and derivatives of 5-isoxazolones. Commercially useful chelating extractants are of two types – a series of substituted 2-hydroxybenzophenone oximes produced by Henkel Corporation under the name LIX reagents and the substituted 8-hydroxyquinolines produced by Sherex (Ashland Chemical Company) and marketed under the name Kelex. Most of these extractants were developed for the specific extraction of copper from acidic leach liquors and from alkaline solutions [22, 23].





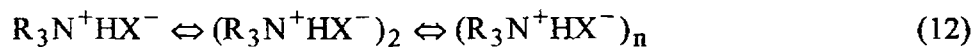
7-[3-(5,5,7,7-tetramethyl-1-octenyl)]-8-hydroxyquinoline (Kelex 100)

### 1.2.2 Extractants involving ion association

Quaternary ammonium compounds with high molecular weights (Aliquat 336) behave chemically as strong base anion exchangers and require lower concentrations of salting out reagents. Commercial processes have been developed which employ primary ( $\text{RNH}_2$ ) [24], secondary ( $\text{R}_2\text{NH}$ ) [25], tertiary ( $\text{R}_3\text{N}$ ) [26] amines and quaternary ammonium salts ( $\text{R}_4\text{N}^+$ ) [27]. The usefulness of amines as extractants depends essentially on the ability of ions to form anionic species in the aqueous phase, which are extracted by amines in an anion exchange process. In order to achieve this exchange, the amine is first converted to the appropriate amine salt to provide an anion to exchange with the metal species.



One important factor influencing the extraction of metals by amines is the aggregation of the amine in the organic phase, which is determined by the nature of the diluent.



Monomer                  Dimer                  Polymer

Another factor influencing metal extraction is the nature of carbon chain, and also the number of carbon atoms in the chain. Some of the metal species which have been reported to be extracted by quaternary ammonium halides (Aliquat 336) are  $\text{CuCl}_2^-$ ,  $\text{CuCl}_4^{2-}$ ,  $\text{FeCl}_4^-$  and  $\text{CdCl}_4^{2-}$  [28].

### 1.2.3 Extractants involving solvation

Oxygenated organic solvents such as alcohols, ketones, ethers and esters show some basicity because of the lone pair of electrons on the oxygen atom and can, therefore, directly solvate protons and metal ions and bring about their extraction. Alcohols solvate better than ketones or ethers. Among ketones, methylisobutyl ketone (MIBK) has found commercial application in the separation of zirconium/hafnium [29] and niobium/tantalum [30].

Esters of organophosphorus acids ( $\equiv\text{P}=\text{O}$ ) and a number of related compounds constitute a class of organic solvents which show remarkable solvating properties, whose essential functional group is the semipolar  $\text{P}=\text{O}$  bond with the oxygen atom having good steric availability. Tributylphosphate (TBP) has been used in solvent extraction and may be taken as a typical example of compounds containing  $\text{P}=\text{O}$  bond. The difference in the degree of extraction of elements is utilised for their mutual separation using TBP [31]. The basicity and hence extractability of organophosphorus compounds is in the order: phosphates < phosphonates < phosphinates < phosphine oxides. Among trialkylphosphine oxides, tri-n-octylphosphine oxide (TOPO) has been used for the recovery of vanadium from phosphate liquors [32,33]. Cyanex 923 and Cyanex 925 belong to the new class of extractants consisting of mixture of trialkylphosphine oxides.

Sulphoxides are pyramidal molecules with a lone pair of electron on both the sulphur and oxygen atoms, capable of donation. A correlation of basicity with

---

extracting power clearly establishes the position of sulphoxides between ketones and phosphine oxides. Thus the sulphoxides find their place as promising extractants for a number of metal ions [34,35].

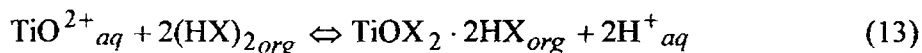
### **1.3 Liquid-liquid extraction of iron(III), titanium(IV) and vanadium(V) : Literature review**

A comprehensive review of literature reveals that the liquid-liquid extraction studies of iron(III), titanium(IV) and vanadium(V) utilises three well-known classes of extractants *viz.*, 1. Acidic extractants, 2. Solvating extractants and 3. Anion exchangers. Sole [36] in a recent review article, highlighted the potential for the recovery of titanium from sulphate leach liquors by solvent extraction. In 1993, Kislik and Eyal [37] have reviewed critically, the acidity dependence on the extraction of titanium(IV) with various extraction systems. Iron control in various hydrometallurgical processes by solvent extraction has been discussed in great detail by Flett and Monhemius [38].

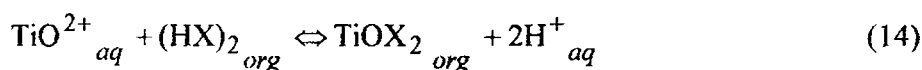
#### ***A. Extraction by acidic extractants***

**Acidic organophosphorus extractants:** Among the various acidic organophosphorus extractants used for the extraction of tetravalent titanium, di-(2-ethylhexyl)phosphoric acid (DEHPA) has been proved to be the most versatile reagent to recover titanium from acidic solutions [39-49]. Biswas and Begum [39] have investigated the extraction behaviour of tetravalent titanium from hydrochloric acid solutions using DEHPA (HX) in kerosene as an extractant over a wide range of aqueous acidities as a function of phase contact time, metal, hydrogen and chloride ion concentrations in the aqueous phase and the extractant concentration in the organic phase. The results suggested that the extraction of titanium occurs via the following reaction:

---



where  $(\text{HX})_2$  refers to the dimeric form of DEHPA. On the other hand, at higher loading of the metal ion, the extraction equilibrium of titanium has been reported as:



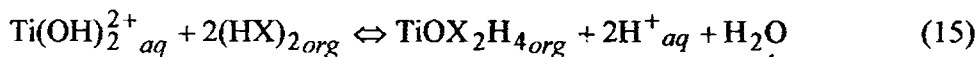
The formation of  $\text{TiOX}_2$  has been further confirmed by IR spectral studies. Further, these authors have also reported slow kinetics for the extraction of titanium(IV) from hydrochloric acid solutions with DEHPA in kerosene as an extractant.

Dual extraction behaviour of titanium (extraction maxima at low acidity, decrease to a minimum at medium acidity and increase at high acidity) has been observed by Sato and Keiichi [40] for the extraction of titanium from hydrochloric acid solutions using DEHPA in kerosene as an extractant.

Islam and Biswas [41,42] and Islam *et al.* [43] have carried out extensive studies on the extraction of titanium from sulphuric acid solutions with a view to investigate the selectivity of titanium(IV) over iron(II) and iron(III) and reported the separation factors as :  $D_{\text{Ti(IV)}} / D_{\text{Fe(III)}} = 60$  and  $D_{\text{Ti(IV)}} / D_{\text{Fe(II)}} = 500$ . In a recent study, Biswas *et al.* [44] have reported  $\text{TiO}^{2+}$  species polymerisation in both aqueous and organic phases and the degree of polymerisation increases as its concentration in the aqueous phase increases.

The extraction of titanium from sulphuric acid solutions by DEHPA has also been investigated by Sato and Nakamura [45] and reported a cation exchange mechanism at low acidities and a solvation mechanism at higher acidities for the extraction of titanium(IV).

---



where  $n \geq 1$  and  $m = 1$ . The stoichiometries of the above extracted complexes were further confirmed by IR and NMR spectroscopic studies.

Sole [50] has studied the extraction of titanium along with other associated metal ions from leach liquors of titaniferrous magnetites using DEHPA as an extractant and found poor selectivity for titanium(IV) over other associated multivalent metal ions.

Recently, Iyatomi *et al.* [51] have described a solvent extraction process for the recovery of titanium(IV) from the waste sulphuric acid solutions of a titanium dioxide industry by employing DEHPA as an extractant. Titanium has been recovered from the organic phase using a mixture of ammonium carbonate and ammonia solution as a stripping agent. Finally, the raffinate from the solvent extraction stream has been subjected to diffusion dialysis treatment to separate associated metal ions such as Fe, Cr and V and thereby regenerating the sulphuric acid.

Kislik and Eyal [46] have investigated the extraction behaviour of titanium from hydrochloric acid solutions by mixtures of mono and di-(2-ethylhexyl)phosphoric acid esters (MEHPA and DEHPA) and reported that MEHPA extracts titanium three orders of magnitude more efficiently than DEHPA. Further, it has also been reported that at higher acidities, MEHPA acts as a chelating agent rather than as a cation exchanger.

A solvent extraction process for the recovery of titanium values from hydrochloric acid leach liquors of ilmenite by employing mono-2-ethylhexyl

---

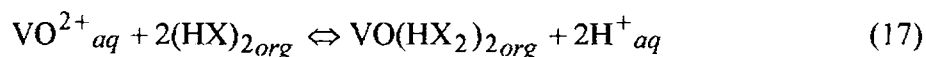


phosphoric acid (MEHPA) as an extractant has been reported by Tolley *et al.* [52]. In this process titanium has been recovered from the loaded organic phase using a mixture of hydrogen peroxide and an inorganic acid as the stripping agent.

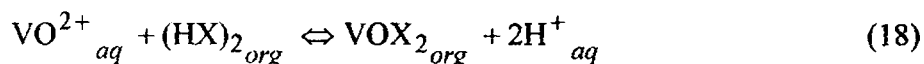
Solvent extraction of titanium(IV), iron(III) and iron(II) from sulphuric acid solutions with di-*o*-tolylphosphoric acid (HDTP  $\equiv$  HA) in benzene containing 20 % hexanol system has been studied by Biswas *et al.* [53] and reported the order of extractability as: Ti(IV) > Fe(III) > Fe(II). The values of separation factors are found to be  $D_{Ti(IV)}/D_{Fe(III)} = 175$  at 0.1 mol/dm<sup>3</sup> HDTP and 3.5 mol/dm<sup>3</sup> sulphuric acid concentrations and  $D_{Ti(IV)}/D_{Fe(II)} = 7800$  at 0.1 mol/dm<sup>3</sup> HDTP and 3.5 mol/dm<sup>3</sup> sulphuric acid concentrations. These values clearly indicate that separation of iron from titanium is promising, if iron is present in the divalent state. Further, these authors also reported the extracted complexes at higher loading of metal ion as TiOA<sub>2</sub>.

Among acidic organophosphorus extractants, di-(2-ethylhexyl)phosphoric acid (DEHPA) has been extensively used for the extraction of vanadium from acidic aqueous solutions. Hirai *et al.* [54] have studied the extraction of vanadium(V) from acidic sulphate and chloride solutions using DEHPA (HX) and found the extracted complexes as VO<sub>2</sub>X·HX. Further, these authors also examined the extraction behaviour of vanadium(V) using bis-(2-ethylhexyl)monothiophosphoric acid (DEHTPA  $\equiv$  HL) and found that VO<sub>3</sub><sup>-</sup> in the aqueous phase was getting reduced to VO<sup>2+</sup> on contact with DEHTPA phase thereby oxidising the extractant to disulfide. The extracted complex has been found to be VOL<sub>2</sub> in this case.

Islam and Biswas [55] have investigated the extraction behaviour of vanadium(IV) from sulphuric acid solutions using DEHPA (HX) in kerosene as an extractant and reported the extraction equilibrium at higher acidities as :



where  $(HX)_2$  refers to the dimeric form of DEHPA. On the other hand, the extraction equilibrium of vanadium(IV) with DEHPA at low acidities has been reported as :



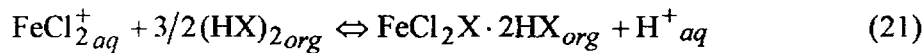
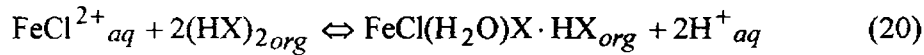
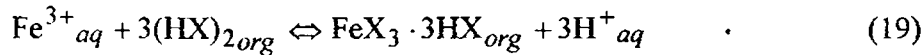
Later studies by Sato and Nakamura [56] confirmed the formation of these complexes by UV-Visible and ESR spectral studies of the loaded organic phase.

Commercial processes for the recovery of vanadium focus either on the extraction of vanadium(V) as anyone of its anionic species using tertiary or quaternary amines or the extraction of vanadium(IV) as  $[VO]^{2+}$  using DEHPA from acidic solutions [57]. In the commercial process for the recovery of vanadium from uranium circuits, iron powder is added to the feed solution to convert iron to ferrous state and all the vanadium to the tetravalent form [58]. This is followed by either sequential extraction of uranium at  $pH < 1.8$  and vanadium(IV) at  $pH 2.0$  or by simultaneous extraction at  $pH 2.0$  using DEHPA followed by selective stripping of vanadium with  $1 \text{ mol/dm}^3$  sulfuric acid and uranium with sodium carbonate.

Tebbe [59] has described a process for the simultaneous oxidation and extraction of vanadium from wet process phosphoric acid using di-(2-ethylhexyl)phosphoric acid (DEHPA) or dioctylphenylphosphoric acid (DOPPA) in combination with trioctylphosphine oxide (TOPO) as the extractant system. US patent 4,594,235 describes a process for the extraction of vanadium as  $VO^{2+}$  from acidic sulphate or chloride solutions using DEHPA followed by precipitation stripping using ammonium hydroxide [60]. The resultant vanadyl hydrate is reacted with carbon to produce vanadium carbide.

Solvent extraction behaviour of iron(III) from chloride solutions using DEHPA dissolved in kerosene has been investigated by Biswas and Begum [61] and reported the extraction equilibria as :

---



Later studies by these authors quantitatively examined the kinetics of the extraction and stripping of Fe(III)-HCl-DEHPA system [62,63].

Sato *et al.* [64] have studied the extraction behaviour of iron(III) from sulphuric, hydrochloric and nitric acid solutions using DEHPA as an extractant and found that the rate of extraction of iron(III) from sulphuric acid solutions is relatively slow in comparison with that from hydrochloric acid or nitric acid solution. Further, these authors have also reported that the mechanism of extraction changes from a cation exchange type at lower acidities to a solvation type at higher acidities [65]. Yu *et al.* [66] have studied the extraction behaviour of iron(III) from sulphuric acid solutions using DEHPA and the subsequent stripping using sulphuric acid. The results showed that the mechanism of extraction and stripping efficiency critically depend on the initial acidity of the aqueous phase. Stripping was easier when hydroxyferric complexes were extracted at moderate pH.

Demopoulos *et al.* [67] have studied the extraction of iron(III) from sulphuric acid solutions using mono-2-ethylhexylphosphoric acid (MEHPA) as an extractant and proposed a solvent extraction process for iron removal from zinc process leach liquors. Later studies by Principe and Demopoulos [68] showed that octylphenyl acid phosphate, a mixed extractant consisting of mono and di-octylphenyl phosphoric acids provide better selectivity for iron over zinc.

It is well known that the stripping of iron(III) from the loaded organic phase extracted with DEHPA is difficult since a high concentration of HCl is required. To overcome this difficulty, several investigators have used a mixture of DEHPA-TBP-kerosene system for the extraction of iron(III) and found that this mixture is effective in the stripping of iron(III) and requires less concentration of acid [69,70].

Sahu and Das [69] have studied the extraction and stripping behaviour of iron(III) from concentrated acid chloride solutions using a mixed solvent system consisting of DEHPA and TBP or MIBK and found that TBP was a better synergist as compared to MIBK. The stripping of iron(III) has been found to be initially increases and then decreases with an increase in the aqueous phase acidity. Further, their results highlight that the stripping of iron(III) from DEHPA-MIBK loaded organic solvent system was better than that from the DEHPA-TBP system.

Among dialkylphosphonic acids, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA  $\equiv$  HL) has been utilised for the extraction of titanium(IV) from sulphuric acid solutions by Jayachandran *et al.* [71] and reported a dual extraction behaviour (maximum at low acidity, decrease to a minimum at medium acidity and increases to a second maximum at high acidity). These authors have found quantitative extraction of titanium in the acidity range of 0.1-0.3 mol/dm<sup>3</sup> and 12-14 mol/dm<sup>3</sup> of sulphuric acid. The extracted species has been reported as TiOL<sub>2</sub>·2HL at lower acidities and as Ti(OH)<sub>3</sub>HSO<sub>4</sub>·4HL at higher acidities.

Toyabe *et al.* [72] have reported a solvent extraction based process for the recovery of vanadium and molybdenum from the sulfate leach liquors of spent catalyst containing Fe, Al, Ni and Co. The process involves roasting of the waste catalyst followed by reduction dissolution in sulfuric acid and recovery of aluminium as ammonium aluminium sulfate. Molybdenum was then removed by solvent extraction using N-lauryl(trialkylmethyl)amine in xylene as an extractant followed

---

by a second solvent extraction step for the recovery of vanadium using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) in xylene as an extractant and subsequent stripping using sulphuric acid.

Jayachandran and Dhadke [73] have studied the extraction of iron(III) from dilute sulphate solutions using 2-ethylhexylphosphonic acid mono 2-ethylhexyl ester (EHEHPA) and reported a cation exchange mechanism for the extraction process. The differences in extraction and stripping conditions were utilised to establish a selective separation condition for iron(III) from associated metal ions such as titanium(IV), cobalt(II), chromium(VI), zinc(II) and copper(II).

The extraction of iron(III) from sulphate solutions by mixture of tertiary amine and alkylphosphonic acid mono-2-alkyl ester (EHEHPA) or dialkyl phosphinic acid has been investigated by Yu and Chen [74] and reported synergism in the extraction of iron (III). Further, these authors also reported that the stripping of iron(III) with sulphuric acid from the mixed solvent system requires lower concentration of acid than that required with phosphonic acid or phosphinic acid.

Recently, Deep *et al.* [75] have studied the extraction of titanium(IV) from hydrochloric acid solutions using mono and di-sulphur analogs of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 302 and Cyanex 301), as extractants and reported the quantitative extraction of titanium at low aqueous acidities. Further, these authors also reported the extracted complexes as  $Ti(OH)_2R_2$  (HR  $\equiv$  Cyanex 301 or Cyanex 302)

The distribution equilibrium of vanadium(IV) between solutions of bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA  $\equiv$  HR) dissolved in EXXSOL D80 and weakly acidic sulfate solutions has been investigated by Zhang *et al.* [76]. The stoichiometry and the chemical structure of the extracted species of vanadium(IV)

---























































































































































































































