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

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UNDER THE SUPERVISION OF
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PECIFIC SEPARATION SCIENCE AND TECHNOLOGY GROUP
REGIONAL RESEARCH LABORATORY (CSIR)
THIRUVANANTHAPURAM - 695 019, KERALA, INDIA.

JULY 2002

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

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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
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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.

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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).

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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, 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^3
$FeCl_2$	170-210
$FeCl_3$	40-60
$MgCl_2$	15-16
$MnCl_2$	7-8
$AlCl_3$	3-6
$TiOCl_2$	3-4
$CrCl_3$	3-7
$VOCl_3$	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 1st leach liquor to $FeCl_3$ for sale, TiO_2 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_2 recovery-90%.
Indian Rare Earths Ltd.	Ilmenite 'OR' grade	Benelite process, reduction roasting, 3 stage leaching with regenerated acid, TiO_2 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,

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

(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.

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

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

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

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

$$\mu_1^{o} + RT \ln m_1 + RT \ln \gamma_1 = \mu_2^{o} + RT \ln m_2 + RT \ln \gamma_2. \qquad (4)$$

where μ^{o}, represents the chemical potential of the solute in a hypothetical ideal 1 molal solution, m, the solute concentration in molality and γ, the molal activity coefficient.

The molal distribution coefficient,

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

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

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

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

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

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

$$S.F. = D_1/D_2 \qquad (8)$$

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 –COOH, >P(O)OH, -SO_3H while the latter are those which chelate with metal ions.

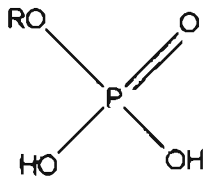
A. Acidic extractants

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).

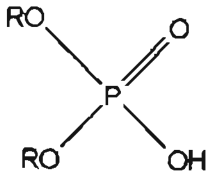
$$M^{n+}{}_{org} + nHA_{org} \Leftrightarrow MA_{n_{org}} + nH^{+}_{aq} \tag{9}$$

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

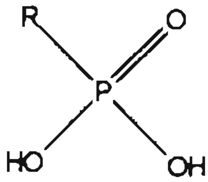
Acidic organophosphorus extractants : This type of extractants include the following:



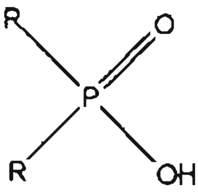
1. Monoalkyl phosphoric acid



2. Dialkylphosphoric acid



3. Monoalkyl phosphonic acid

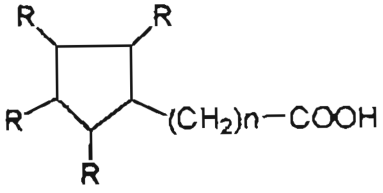


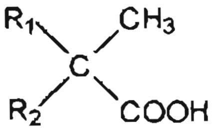
4. Dialkylphosphinic acid

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

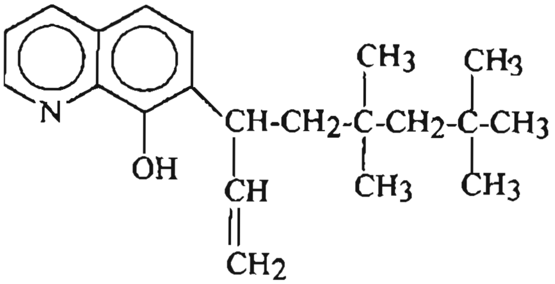

Versatic 911 acid ($R_1, R_2 = C_4$–C_5)
Versatic 10 acid ($R_1, R_2 = C_6$)

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].

$CH_3(CH_2)_3\ CH(C_2H_5)\ C(=NOH)\ CH(OH)\ CH(C_2H_5)\ (CH_2)_3\ CH_3$
5,8-Diethyl-7-hydroxy-6-dodecanone oxime (LIX 63)



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 (RNH_2) [24], secondary (R_2NH) [25], tertiary (R_3N) [26] amines and quaternary ammonium salts (R_4N^+) [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.

$$R_3N_{org} + HX_{aq} \Leftrightarrow R_3N^+HX^-{}_{org} \tag{10}$$

$$R_3N^+HX^-{}_{org} + MY^-{}_{aq} \Leftrightarrow R_3N^+HMY^-{}_{org} + X^-{}_{aq} \tag{11}$$

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.

$$\underset{\text{Monomer}}{R_3N^+HX^-} \Leftrightarrow \underset{\text{Dimer}}{(R_3N^+HX^-)_2} \Leftrightarrow \underset{\text{Polymer}}{(R_3N^+HX^-)_n} \tag{12}$$

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 $CuCl_2^-$, $CuCl_4^{2-}$, $FeCl_4^-$ and $CdCl_4^-$ [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 ($\equiv$P=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 P=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 P=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:

$$\mathrm{TiO}^{2+}{}_{aq} + 2(\mathrm{HX})_{2\,org} \Leftrightarrow \mathrm{TiOX}_2 \cdot 2\mathrm{HX}_{org} + 2\mathrm{H}^{+}{}_{aq} \qquad (13)$$

where $(HX)_2$ 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:

$$\mathrm{TiO}^{2+}{}_{aq} + (\mathrm{HX})_{2\,org} \Leftrightarrow \mathrm{TiOX}_{2\,org} + 2\mathrm{H}^{+}{}_{aq} \qquad (14)$$

The formation of $TiOX_2$ 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 : $D_{Ti(IV)} / D_{Fe(III)} = 60$ and $D_{Ti(IV)} / D_{Fe(II)} = 500$. In a recent study, Biswas *et al.* [44] have reported 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)

$$\mathrm{Ti(OH)_2^{2+}}_{aq} + 2\mathrm{(HX)_2}_{org} \Leftrightarrow \mathrm{TiOX_2H_4}_{org} + 2\mathrm{H^+}_{aq} + \mathrm{H_2O} \qquad (15)$$

$$\mathrm{Ti(OH)_2HSO_4^+}_{aq} + \mathrm{HSO_4^-}_{aq} + \mathrm{mH_2X_2}_{org} \Leftrightarrow \mathrm{Ti(OH)_2(HSO_4)_2 \cdot 2mHX}_{org} \qquad (16)$$

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 ≡ 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^3 HDTP and 3.5 mol/dm^3 sulphuric acid concentrations and $D_{Ti(IV)}/D_{Fe(II)}$ = 7800 at 0.1 mol/dm^3 HDTP and 3.5 mol/dm^3 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 $TiOA_2$.

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 $VO_2X{\cdot}HX$. Further, these authors also examined the extraction behaviour of vanadium(V) using bis-(2-ethylhexyl)monothiophosphoric acid (DEHTPA≡HL) and found that VO_3^- in the aqueous phase was getting reduced to VO^{2+} on contact with DEHTPA phase thereby oxidising the extractant to disulfide. The extracted complex has been found to be VOL_2 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 :

$$VO^{2+}{}_{aq} + 2(HX)_{2org} \Leftrightarrow VO(HX_2)_{2org} + 2H^+{}_{aq} \qquad (17)$$

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 :

$$VO^{2+}_{aq} + (HX)_{2_{org}} \Leftrightarrow VOX_{2_{org}} + 2H^{+}_{aq} \qquad (18)$$

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 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 :

$$Fe^{3+}{}_{aq} + 3(HX)_{2org} \Leftrightarrow FeX_3 \cdot 3HX_{org} + 3H^+{}_{aq} \qquad (19)$$

$$FeCl^{2+}{}_{aq} + 2(HX)_{2org} \Leftrightarrow FeCl(H_2O)X \cdot HX_{org} + 2H^+{}_{aq} \qquad (20)$$

$$FeCl_{2aq}^{+} + 3/2(HX)_{2org} \Leftrightarrow FeCl_2X \cdot 2HX_{org} + H^+{}_{aq} \qquad (21)$$

$$FeCl_{3aq} + HCl_{aq} + 3/2(HX)_{2org} \Leftrightarrow H_2XFeCl_4 \cdot 2HX_{org} \qquad (22)$$

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 ≡ 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^3 and 12-14 mol/dm^3 of sulphuric acid. The extracted species has been reported as $TiOL_2 \cdot 2HL$ at lower acidities and as $Ti(OH)_3HSO_4 \cdot 4HL$ 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 ≡ Cyanex 301 or Cyanex 302)

The distribution equilibrium of vanadium(IV) between solutions of bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA ≡ 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) has been determined on the basis of slope analysis and IR spectra, respectively and a possible structure for the extracted complex, $VOR_2 \cdot 2HR$ has been proposed. In later studies, these authors have developed selective solvent extraction procedure for the recovery of vanadium from spent hydrodesulfurisation catalyst using BTMPPA or bis(2-ethylhexyl)phosphinic acid (PIA-8) or EHEHPA as an extractant [77-78].

Miralles *et al.* [79] have studied the extraction equilibrium of iron(III) in nitrate solutions with BTMPPA (Cyanex 272 ≡ HR) in Isopar-H as an extractant and reported the extracted complexes as FeR_3, $FeR_3 \cdot 3HR$ and $Fe(NO_3) \cdot 3HR$. Further, these authors have also studied the extraction of iron(III) using BTMPPA from different ionic media and reported that the extraction efficiency varies in the order : nitrate > chloride > sulphate, which is the order of complexation of iron(III) with the anion in the aqueous phase. BTMPPA has been proposed as a potential extractant for iron removal in the cobalt processing plant at the Queensland Nickel (QNI), Australia [80].

The extraction behaviour of iron(III) with bis-(2-ethylhexyl)phosphinic acid (PIA-8) and bis-(2-ethylhexyl)phosphoric acid (DEHPA) has been investigated from acidic nitrate solutions by Naik and Dhadke [81] and reported the extracted complexes as $FeR_3 \cdot 3HR$ (HR ≡ PIA-8 or DEHPA). Further, these authors also reported better selectivity and stripping efficiency with PIA-8 than DEHPA. In the later studies, these authors have reported quantitative extraction for iron(III) in the pH range 2 - 4.5 [82].

Sandhibigraha *et al.* [83] investigated the extraction of iron(III) from chloride solutions using DEHPA, EHEHPA, BTMPPA and their mixtures and reported synergistic enhancement in the extraction of iron(III) using binary mixtures of the extractants. Results showed that BTMPPA was a better synergist compared to EHEHPA or DEHPA. Later studies by these authors examined the stripping behaviour of iron(III) using H_2SO_4 and HCl from the loaded DEHPA, EHEHPA and BTMPPA phases and found that a higher acid concentration is required for the stripping of iron(III) from loaded DEHPA phase when compared to EHEHPA or BTMPPA [84]. Better stripping efficiencies for iron(III) could be attained using lower acid concentrations when a mixed solvent system consisting of 60% DEHPA and 40% EHEHPA has been used for the extraction.

Carboxylic acids: Monocarboxylic acids such as versatic 10 acid has been well studied for the extraction of iron(III) from acidic solutions. A distinct advantage of carboxylic acid extractants has been their acidity and thermal stability to allow removal of iron(III) at elevated temperatures by direct hydrolysis with water or dilute acids in the hydrolytic and precipitation stripping processes [85]. Monhemius and co-workers [86,87] developed hydrolytic stripping by precipitating iron directly as hematite by treating the loaded organic phase containing Fe(III) with water in an autoclave at 423 - 473K. Konishi *et al.* [88,89] have reported the detailed studies on the hydrolysis of iron(III) carboxylate solutions for preparation of high purity iron oxide powders. Stefanokis and Monhemius [90] have studied the extraction of iron(III) from nitrate solutions using versatic 10 acid and reported that versatic acid can be used as a selective extractant for iron removal in the production of smelter grade alumina. Further, a chemically based computer model has been developed for the iron(III) extraction from aluminium nitrate solutions using versatic acid and compared with the experimental results [91]. In later studies, Monhemius *et al.* [92] showed that pigment grade iron oxides can be prepared from iron(III) carboxylate solutions obtained from the extraction and recovery of iron(III) from zinc process solutions using versatic acid.

B. *Extraction by solvating extractants*

Among solvating type of extractants, neutral organophosphorus extractants such as tributylphosphate (TBP) and trialkylphosphine oxides have been extensively used for the extraction of titanium(IV), vanadium(V) and iron(III) from acidic aqueous solutions.

Allal and co-workers [93] have investigated the extraction behaviour of tetravalent titanium from hydrochloric acid and calcium chloride solutions using tributylphosphate (TBP) and trioctylphosphine oxide (TOPO). The results showed that when mixed together, TBP and decanol are very suitable for the extraction of titanium since the kinetics of the extraction reaction is very fast and an extraction yield as high as 95% can be obtained from 10 mol/dm^3 HCl. The extraction equilibrium of titanium has been described as:

$$Ti^{4+}_{aq} + 4Cl^-_{aq} + 2L_{org} \Leftrightarrow TiCl_4 \cdot 2L_{org} \qquad (23)$$

where L = TBP or TOPO. Further, an equilibrium constant value of 0.72 has been reported for TBP extraction and 2.95 for TOPO. These authors also studied the influence of temperature on the extraction of titanium using TOPO and found that an increase in temperature leads to a decrease in extraction efficiency and the extraction process was found to be exothermic.

The extraction of titanium from sulphuric acid solutions using TBP in CCl_4 as an extractant has been investigated by Tedesco and Rumi [94] and reported the extracted complexes as $TiOSO_4 \cdot TBP$ and $TiOSO_4 \cdot 2TBP$. These authors have also reported the co-extraction of H_2SO_4 and identified the organic phase species as $H_2SO_4 \cdot TBP$ and $H_2SO_4 \cdot 2TBP$.

Sheng *et al.* [95] have used TBP for the separation of titanium from aluminium and iron in the product stream of high temperature chlorination of fly ash by HiChlor process. Titanium has been selectively extracted using 30 vol. % TBP with 8 vol. % isodecanol as modifier at hydrochloric acid concentrations > 9 mol/dm^3. Further, these authors also stated that the addition of $AlCl_3$ as salting out agent enhances the extraction efficiency of titanium. Stripping of titanium from the loaded organic phase has been achieved using 1 mol/dm^3 HCl.

Sulphuric acid co-extraction by TOPO has also been reported by Sato *et al.* [96] and identified the extracted species as $H_2SO_4 \cdot TOPO$ and $H_2SO_4 \cdot 2TOPO$. In the later studies, these researchers demonstrated that sulphuric acid present in the organic phase as the species $H_2SO_4 \cdot TOPO$ is displaced by titanium complex thereby resulting in the extraction of titanium as the complex, $TiO(HSO_4)_2 \cdot 2TOPO$ [97]. From IR spectral studies, these authors found that titanium extracted into TOPO solution is bonded to the phosphoryl oxygen suggesting the extracted species as $[Ti(OH)(SO_4)(HSO_4)(TOPO)_2]$, in an octahedral arrangement. Sato *et al.* [97] have also studied the solvent extraction behaviour of titanium from hydrochloric acid solutions using TOPO in benzene as an extractant and found the extracted complex as $TiCl_4 \cdot 2TOPO$.

A solvent extraction process for the preparation of titanium dioxide pigment from sulphuric acid leach solutions of ilmenite has been described by Watanabe [98]. Titanium was extracted from the leach solutions using 20% trioctylphosphine oxide (TOPO) and 5% dioctylacetamide in a hydrocarbon diluent as an extractant and the strip liquor was subjected to hydrolysis to produce TiO_2. US Patent 5,061,460 [99] describes a process for the extraction and recovery of titanium from a sulphuric acid solution containing multivalent metal ions using a mixed solvent system consisting of TOPO and a primary amine, Primene JMT. Denecker *et al.* [100], Cordelet *et al.* [101] and Fitoussi *et al.* [102] have proposed dibutylbutyl phosphonate (DBBP) as an extractant for titanium from sulphate leach liquors of ilmenite ore. Titanium was recovered from the loaded organic phase using sulphuric acid as the stripping agent.

Shibata and co-workers [103] have investigated the extraction of titanium and other metal ions such as Fe(III), Fe(II), Zn(II), Cu(II) and Co(II) from hydrochloric acid and sulphuric acid solutions using a series of trialkylphosphine oxides such as Cyanex 921 (trioctylphosphine oxide), Cyanex 923 (a mixture of four trialkylphosphine oxides) and Cyanex 925 (di-(2,4,4-trimethylpentyl) octylphosphine oxide) and reported that extraction of titanium increases with increasing hydrochloric acid concentration, reaching 99 % at 9 mol/dm^3 HCl with simultaneous extraction of other metal ions. On the other hand, it has been reported that the extraction of titanium from sulphuric acid solutions is selective over wide ranges of pH and co-extraction of Fe(III) and Fe(II) is less than 20 %, while Zn(II), Cu(II) and Co(II) are not extracted. In the later studies, these authors have developed a computer program for the simulation of counter current multistage extraction process for the recovery of titanium using Cyanex 923 as an extractant [104].

Sole [50] has compared the degree of extraction of titanium by TOPO and Cyanex 923 as a function of time and reported that the extraction of titanium requires an equilibration time of 15-20 min. for TOPO system and 10-15 min. for Cyanex 923 system. Further, it has also been reported that the loading capacity of titanium by Cyanex 923 is substantially higher than that of TOPO and poor phase disengagement with Cyanex 923. In the later studies, Sole and co-workers [105] have reported a solvent extraction process for the recovery of titanium from sulphuric acid leach liquors of titaniferrous magnetite ore. This process involves five stages of counter current extraction with a feed solution containing approximately 50 g/dm^3 iron, 5 g/dm^3 titanium, 1 g/dm^3 vanadium and 80 g/dm^3 sulphuric acid using an organic phase comprising 10 vol. % TOPO in Kerosol 200 as an extractant (org. : aq. ratio = 2.0). The loaded organic phase was then stripped in seven stages using 100 g/dm^3 sulphuric acid with org:aq ratio of unity. Under these conditions an average of 80 % titanium was recovered from the leach liquor. Negligible amounts of vanadium and aluminium are extracted by this system. On the other hand, 11 % of iron was found to be co-extracted. Gupta *et al.* [106] have studied the extraction behaviour of 3d transition metals such as Ti(IV), V(IV), Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) from hydrochloric acid solutions using Cyanex 923 and reported that mutual separation among some metal ions is possible by utilising the difference in the extraction and stripping behaviour.

Among neutral organophosphorus extractants, tributylphosphate (TBP) has been widely studied for the extraction of vanadium [107-110]. Tedesco and Rumi [107] investigated the extraction of vanadium(V) from hydrochloric acid solutions using TBP in carbon tetrachloride as an extractant and reported the extraction equilibrium as:

$$VO_2Cl_{aq} + nTBP_{org} \Leftrightarrow VO_2Cl \cdot nTBP_{org} \qquad (24)$$

where n = 2 or 3. Further, these authors have also studied the reduction of vanadium(V) to vanadium(IV) in hydrochloric acid solutions and reported that the extend of reduction depends on the acid concentration and time.

Komasawa *et al.* [108] have studied the extraction behaviour of vanadium(IV) from hydrochloric acid (2-5 mol/dm^3) solutions using TBP in xylene as an extractant and reported the extracted complexes as $VOCl_2 \cdot (HCl) \cdot 4TBP$ and $VOCl_2 \cdot 4TBP$. The equilibrium constants of the extracted complexes have been reported as 1.41×10^{-5} and 9.19×10^{-5}, respectively. Sato [109] and Sato *et al.* [110] have studied the extraction of vanadium(IV) from dilute hydrochloric acid solutions using TBP or TOPO as an extractant and reported the extracted complexes as $VOCl \cdot nL$ where L ≡ TBP/TOPO and n = 1 or 2.

A simple and rapid method for extracting vanadium(V), niobium(V) and tantalum(V) from halide media using triphenylphosphine oxide (TPPO) in xylene as an extractant has been reported by Kakade *et al.* [111]. Further, these authors have reported the extracted species as $VOX_3 \cdot 2TPPO$, where X = Cl^- or Br^-. Gaudh and

Shinde [112] have also reported a separation procedure for vanadium(V) from Nb and Ta using tris(2-ethylhexyl)phosphate in toluene as an extractant.

Singh *et al.* [113] have studied the extraction of vanadium(IV) from hydrochloric acid solutions using triisoamylphosphate (TAP) in carbon tetrachloride as an extractant and reported the extracted species as $VOCl_2.TAP$ and $VOCl_2.2TAP$ at 3.6 mol/dm^3 HCl and 7.0 mol/dm^3 HCl, respectively.

Specker and Cremer [114] were the first to study the extraction of iron(III) using 1-5 % TBP in benzene from hydrochloric acid solutions and they reported the extracted complexes as $FeCl_3 \cdot 3TBP$ at 4 mol/dm^3 HCl and $HFeCl_4 \cdot 2TBP$ at 6-9 mol/dm^3 HCl solutions. Sahu and Das [115] studied the extraction of iron from concentrated acid chloride solutions (~100g /dm^3 Fe(III)) using TBP and found that the extraction of iron(III) proceeds by the mechanism:

$$FeCl_{3aq} + HCl_{aq} + 2TBP_{org} \Leftrightarrow HFeCl_4 \cdot 2TBP_{org} \qquad (25)$$

Further, these authors also reported that the use of TBP-DEHPA mixed-solvent system, resulted in a synergistic enhancement in the extraction of iron(III). Reddy and Bhaskara Sarma [116] studied the extraction of iron(III) at macro level concentrations using mixtures of tributylphosphate and methylisobutyl ketone and reported that the mixed solvent system could provide better phase separation characteristics than when used individually for the extraction of iron(III).

Thornhill *et al.* [117] have described a solvent extraction method for the separation of iron(III) from hydrochloric acid solutions containing Fe, Co, Cu and Ni obtained from nickel matte leaching using 4 vol.% TBP as the extractant.

The selective recoveries of titanium(IV) and iron(III) from the synthetic hydrochloric acid leach liquors of ilmenite ore (1.8-11 mol/dm^3 HCl) containing

0.25-0.57 mol/dm^3 titanium and 0.27-0.29 mol/dm^3 iron have been investigated by Narita *et al.* [118] using TBP in benzene as an extractant. Iron was found to be extracted into TBP phase over a wide range of hydrochloric acid concentration studied and the extraction was considerably accelerated by the salting out effect of the co-existing titanium. On the other hand, titanium was found to be not extracted at hydrochloric acid concentrations lower than 6 mol/dm^3. However, it has been observed that titanium was extracted as $TiCl_4 \cdot 3TBP$ at a concentration range of chloride ion higher than 7 mol/dm^3. Further, these authors have stated that iron and titanium can be separated by controlling the aqueous phase acidity of the leach liquors.

Chen *et al.* [119] have reported a process for the manufacture of high purity TiO_2. This process involves leaching of ilmenite ore with 31% hydrochloric acid and phosphoric acid at 363 K to obtain a crude HCl-Ti liquor and the feed adjustment to maintain a free acid concentration > 9 mol/dm^3, filtration and solvent extraction of iron using TBP in benzene (org. : aq. ratio = 1:1.3). The loaded organic phase was then washed with 0.5 mol/dm^3 hydrochloric acid and subsequently stripped with 4 mol/dm^3 hydrochloric acid (org./aq. ratio = 1.3-2.1) to obtain a refined HCl-Ti liquor.

A process for the recovery of hydrochloric acid from waste steel pickle liquors by solvent extraction removal of iron using a mixed ligand system consisting of tributylphosphate and a tertiary amine as the extracting solvent has been described by Watanabe and Nishimura [120]. Iron removal from nickel/cobalt process liquors at Falconbridge Matte leach process, Norway has been carried out by solvent extraction of iron(III) using tributylphosphate as an extractant [121]. Copper and cobalt present in the nickel leach liquor is removed by extraction using triisooctyl amine in subsequent stages. Tributylphosphate has also been used for iron removal

Duyvestyn *et al.* [123] have described a solvent extraction process for the production of titanium dioxide pigment from hydrochloric acid leach solutions of ilmenite. In this process, the leachate was reduced and cooled for partial removal of iron as $FeCl_2$ crystals. Iron(III) and titanium(IV) were then co-extracted using Cyanex 923 (a mixture of four trialkylphosphine oxides) as an extractant followed by a second solvent extraction step to recover iron(III) using trioctyl amine (Alamine 336) as the solvent. The raffinate containing titanium(IV) was hydrolysed by water addition or spray hydrolysis into pigment grade TiO_2. Iron chloride was then converted into iron oxide and the regenerated hydrochloric acid was recycled into the leaching stage.

The extraction behaviour of iron(III) from perchlorate solutions using trioctylphosphine oxide (TOPO) has been studied by Matsuyama *et al.* [124] and the extracted species was identified as $Fe(ClO_4)_3{\cdot}(TOPO)_4$. Further, these authors have studied the kinetics of the extraction process and found that the addition of chloride ion to the system enhances the extraction rate due to the formation of $FeCl^{2+}$. Sekine *et al.* [125] have also pointed out that in the $HClO_4$-TOPO system iron(III) is extracted as hydrolysed species $FeOH^{2+}$ and the extraction rate is accelerated in the presence of anions such as chloride, bromide and nitrate.

Biswas *et al.* [126] have described a two step solvent extraction process for the recovery of iron(III) and titanium(IV) from the hydrofluoric acid leach solutions of ilmenite ore. Iron and titanium in the fluoride leach solution were precipitated, oxidised and dissolved in hydrochloric acid followed by a two stage extraction of iron(III) using MIBK. Subsequently, titanium(IV) was extracted using DEHPA at pH ~ 0 and recovered from the loaded organic phase using sodium carbonate as the strippant.

A solvent extraction process have been described for the extraction of iron from ilmenite leach liquors by Yamamura and co-workers [127]. The leach liquor is oxidised and subjected to three stages of extraction of iron using methylisobutyl ketone (MIBK) in benzene as an extractant. Iron was then recovered from the organic phase by stripping with water in four stages

US patent 5,489,423 by Mikami and Iyatomi [128] describes another process for the recovery of acid from waste sulphate liquors of ilmenite processing industry. The waste acid is oxidised with chlorine to convert ferrous iron to ferric iron followed by extraction of iron(III) using MIBK as the extractant. Titanium was then extracted in the second step of solvent extraction using DEHPA as the extractant. Metal oxides were prepared from the strip liquors by calcination and the acid was recovered from the raffinate. Matsumoto and Hayashi [129] have also reported a process for the recovery of sulphuric acid from waste sulphate liquors of titanium dioxide industry by electrolytic oxidation of the waste liquor followed by solvent extraction and separation of iron(III) using thenoyltrifluoroacetone (HTTA) in benzene as an extractant.

C. Extraction by anion exchangers

Very few reports are available on the solvent extraction of titanium(IV) using anion exhangers such as amines. High molecular weight amines have been used for the extraction of titanium(IV) at low aqueous acidities [130,131]. However, their utility was restricted due to the problem of emulsion formation and interference from co-existing metal ions. Majority of the reports on the extraction of titanium(IV) using amines have focussed on the analytical applications.

Recently, Lozano and Juan [132] have reported a solvent extraction process for the recovery of vanadium from spent sulphuric acid catalyst using Primene 81R in kerosene as an extractant. These authors have reported the extraction mechanism in the pH range 2.0-2.5 as :

$$5RNH_{2_{org}} + 5H^{+}{}_{aq} + HV_{10}O_{28}{}^{5-}{}_{aq} \Leftrightarrow [(RNH_3)_5{}^{+}.(HV_{10}O_{28})^{5-}]_{org} \qquad (26)$$

Nekovar and Schrotterova [133] have studied the extraction of vanadium(V) from acidic sulphate solutions using Primene JMT and found that extraction efficiency was higher in the pH range in which polymeric anionic species of vanadium(V) are present.

Tertiary amines were found to be better extractants for vanadium in the pH range 1.5 to 4.0 [134]. On the other hand, quaternary amines were found to be effective extractants for vanadium in the pH range 1.5 to 12 reaching optimum values between pH 6-9 [135]. Tricaprylmethyl ammonium chloride (Aliquat 336), a liquid anion exchanger has been used for the commercial recovery of vanadium and chromium from alkaline leach liquors obtained from titaniferrous magnetite ore [136]. Separation is based on preferential extraction of vanadium at pH 9.0 and chromium at pH 13.5. Chromium is first extracted and stripped with NaCl. The raffinate is then used for vanadium extraction using Aliquat 336 followed by stripping with NH_4Cl solution.

Alamine 336 has been used commercially for the recovery of vanadium from uranium circuits involving sulphuric acid leach liquors of the carnotite ores [137]. This separation method involves simultaneous extraction of uranium and vanadium at pH 2.0 followed by selective stripping of vanadium by H_2SO_4 and that of uranium by 1.0 mol/dm^3 Na_2CO_3.

Recently, Tangri and co-workers [138] have reported a solvent extraction process for the recovery of high purity V_2O_5 (> 99.9%) from spent catalyst obtained from the manufacture of sulphuric acid by contact process using Alamine 336 as an extractant. These authors have reported the extraction mechanism of vanadium at pH 2 to 6.5 as:

$$4R_3NHHSO_{4_{org}} + H_2V_{10}O_{28}{}^{4-}{}_{aq} \Leftrightarrow (R_3NH)_4.H_2V_{10}O_{28_{org}} + 4HSO_4^-{}_{aq} \quad (27)$$

Hirai and Komasawa [139] studied the extraction of vanadium(V) from hydrochloric acid solutions using tri-n-octylmethyl ammonium chloride as an extractant and reported the extracted species as $VO_2Cl{\cdot}2R$ and $(VO_2)_2Cl_2{\cdot}2R$ where R denotes monomeric species of the extractant in benzene diluent. Further, these authors have also reported that the extracted species as $VO_2Cl{\cdot}R$ and $VO_2Cl{\cdot}2R$ when chloroform is used as a diluent. Commercially available amines such as ADOGEN 364 [140], Amberlite LA-2 [141] and ADOGEN 464 [140] have also been used for the extraction of vanadium.

Brown *et al.* [142] have described a process for the recovery of vanadium from acidic sulphate solutions containing iron by solvent extraction using a mixed solvent system consisting of tricapryl amine and tributylphosphate. The extraction stage is preceded by an oxidation step using hydrogen peroxide to convert tetravalent vanadium to pentavalent state.

Hubred *et al.* [143] have developed a separation procedure for vanadium(V) from cobalt, molybdenum, nickel and tungsten in which a quaternary ammonium salt is used to co-extract V(V), Mo(VI) and W(VI) followed by a second step solvent extraction using oxime extractants to recover Mo(VI) and W(VI) from the strip solution.

Lakshmanan *et al* [144] have described a process for the recovery of vanadium from fly ash. The process includes steps for the separation of carbon, followed by alkaline pressure leaching of fly ash and solvent extraction for the recovery of vanadium from the leach liquor using trioctylmethylammonium chloride (Aliquat 336) as an extractant.

Amines or amine salts have been studied by several investigators for the extraction of iron(III) from acid solutions Alguacil and Amer [145] studied the extraction of iron(III) from aqueous sulphate solutions using a primary amine, Primene 81R and found that extraction occurred by an adduct formation reaction between Primene 81R sulphate and the $(Fe(OH)SO_4)_2$ species in the aqueous phase. On the basis of experimental data and spectral studies, a dimeric structure was suggested for the extracted complex, $3(RNH_3)_2SO_4 \cdot (Fe(OH)SO_4)_2$ Later studies by these authors showed that toluene or benzene is the most suitable diluent for the Primene 81R system [146].

Chen *et al.* [147] have studied the extraction of iron(III) from sulphate solutions using mixed solvent systems and found that the mixtures of primary amines and TBP / DEHPA / MEHPA / trialkylphosphine oxides as extractant systems enabled easy stripping of iron(III) with sulphuric acid. Further, these authors showed that a mixture of primary amine and TBP when used as the extractant, gave better separation for iron from aluminium present in the sulfuric acid leach liquors of bauxite. Studies by Mahi *et al.* [148] showed that Alamine 336 is a selective extractant for iron removal from alumina process chloride liquors.

A process for the removal of iron from zinc process sulphate liquors by solvent extraction using a primary amine, Primene JMT as an extractant has been described by Juan and Perales [149]. Iron was recovered from the organic phase by precipitation stripping using ammonium sulphate. Wu and Yu [150] have reported that tertiary amines can be used as extractants for the recovery and removal of iron(III) from zinc sulphate solutions. Kerney [151] have studied the extraction and stripping of iron(III) from zinc process leach liquors using a mixture of Primene JMT and EHEHPA as the extractant and found better extraction and stripping efficiencies.

Chapter 2

Studies on the extraction and separation of iron(III) from titania waste chloride liquors using neutral solvating extractants

Part A

Liquid-liquid extraction separation of iron(III) from titania wastes using TBP-MIBK mixed solvent system

A survey of literature showed that acidic organophosphorus extractants such as di-(2-ethylhexyl)phosphoric acid (DEHPA) and neutral solvating extractants such as tributylphosphate (TBP) and methylisobutyl ketone (MIBK) have been widely used for the extraction of iron(III) from acidic chloride solutions. The use of acidic organophosphorus extractants for the extraction of iron(III) have some disadvantages like slow kinetics and requires high mineral acid concentration for the recovery of iron(III) from the loaded organic phase. On the other hand, neutral organophosphorus extractants such as tributylphosphate (TBP), when used for the extraction of iron(III) resulted in third phase formation and poor phase disengagement [152]. Hence a modifier has to be introduced in the organic phase. Very high concentration of HCl (> 6 mol/dm^3) is required to achieve complete extraction of iron(III) with MIBK [153]. In order to overcome the above limitations, in the present study, a mixed solvent system consisting of TBP and MIBK has been explored for the selective extraction of iron(III) from the waste chloride liquors of titanium minerals processing industry and the results are presented in this chapter.

2.1 Experimental

Reagents

Tributylphosphate and methylisobutyl ketone, supplied by Aldrich Chemical Company, USA were used without further purification. Distilled kerosene (boiling range 160-200°C, composed of aliphatic hydrocarbons) was used as a diluent. All other reagents and chemicals used were of analytical reagent grade.

Iron(III) stock solution was prepared by dissolving 325 g of $FeCl_3.H_2O$ in concentrated hydrochloric acid and diluted to 1 dm^3 with distilled water. Titanium(IV) solutions were prepared from $TiCl_4$ (99%, Spectrochem, India) solution by diluting to the required concentration with hydrochloric acid. Vanadium(V) stock solution was prepared by dissolving 5.85 g of ammonium monovanadate in hydrochloric acid and diluting to 1 dm^3 with distilled water. Stock solutions of magnesium(II), aluminium(III), chromium(III) and manganese(II) were prepared by dissolving 12.32 g of $MgSO_4.7H_2O$, 18.75 g of $Al(NO_3)_3.9H_2O$, 25 g of $CrK(SO_4)_2.12H_2O$ and 8.45 g of $MnSO_4.H_2O$ in 1 dm^3 each of distilled water, respectively. Suitably diluted stock solutions of the above mentioned metal ions were used in the extraction and analytical studies.

Apparatus

A Hitachi (Japan) 220 double beam microprocessor controlled spectrophotometer was used for measuring absorbances. A GBC (Australia) 902 atomic absorption spectrometer was used for analysis of metal ions in multicomponent mixtures. An Orion (USA) 720A Ion Analyser was used for the pH measurements.

Liquid-liquid extraction procedure

Solvent extraction and stripping experiments were carried out by shaking required volumes of aqueous and organic phases in a glass stoppered vial using a mechanical shaker at 303 ± 1K. Preliminary experiments showed that the extraction equilibrium was attained within couple of minutes. After phase separation, the concentration of a particular metal ion remaining in the aqueous phase was determined by standard analytical procedures. The concentration of metal ion in the organic phase was then obtained by material balance. The distribution ratio, D, was taken as the ratio of the concentration of metal ion in the organic phase to that present in the aqueous phase. All the extraction experiments were performed in duplicate and the general agreement in the distribution ratio values obtained was within ± 5%. The batch type counter current extraction and stripping studies were performed at a laboratory scale using separatory funnels of suitable volume.

Analytical procedure

Iron(III) at macro level concentrations was analysed volumetrically by the standard $SnCl_2$ reduction–$K_2Cr_2O_7$ titration method [154]. Iron(III) in the analyte is reduced to iron(II) by the addition of 5% $SnCl_2$ solution at 90°C. The excess $SnCl_2$ was removed by adding 10% $HgCl_2$ and the ferrous iron was estimated by titrating with standard $K_2Cr_2O_7$ (0.1 N) solution using diphenylamine-4-sulphonic acid (0.01% in con.H_2SO_4) as an indicator. At low concentrations, Iron(III) was assayed spectrophotometrically by 1,10-phenanthroline method [155]. Iron(III) in the aqueous phase sample was reduced to iron(II) using 10% hydroxylammonium chloride and complexed with 1,10-phenanthroline (0.25%) in sodium acetate buffer (0.2 mol/dm^3) solutions of pH=5.0. The absorbances were recorded at 515 nm and the metal concentration was computed from the calibration plot.

Both titanium(IV) and vanadium(V) were determined spectrophotometrically as their H_2O_2 complexes in 1.0 mol/dm^3 sulphuric acid solutions at 410 and 540 nm, respectively [156,157]. The metal concentrations in the aqueous phase were then computed *from the respective calibration graphs.*

Chromium(III) was analysed spectrophotometrically as the chromium(VI) complex with diphenylcarbazide in 0.1 mol/dm^3 H_2SO_4 solutions after oxidation using potassium permanganate [158]. The absorbances were recorded at 540 nm and the metal concentrations were then computed from the calibration graph.

The determination of aluminium(III) was carried out spectrophotometrically using Eriochrome Cyanine R indicator (0.1%) as the complexing agent in dilute sodium acetate buffer solutions of pH = 6.1 [159]. Absorbances were measured at 535 nm after allowing 30 min. for colour development. The metal concentration was then read from the calibration plot.

Magnesium(II) was determined colorimetrically as its complex with Eriochrome black T indicator (0.1% in methanol) in ammonia buffer solutions of pH = 10.1 [160]. Absorbances were recorded at 520 nm and the corresponding metal concentrations were calculated from the calibration graph.

Analysis of manganese(II) was carried out volumetrically by titration with EDTA after addition of 0.5 g of hydroxylammonium chloride to prevent oxidation [161]. EDTA solution was standardised by titration with $ZnSO_4$ in ammonia buffer solutions of pH = 10 using Eriochrome black T in KCl as the indicator.

All the metal ions present in multicomponent mixtures were analysed using atomic absorption spectroscopy.

2.2 Results and Discussion

2.2.1 *Extraction equilibrium*

Iron(III) extraction with TBP, MIBK and TBP + MIBK mixtures

The extraction of iron(III) from solutions containing 1 mol/dm^3 iron(III) chloride and 2 mol/dm^3 hydrochloric acid using TBP, MIBK and their mixtures has been investigated and the results are shown in Table 2.1. Iron(III) extraction increases with increasing TBP concentration in kerosene in the organic phase. Here, isodecanol (20 vol. %) has been used as a modifier in the organic phase when TBP alone was used as an extractant whereas the mixed solvent system does not contain a modifier. On the other hand, it was found that the extraction of iron(III) with MIBK alone was negligible upto 40 vol.% concentration. However, with the mixtures of MIBK + TBP, a small synergistic enhancement in the extraction of iron(III) has been observed. It is clear from these experiments that a mixed solvent system (70 vol.% TBP and 30 vol.% MIBK) can extract iron(III) chloride more effectively from lower acid concentrations as compared to TBP or MIBK alone. Further, the phase disengagement is also fast (within couple of minutes) as compared to individual extractants (15-20 min). Hence a solvent mixture consisting of 70 vol.% TBP and 30 vol.% MIBK was used in the subsequent experiments for the optimisation of extraction and stripping conditions. The log-log plots for TBP and TBP + MIBK mixtures are straight lines with slope values of 1.9, indicating the association of 2 moles of TBP in the extracted complexes (Fig. 2.1).

Table 2.1 Iron(III) extraction with TBP, MIBK and TBP + MIBK mixtures. [$FeCl_3$] = 1.0 mol/dm^3, [HCl] = 2.0 mol/dm^3.

Concentration of solvent (volume %)		Distribution ratio for iron(III) extraction (D)
TBP	60	0.72
	70	0.88
	80	1.07
	90	1.40
	100	1.73
MIBK.	10	negligible
	20	negligible
	30	negligible
	40	negligible
TBP:MIBK (mixture)	70:30	1.18
	75:25	1.33
	80:20	1.40
	85:15	1.56
	90:10	1.73

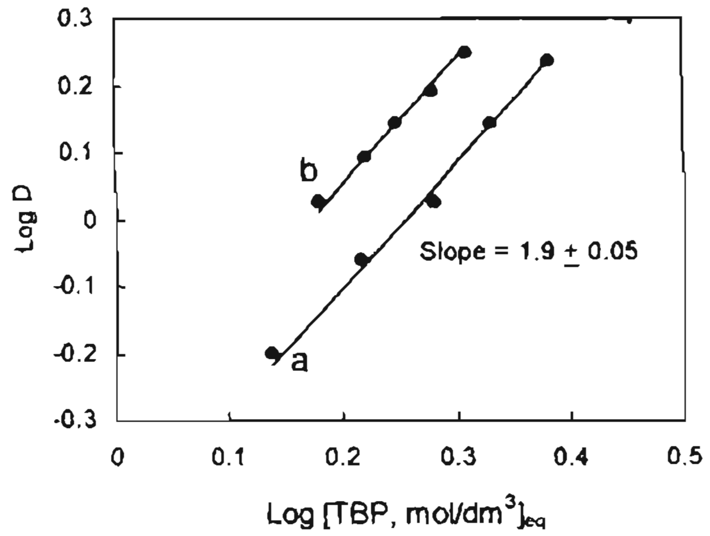


Figure 2.1 Effect of TBP concentration on the extraction of iron(III). (a) TBP-isodecanol-kerosene system (b) TBP + MIBK system. Aq. phase : $[FeCl_3]$ = 1 mol/dm^3, [HCl] = 2 mol/dm^3.

Effect of hydrochloric acid concentration

The extraction behaviour of iron(III) (1 mol/dm^3), magnesium(II) (0.05 mol/dm^3), aluminium(III) (0.03 mol/dm^3), titanium(IV) (0.02 mol/dm^3), vanadium(V) (0.01 mol/dm^3), chromium(III) (0.002 mol/dm^3) and manganese(II) (0.03 mol/dm^3) present in the waste chloride liquors of titanium minerals processing industry has been investigated as a function of hydrochloric acid concentration (0.5 to 3.0 mol/dm^3 HCl) using a mixed-solvent system consisting of 70 vol. % TBP and 30 vol. % MIBK. The extraction of iron(III) was found to increase with the increase of hydrochloric acid concentration in the aqueous phase. On the other hand, magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III) and manganese(II) were found to be not extracted into the organic phase under the present experimental conditions.

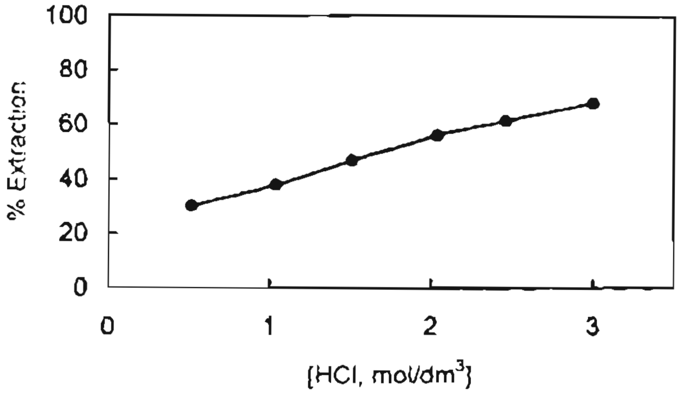


Figure. 2.2 Extraction behaviour of iron(III) (1 mol/dm^3) using 70 vol.% TBP and 30 vol.% MIBK mixed solvent system from hydrochloric acid solutions.

The effect of hydrogen (1.0 to 4.0 mol/dm^3) and chloride (4.0 to 6.0 mol/dm^3) ion concentrations on the extraction of iron(III) chloride (1 mol/dm^3) has been investigated from HCl + $CaCl_2$ mixtures using a mixed-solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK and the results are depicted in Fig. 2.3. The log [Cl$^-$] versus log D plot is a straight line with a slope of 3.9, indicating the association of four chloride ions with iron in the extracted complex. The log [H$^+$] versus log D plot gave a straight line with a slope of unity indicating the extracted species as $HFeCl_4$.

Based on the preceding studies, the extraction equilibrium for iron(III) using a mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK can be represented as :

$$Fe^{3+}{}_{aq} + H^{+}{}_{aq} + 4Cl^{-}{}_{aq} + 2S_{org} \rightleftharpoons HFeCl_4 \cdot 2S_{org} \qquad (28)$$

where S represents TBP. The above extraction equilibrium is in good agreement with the earlier reports by Sahu and Das [115] and Narita *et al.* [118]. On the other hand,

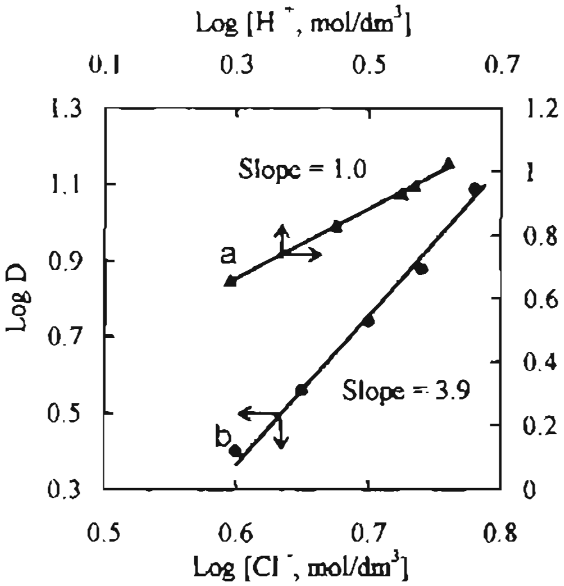


Figure 2.3 (a) Effect of hydrogen ion concentration on the extraction of iron(III); [$FeCl_3$] = 1 mol/dm^3, [Cl^-] = 5 mol/dm^3. (b) Effect of chloride ion concentration on the extraction of iron(III); [$FeCl_3$] = 1 mol/dm^3, [H^+] = 2 mol/dm^3.

Reddy and Bhaskara Sarma [116] have reported the extracted complex as $HFeCl_4\cdot3TBP$ for the iron(III) extraction from HCl solutions using TBP.

2.2.2 *Loading capacity of the mixed solvent system*

Aliquot of 10 cm^3 of the mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK was repeatedly contacted at 303 $\pm$ 1 K for 10 min. with equal volumes of aqueous phase containing 55.85 g/dm^3 iron(III) in 2.0 mol/dm^3 hydrochloric acid. The aqueous phases were analysed for iron(III) after each stage of extraction and the amount of iron(III) transferred into the organic phase was determined. The cumulative concentration of iron in the organic phase after each stage of contact was determined and plotted against number of stages of contact (Fig. 2.4). The loading capacity of the mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK for the extraction of iron(III) was calculated and found to be 48 g of Fe(III)/dm^3 of the solvent.

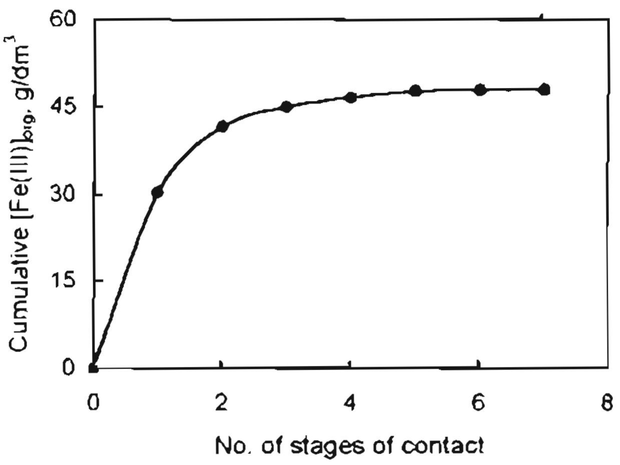


Figure 2.4 Loading capacity of 70 vol.% TBP + 30 vol.% MIBK solvent system for iron(III) extraction. [HCl] = 2.0 mol/dm^3.

2.2.3 *Recycling capacity of the mixed solvent system*

Experiments have also been performed to determine the recycling capacity of the mixed solvent system, first by loading with iron(III) and then stripping with deionised water of pH=2.0. The stripped organic phase was then used for the extraction. The results revealed practically insignificant change in the extraction efficiency of mixed solvent system upto ten cycles of extraction.

2.2.4 *Extraction and Stripping isotherms*

A solvent mixture consisting of 70 vol.% TBP and 30 vol.% MIBK was used to generate an extraction isotherm for iron(III) from 2 mol/dm^3 hydrochloric acid solutions. The McCabe-Thiele plot for a feed solution containing 55.85 g/dm^3 iron(III) showed that almost quantitative extraction of iron was possible in two counter current stages at an aq. : org. ratio of 1:2 (Fig. 2.5). The loaded organic phases obtained from these experiments were used to carry out stripping studies

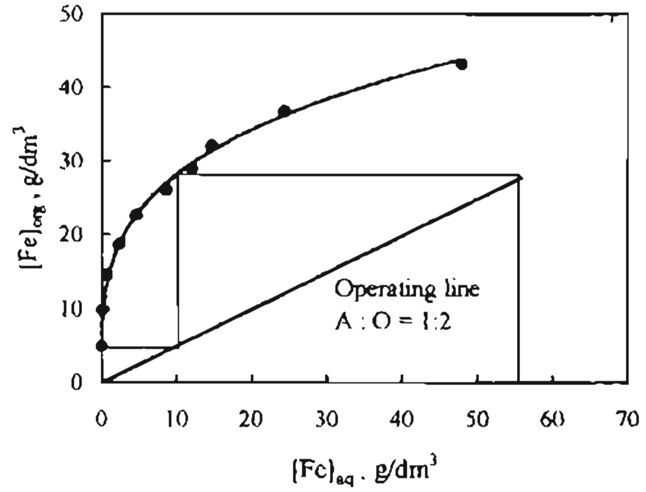


Figure 2.5 McCabe-Thiele plot for iron(III) extraction. $[Fe^{3+}]$ = 55.85 g/dm^3, [HCl] = 2 mol/dm^3.

using distilled water of pH = 2.0. McCabe-Thiele plot for a loaded organic phase containing 27.92 g/dm^3 iron(III) showed that quantitative stripping of iron is possible in three counter current stages with an org. : aq. ratio of 2:3 (Fig. 2.6).

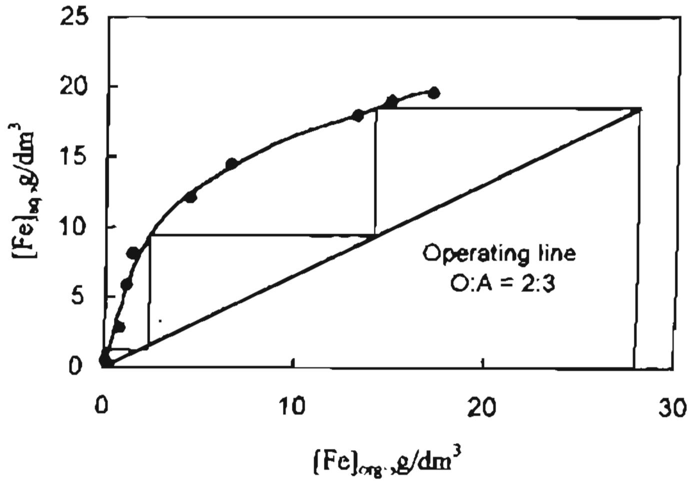


Figure 2.6 McCabe-Thiele plot for iron(III) stripping. $[Fe^{3+}]_{org}$ = 27.92 g/dm^3.

2.2.5 *Extraction of iron(III) from waste chloride liquors of titania industry*

The developed solvent extraction procedure using a mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK was applied for the recovery of high purity iron(III) chloride from the waste liquors of titanium minerals processing industry. The composition of the waste chloride liquor containing multivalent metal chlorides is given in Table 2.2. As it is well known that ferrous iron is less extractable than ferric iron when extracted with solvating extractants, in the present study, the waste chloride liquor was chlorinated to convert ferrous to ferric iron by passing chlorine gas (in a stoichiometric amount to the divalent iron ions).

$$2FeCl_2 + Cl_2(g) \rightarrow 2FeCl_3 \qquad (29)$$

A batch type counter current extraction and stripping studies were carried out at laboratory scale using separatory funnels at 303 ± 1 K. The extraction process for the recovery of iron(III) chloride from the waste liquor comprises the steps of (1) chlorination of waste chloride liquor and adjustment of acidity in the feed (2) selective extraction of iron(III) chloride from the chlorinated waste chloride liquor in three stages of counter current extraction (aq. : org. = 1:2) using a mixed solvent

Table 2.2 Composition of waste chloride liquor from TiO_2 industry.

Constituent	g /dm^3
$FeCl_2$	215 66
$FeCl_3$	48.67
$MgCl_2$	13.41
$MnCl_2$	5.96
$AlCl_3$	13.36
$TiOCl_2$	0.22
$CrCl_3$	0.78
$VOCl_3$	1.16
HCl	33.32

system consisting of 70 vol.% TBP and 30 vol.% MIBK and (3) backwashing of the loaded organic phase using distilled water (pH = 2.0) in three stages (org. : aq. = 2:3) to recover high purity iron(III) chloride. The schematic diagram of the process adopted is shown in Fig. 2.7. Typical results of the process are given in Table 2.3. The present study clearly shows that the mixed solvent system can be used as a selective extractant for the recovery of high purity iron(III) chloride (99.9 %) with an yield of 99.9 % from a multivalent metal chloride feed, present in the waste chloride liquors of titanium minerals processing industry. By converting ferric chloride into iron oxide of various purities by the known methodologies, it has applications in paint, pigment and electronic industries. Further, ferric chloride may be used as a flocculating agent in the sewage water treatment plants.

Table 2.3 Extraction of iron(III) chloride from waste liquors of titanium minerals processing industry using 70 vol.% TBP + 30 vol.% MIBK mixed-solvent system.*

Constituent	Amount of metal chloride (gms)		
	Feed	Raffinate	Strip solution
$FeCl_3$	162.240	0.090	162.150
$TiOCl_2$	0.110	0.107	< 0.003
$MgCl_2$	6.705	6.532	0.173
$MnCl_2$	2.980	2.975	0.005
$AlCl_3$	6.679	6.674	< 0.005
$VOCl_3$	0.579	0.576	< 0.003
$CrCl_3$	0.396	0.393	< 0.003
HCl	72.9	34	38.9

*purity of iron(III) chloride = 99.9 %, product yield = 99.9 %

The present investigations clearly highlight that high purity iron(III) chloride can be selectively recovered from titania waste chloride liquors through a solvent extraction process using a mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK. Further, the problems associated with the TBP and MIBK when used individually for the extraction of iron(III) could be overcome by using the mixed solvent system.

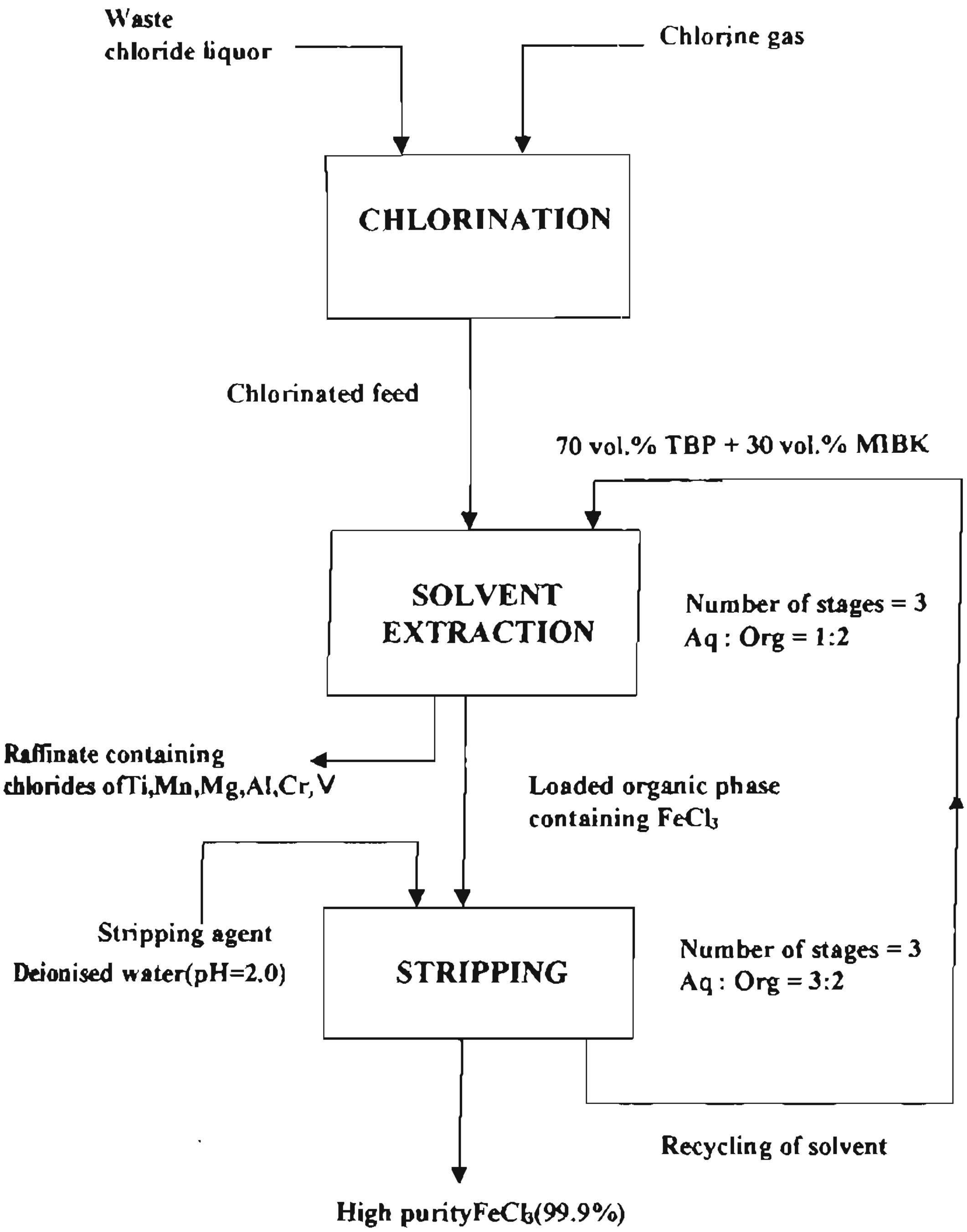


Figure 2.7 Schematic flow diagram of the solvent extraction process.

Part B

Studies on the extraction of iron(III) from acidic chloride solutions using Cyanex 923

It is clear from the literature review that the extraction of iron(III) from dilute hydrochloric acid solutions has been well studied using neutral organophosphorus extractants such as tributylphosphate (TBP) and trioctylphosphine oxide (TOPO). However, studies on the extraction of iron(III) from hydrochloric acid solutions using Cyanex 923 (TRPO) is lacking. Hence in the present work, Cyanex 923 has been explored as an extractant for iron(III) from acidic chloride solutions.

Cyanex 923 (TRPO) is a mixture of four trialkyklphosphine oxides, which exhibit extraction properties similar to trioctylphosphine oxide (TOPO) and is commercially available from Cytec, Canada.

$R_3P=O$ $R_2R'P=O$ R = hexyl
$R'_3P=O$ $R'_2RP=O$ R' = octyl

Trialkyl phosphine oxide
(CYANEX 923≡TRPO)

The above solvent mixture has the advantage of being a liquid and is completely miscible with all commonly used hydrocarbons. Cyanex 923 has been suggested as a potential extractant for trivalent lanthanides and yttrium [162] and also for the extraction of thorium(IV) and uranium(VI) [163].

In the present study, the extraction behaviour of iron(III) from acidic chloride solutions has been investigated using Cyanex 923 as an extrattant with a view to elucidate the nature of complexes extracted into the organic phase and also to investigate the selectivity of iron(III) over other associated metal ions present in the waste chloride liquors of titanium minerals processing industry.

2.3 Experimental

Reagents

Cyanex 923, supplied by Cytec, Canada, contains trialkylphosphine oxides (93%), including dioctylhexylphosphine oxide (40-44%), dihexyloctylphosphine oxide (28-30%), trihexylphosphine oxide (8%) and trioctylphosphine oxide (14%) [164]. Cyanex 923 was purified by the method described elsewhere [165] Trioctylphosphine oxide (TOPO) was obtained from E-Merck Limited, India. Xylene of analytical reagent quality was used as a diluent in the present work.

Extraction and analytical procedure

The liquid-liquid extraction and the analytical methods followed for the determination of the metal ions were the same as described in Part A of this chapter. Preliminary experiments showed that extraction equilibrium is attained within 5 min. for all the metal ions.

2.4 Results and discussion

2.4.1 *Extraction equilibrium*

Effect of hydrochloric acid concentration

The effect of hydrochloric acid concentration (0.4 to 2.0 mol/dm^3) on the extraction of iron(III) (3.6×10^{-4} mol/dm^3) has been investigated using 0.2 mol/dm^3 TRPO in xylene as an extractant and the results are given in Fig. 2.8. It is clear from

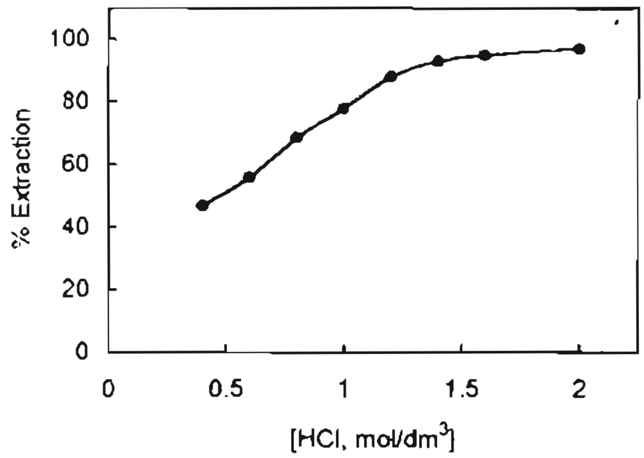


Figure 2.8 Effect of hydrochloric acid concentration on the extraction of iron(III) (3.6×10^{-4} mol/dm^3) using 0.2 mol/dm^3 TRPO in xylene.

the figure that the extraction of iron(III) increases with increase in hydrochloric acid concentration in the aqueous phase and this can be attributed to the common ion effect.

Effect of hydrogen and chloride ion concentrations

The effect of hydrogen ion (0.4 to 2.0 mol/dm^3) and chloride ion (1.0 to 2.0 mol/dm^3) concentrations on the extraction of iron(III) (3.6×10^{-4} mol/dm^3) has been investigated using 0.1 mol/dm^3 TRPO in xylene as an extractant by employing HCl + NaCl mixtures in the aqueous phase and the results are presented in Fig. 2.9. The log [Cl$^-$] vs. log D plot is a straight line with a slope of 4.0 indicating the association of four chloride ions with iron(III) in the extracted complexes. The log [H$^+$] vs. log D plot has a slope of unity, indicating the extracted species as $HFeCl_4$.

Effect of metal ion concentration

The effect of metal ion concentration (3.6×10^{-4} to 1×10^{-2} mol/dm^3) on the extraction process has been studied from 2.0 mol/dm^3 hydrochloric acid solutions

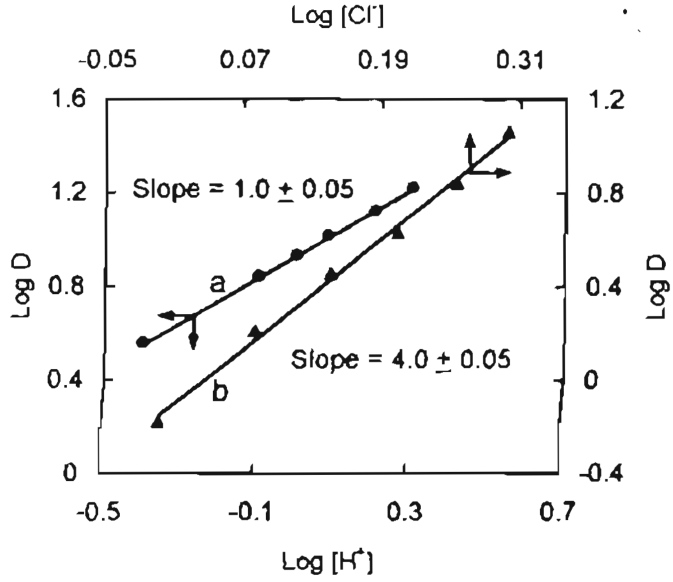


Figure 2.9 (a) Effect of hydrogen ion concentration on the extraction of iron(III). [Fe(III)] = 3.6×10^{-4} mol/dm^3, [Cl$^-$] ≈ 2.0 mol/dm^3. (b) Effect of chloride ion concentration on the extraction of iron(III), [H$^+$] = 1.0 mol/dm^3. Org. ph. : 0.1 mol/dm^3 TRPO in xylene.

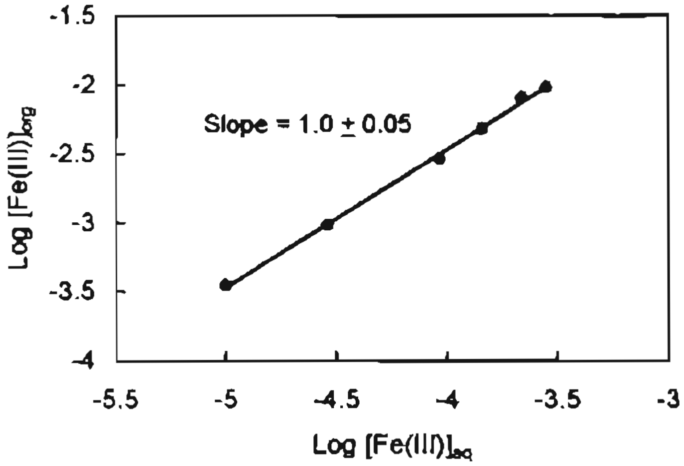


Figure 2.10 Effect of metal ion concentration on the extraction of iron(III) from 2.0 mol/dm^3 HCl solutions using 0.2 mol/dm^3 TRPO in xylene.

using 0.2 mol/dm^3 TRPO in xylene and the results are depicted in Fig. 2.10. The extraction of iron(III) was found to be independent of initial aqueous phase metal concentration under the present experimental conditions. The log-log plot of the equilibrium organic phase metal concentration against the aqueous phase metal concentration is linear with a slope equal to 1.0, indicating that a mononuclear species is getting extracted into the organic phase.

Effect of extractant concentration

The effect of TRPO concentration (0.02 to 0.2 mol/dm^3) on the extraction of iron(III) has been studied at constant metal ion (3.6×10^{-4} mol/dm^3) and hydrochloric acid (2.0 mol/dm^3) concentrations and the results are presented in Fig. 2.11. The extraction of iron(III) increases linearly with increasing extractant concentration and from the slope of the plot, log D vs. log [TRPO], it is clear that two molecules of Cyanex 923 are involved in the extracted complexes of iron(III). The existence of a similar disolvated species in the organic phase has been reported by several investigators for the extraction of iron(III) from hydrochloric acid solutions using neutral oxo-donors such as TBP [115,118]. For comparison, the extraction of iron(III) (3.6×10^{-4} mol/dm^3) has also been investigated from 2.0 mol/dm^3 hydrochloric acid solutions using trioctylphosphine oxide (TOPO) (0.02 to 0.1 mol/dm^3) *in xylene as an extractant and observed a similar extraction behaviour for* iron(III). The equilibrium constants for the extraction of iron(III) have been calculated from the distribution data and were found to be log $K_{ex,TRPO}$ = 1.78 and $K_{ex,TOPO}$ = 1.81 for TRPO and TOPO, respectively. It is clear from the results that the extraction efficiency of iron(III) with TRPO is almost equal to that of TOPO, which is in accordance with their basicity values (K_H = nitric acid uptake constant, $K_{H,TRPO}$ = 8.5, $K_{H,TOPO}$ = 8.9 [163]).

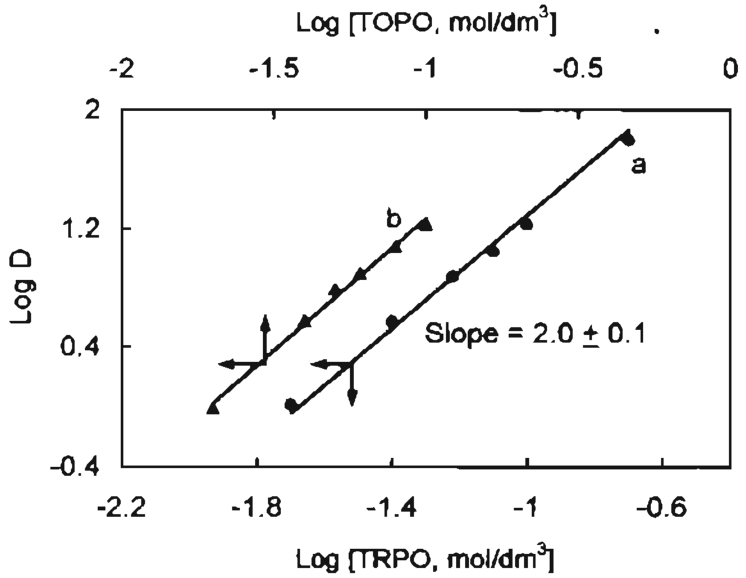


Figure 2.11 Effect of extractant concentration on the extraction of iron(III).
Aq. ph.: [Fe(III)] = 3.6×10^{-4} mol/dm^3), [HCl] = 2.0 mol/dm^3, Org. ph. : (a) TRPO (b) TOPO.

From the preceding studies, the extraction equilibrium of iron(III) with Cyanex 923 (TRPO) when extracted from hydrochloric acid solutions can be represented as :

$$Fe^{3+}{}_{aq} + aH^{+}{}_{aq} + (3+a)Cl^{-}{}_{aq} + yTRPO_{org} \overset{K_{ex,TRPO}}{\Leftrightarrow} H_aFeCl_{3+a}\cdot yTRPO_{org} \quad (30)$$

where a = 1 and y = 2.

2.4.2 *Dependence of extraction on the nature of diluent*

The extraction of iron(III) from 1 mol/dm^3 hydrochloric acid solutions using 0.2 mol/dm^3 TRPO in various diluents has been studied and the results are shown in Table. 2.4. Results clearly show that the extraction of iron(III) varies with the nature of the diluent. When chloroform is used as a diluent, very little extraction of iron(III) has been observed. This may be due to strong acid-base interaction between the basic extractant, TRPO and the acidic diluent, chloroform through hydrogen bonding.

Table 2.4 Dependence of extraction of iron(III) on the nature of diluent. [Fe(III)] = 3.6×10^{-4} mol/dm^3, [HCl] = 1.0 mol/dm^3, [TRPO] = 0.2 mol/dm^3.

Diluent	Dielectric constant(ε) [166]	% Extraction
Methylisobutyl ketone	13.11	98
Chloroform	4.90	9
Xylene	2.26	80
Toluene	2.24	78
Benzene	2.28	78
Cyclohexane	2.02	89
Kerosene	2.00	87

Among the benzene derivatives employed as diluents, the iron(III) extraction varies in the order : xylene > toluene ~ benzene. The interaction of these aromatic hydrocarbons with the solute are stronger than that of non-aromatic hydrocarbons such as cyclohexane. Strong interactions of the diluent with the extractant can result in lower extractions of the metal ions. Hence, in the present study, the extraction of iron(III) is higher in cyclohexane than in aromatic hydrocarbons. The results also clearly demonstrate that the diluents such as kerosene, benzene, xylene and toluene, having low dielectric constants, show high extraction of iron(III). On the other hand, diluents having higher dielectric constant, such as chloroform, gave poor extraction. However, in the present work, methylisobutyl ketone having high dielectric constant, shows high extraction for iron(III). This can be attributed to the synergistic effect of the mixed-solvent system.

2.4.3 *Stripping studies*

The effect of hydrochloric acid concentration on iron(III) stripping from a loaded organic solvent system consisting of 0.2 mol/dm^3 TRPO in xylene ([Fe(III)]$_{org}$ = 3.6×10^{-4} mol/dm^3) has been investigated and the results are shown in

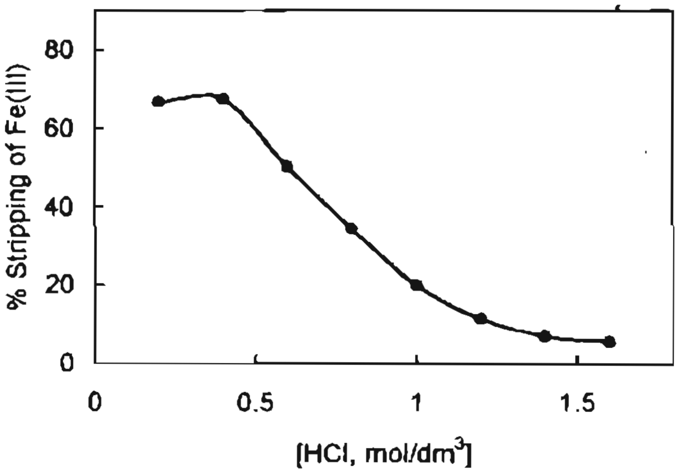


Figure 2.12 Effect of hydrochloric acid concentration on iron(III) stripping from loaded TRPO system. $[Fe(III)]_{org.}$ = 3.6×10^{-4} mol/dm^3, [TRPO] = 0.2 mol/dm^3 in xylene.

Fig. 2.12. It is clear from the results that the percentage of iron(III) stripped from the loaded solvent decreases with increasing HCl concentration. Trial experiments showed that complete iron(III) stripping from loaded organic phase is possible in two counter current stages at an org. : aq. phase ratio of 1 : 3 using 0.4 mol/dm^3 HCl as a stripping agent.

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*

The effect of hydrochloric acid concentration (0.2 to 2.0 mol/dm^3) on the extraction of iron(III) (3.6×10^{-4} mol/dm^3), iron(II) (3.6×10^{-4} mol/dm^3), magnesium(II) (1.0×10^{-3} mol/dm^3), aluminium(III) (1.0×10^{-3} mol/dm^3), titanium(IV) (1×10^{-3} mol/dm^3), vanadium(V) (0.25×10^{-3} mol/dm^3), chromium(III) (1.0×10^{-3} mol/dm^3) and manganese(II) (1.0×10^{-3} mol/dm^3) and has been investigated using 0.2 mol/dm^3 TRPO in xylene as an extractant and the results are shown in Fig. 2.8. The extraction of both iron(II) and iron(III) increases with increase in the aqueous phase

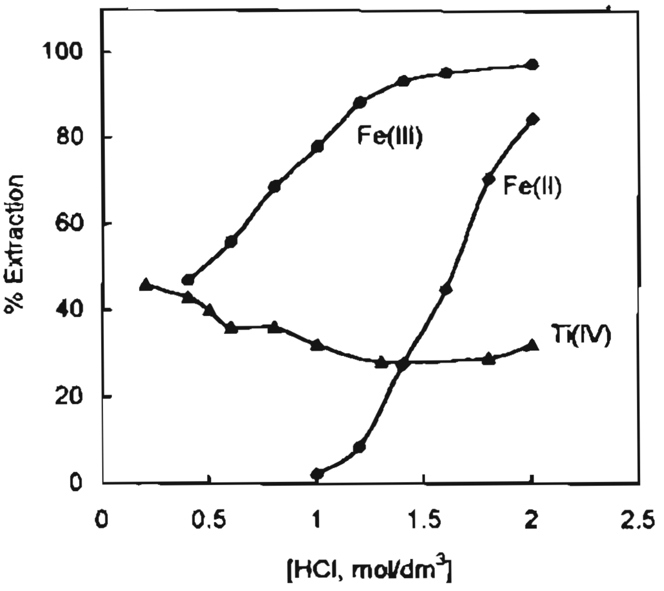


Figure 2.13 Effect of hydrochloric acid concentration on the extraction of iron(III) (3.6×10^{-4} mol/dm^3), iron(II) (3.6×10^{-4} mol/dm^3) and titanium(IV) (1×10^{-3} mol/dm^3), using 0.2 mol/dm^3 TRPO in xylene.

hydrochloric acid concentration. However, it has been observed that iron(III) is extracted only from more concentrated acidic solutions than iron(II). The percentage extraction of titanium(IV) was found to decrease moderately from 46 % to 32 % with increase of HCl concentration from 0.2 to 2.0 mol/dm^3. On the other hand, other metal ions such as magnesium(II), aluminium(III), vanadium(V), chromium(III) and manganese(II) were found to be not extracted under the present experimental conditions. The above studies reveal the poor selectivity for iron(III) using TRPO as an extractant from acidic chloride solutions.

Chapter 3

Studies on the liquid-liquid extraction of titanium(IV) from acidic chloride solutions using acidic organophosphorus extractants

Titanium finds the widest application as titanium dioxide pigment in the paint industry. Due to its excellent corrosion resistance in a chloride environment and also because of its special properties of high resistance, titanium has also been widely used in the aerospace industry. Selective separation and recovery of titanium from industrial wastes is gaining more importance because of the greater need for high purity products. Further, 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.

A survey of literature showed that di-(2-ethylhexyl)phosphoric acid (DEHPA) has been widely used for the extraction of titanium(IV) from acidic solutions [39-45]. Sole [50] has investigated the extraction of titanium(IV) from sulphuric acid leach liquors of titaniferrous magnetite using DEHPA and reported poor selectivity for titanium over other associated metal ions due to their co-extraction. As compared to dialkylphosphoric acids, studies on the extraction of tetravalent titanium from acidic chloride solutions using dialkylphosphinic acids or phosphonic acids are lacking. Hence in the present work, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (Ionquest 801 ≡ EHEHPA) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272 ≡ BTMPPA) have been explored for the extraction of titanium(IV) from hydrochloric acid solutions with a view to elucidate the nature of complexes extracted into the organic phase and also to investigate the selectivity between titanium(IV) and other associated multivalent metal ions present in the waste chloride liquors of titanium minerals processing

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industry. For comparison, extraction behaviour of titanium(IV) from hydrochloric acid solutions has also been studied using bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302 ≡ BTMPTPA) in xylene as an extractant.

3.1 Experimental

Reagents

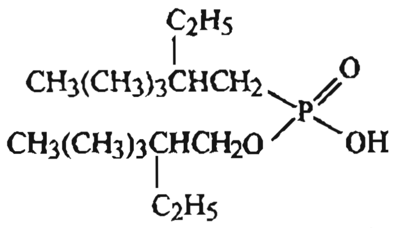
Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272 ≡ BTMPPA) and bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302 ≡ BTMPTPA), supplied by Cytec, Canada were used as extractants after purification. BTMPPA was purified by the copper salt precipitation method as described below [167] : First, BTMPPA was washed successively with solutions of sodium carbonate, sulphuric acid and water. Its copper(II) complex was prepared by shaking a hexane solution of BTMPPA with a copper sulphate solution of pH ~ 4.3 adjusted by dropwise addition of sodium hydroxide solution. The hexane solution was dried by using a rotary evaporator, the solid was washed with acetone to remove impurities and then the complex was decomposed with hydrochloric acid. The purity of BTMPPA was determined by potentiometric titration in 75% isopropanol with sodium hydroxide and found to be >99% pure.

BTMPTPA was purified by the cobalt salt precipitation method as described below [168] : An approximately 0.5 mol/dm^3 solution of BTMPTPA in hexane was prepared and was added half its volume of a saturated sodium sulphate solution in which an amount of sodium hydroxide equivalent to BTMPTPA plus a 20% excess has been dissolved. The phases were mixed vigorously for 10 min. and then allowed to separate. The organic phase containing sodium salt of BTMPTPA was separated and contacted with a 0.5 mol/dm^3 solution of cobalt sulphate whereby the organic phase becomes saturated with the cobalt salt of BTMPTPA. The precipitated cobalt-

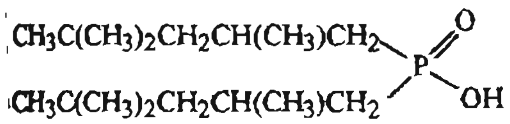
BTMPTPA complex was washed with ice cold acetone, filtered and air dried. The complex was decomposed with a mixture of 4 mol/dm^3 H_2SO_4 and diethylether and the impurities were removed by evaporation in a rotary evaporator. The purity of BTMPTPA was determined by potentiometric titration in 75% isopropanol with N-tetrabutylammonium hydroxide and was found to be >99% pure.

2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) with a trade name, Ionquest 801, supplied by Albright and Wilson, USA was purified by the copper salt precipitation method as described earlier. Kerosene (boiling range 160-200° C; composed of aliphatic hydrocarbons) was used as the diluent for EHEHPA. Kerosene was purified by washing with con. H_2SO_4, 0.1 mol/dm^3 NaOH and water, respectively. To improve the phase disengagement, 20 vol.% isodecanol was used as a modifier along with EHEHPA in the organic phase.

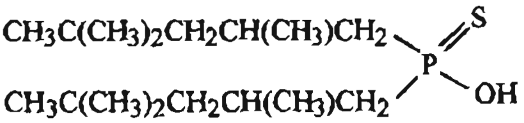
The molecular structures of the extractants are:



2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester
(EHEHPA)



bis(2,4,4-trimethylpentyl)phosphinic acid
(BTMPPA)



bis(2,4,4-trimethylpentyl)monothiophosphinic acid
(BTMPTPA)

Liquid-liquid extraction and analytical procedures for the determination of metal ions were the same as described in Chapter 2. All the computer programs were written in FORTRAN 77 and executed on a 32 bit mini computer (HCL HORIZON III).

3.2 Preparation of metal complexes

The complexes of titanium(IV) with EHEHPA and BTMPPA were prepared by following the general procedure : The loading of the extractant in the organic phase was carried out by repeated contacts of fresh portions of metal solution for required time. The loaded organic phase was then subjected to evaporation of diluent in a rotary evaporator and dried in a desiccator. A Nicolet FTIR 560 Magna Spectrometer using KBr (neat), was used to obtain the IR spectra of the metal complexes. For comparison, IR spectra of pure extractants were also recorded.

3.3 Results and discussion

3.3.1 *Effect of phase contact time*

The effect of phase contact time on the distribution ratio for the extraction of titanium(IV) (0.01 mol/dm^3) from 1.0 mol/dm^3 hydrochloric acid solutions using EHEHPA (0.2 mol/dm^3) in kerosene as an extractant has been studied and the results are shown in Fig. 3.1. It is found that the distribution ratio increases with increasing phase contact time upto 90 min. and thereafter the curve levels off. It is clear from the results that the time required for attaining the extraction equilibrium for this system is about 90 min. The distribution ratios for the extraction of titanium(IV) (2.5×10^{-3} mol/dm^3) from 0.14 mol/dm^3 hydrochloric acid with 0.05 mol/dm^3 BTMPPA in xylene have been measured at different phase contact times and the results are depicted in Fig.3.2. It is clear from the experiments that the extraction equilibrium time for this system is about 2h.

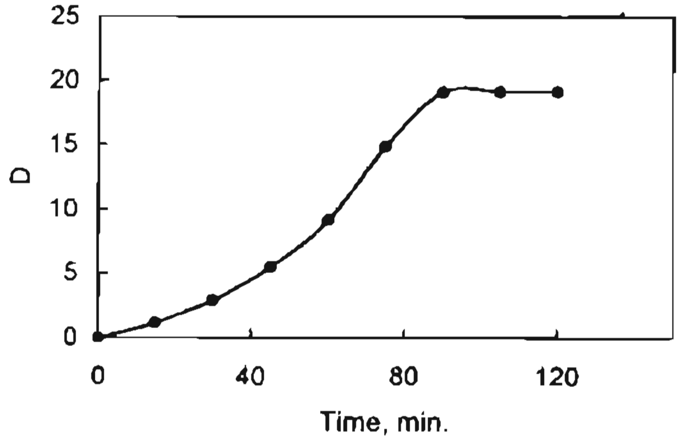


Figure 3.1 Dependence of distribution ratio on phase contact time. [Ti(IV)] = 0.01 mol/dm^3, [HCl] = 1.0 mol/dm^3, [EHEHPA] = 0.2 mol/dm^3.

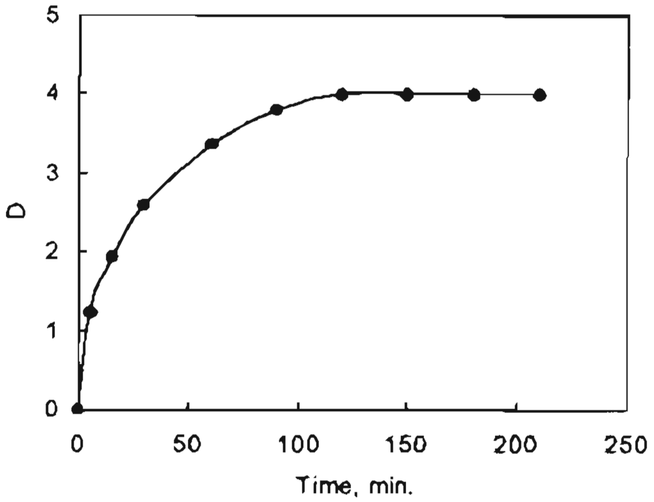


Figure 3.2 Dependence of distribution ratio on phase contact time. [Ti(IV)]=2.5×10^{-3} mol/dm^3, [HCl] = 0.14 mol/dm^3, [BTMPPA] = 0.05 mol/dm^3.

On the other hand, the extraction equilibrium of titanium(IV) (1×10^{-3} mol/dm^3) from 0.1 mol/dm^3 hydrochloric acid solutions using 0.1 mol/dm^3 BTMPTPA as an extractant is found to be faster and an equilibrium was achieved within 5 min.

3.3.2 *Extraction of tetravalent titanium from acidic chloride solutions using dialkylphosphonic or phosphinic acids*

Extraction equilibrium

The extraction equilibrium of titanium(IV) from hydrochloric acid solutions with acidic organophosphonic or phosphinic extractants may be represented as:

$$\mathrm{TiO}_{aq}^{2+} + 2(\mathrm{HX})_{2\,org} \overset{K_{ex}}{\Leftrightarrow} \mathrm{TiO}(\mathrm{HX}_2)_{2\,org} + 2\mathrm{H}_{aq}^{+} \qquad (31)$$

where K_{ex} denotes the equilibrium constant and $(HX)_2$ refers to the dimeric form of extractant (EHEHPA or BTMPPA or BTMPTPA). It has been reported elsewhere that these extractants will exist as dimers under the present experimental conditions [39,169].

$$K_{ex} = \frac{[\mathrm{TiO}(\mathrm{HX}_2)_2][\mathrm{H}^+]^2}{[\mathrm{TiO}^{2+}][(\mathrm{HX})_2]^2} \qquad (32)$$

Titanium(IV) in the aqueous phase forms a variety of complexes in the presence of chloride ions. Then the total Ti(IV) concentration can be expressed as:

$$\begin{aligned}[\mathrm{Ti}^{4+}]_{\mathrm{Total}} &= [\mathrm{TiO}^{2+}] + [\mathrm{TiOCl}^{+}] + [\mathrm{TiOCl}_2] \\ &= \mathrm{TiO}^{2+}\,(1 + \beta_1[\mathrm{Cl}^-] + \beta_2[\mathrm{Cl}^-]^2) \qquad (33)\end{aligned}$$

where β_1 and β_2 are stability constants of the following reactions:

$$\mathrm{TiO}^{2+} + \mathrm{Cl}^- \overset{\beta_1}{\Leftrightarrow} \mathrm{TiOCl}^+ \qquad (34)$$

$$\mathrm{TiO}^{2+} + 2\mathrm{Cl}^- \overset{\beta_2}{\Leftrightarrow} \mathrm{TiOCl}_2 \qquad (35)$$

The values of stability constants, $\beta_1 = 3.55$ and $\beta_2 = 1.41$ were obtained from literature [170]. The distribution ratio, D, of titanium(IV) can be written from Eqs.(32) and (33) as:

$$D = \frac{K_{ex}\,[(\mathrm{HX})_2]^2}{[\mathrm{H}^+]^2\,(1+\beta_1[\mathrm{Cl}^-]+\beta_2[\mathrm{Cl}^-]^2)} \qquad (36)$$

The equilibrium constant (K_{ex}) of the extracted complexes was determined by non-linear regression analysis using the following procedure :

1. A value of K_{ex} is assumed
2. Values of D under the given conditions are calculated from Eq.36 and compared with the experimental values
3. The value of the equilibrium constant which leads to a minimum root mean square fractional error, y, where

$$y = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{D_{cal,i} - D_{\exp,i}}{D_{\exp,i}}\right\}^2} \qquad (37)$$

for all the experimental data are taken as the equilibrium constant for the system under consideration.

Effect of extractant concentration

The effect of EHEHPA concentration (0.05 to 0.3 mol/dm^3) on the extraction of titanium(IV) (0.01 mol/dm^3) from 1.0 mol/dm^3 hydrochloric acid solutions has been investigated and the results are depicted in Fig. 3.3. The effect of concentration of BTMPPA (0.01 to 0.1 mol/dm^3) and BTMPTPA (0.05 to 0.2 mol/dm^3) on the extraction of titanium(IV) has also been studied by keeping the metal (2.5×10^{-3} mol/dm^3 in the case of BTMPPA and 1×10^{-3} mol/dm^3 in the case of BTMPTPA) and acid (0.14 mol/dm^3 for BTMPPA and 0.1 mol/dm^3 for BTMPTPA) concentrations constant and the results are shown in Fig. 3.4. It is clear from the figures that the extraction of titanium increases with increase in extractant concentrations. From the slope of the plots, log $D[H^+]^2\{1+\beta_1[Cl^-]+[\beta_2[Cl^-]^2\}$ versus log $[(HX)_2]$, it is inferred that two dimeric molecules of the extractant (HX ≡ EHEHPA or BTMPPA or BTMPTPA) are involved in the extracted complexes of titanium(IV).

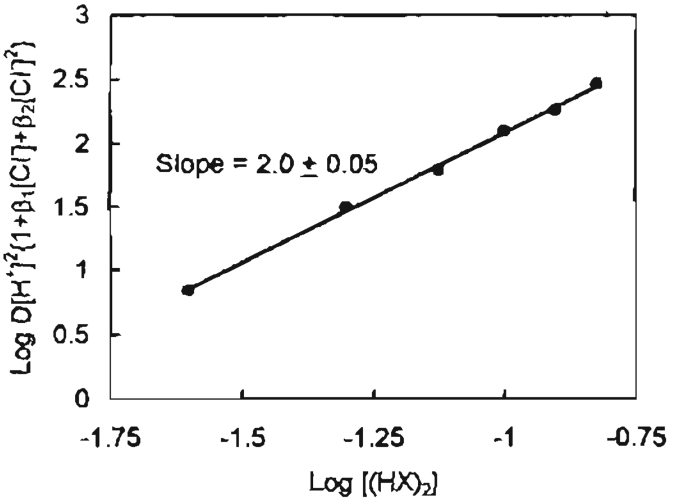


Figure 3.3 Effect of EHEHPA concentration on the extraction of titanium(IV). [Ti(IV)] = 0.01 mol/dm^3, [HCl] = 1.0 mol/dm^3.

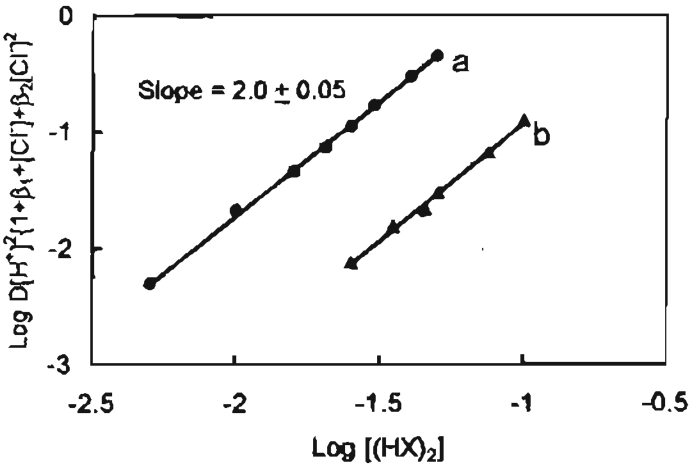


Figure 3.4 Effect of extractant concentration on the extraction of titanium(IV). (a) BTMPPA, [Ti(IV)] = 2.5×10^{-3} mol/dm^3, [HCl] ≈ 0.14 mol/dm^3. (b) BTMPTPA, [Ti(IV)] = 1.0×10^{-3} mol/dm^3, [HCl] = 0.10 mol/dm^3.

Effect of acidity

The extraction of titanium(IV) with EHEHPA (0.05 mol/dm^3), BTMPPA (0.05 mol/dm^3) and BTMPTPA (0.2 mol/dm^3) as a function of hydrochloric acid concentration has been studied and the results are shown in Figs. 3.5 and 3.6. In all the extraction systems, the extraction behaviour showed an inverse dependence with acidity. The plots of log $D\{1+ \beta_1[Cl^-] + \{\beta_2[Cl^-]^2\}$ versus log $[H^+]$ gave a slope of -2.0, confirming the formation of the complex, $TiO(HX_2)_2$. The acidity dependence of 2.0 also indicates the extraction of titanium(IV) as TiO^{2+} rather than the extraction of Ti^{4+}.

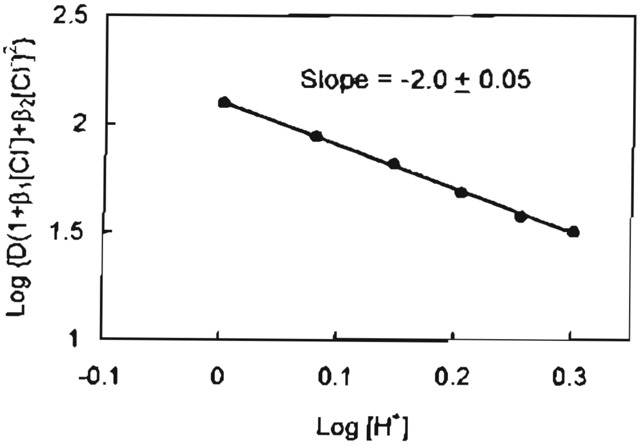


Figure 3.5 Effect of hydrogen ion concentration on the extraction of titanium(IV). [EHEHPA] = 0.2 mol/dm^3, [Ti(IV)] = 0.01 mol/dm^3.

Effect of metal ion concentration

The effect of titanium concentration on the extraction process has been investigated using EHEHPA (0.1 mol/dm^3), BTMPPA (0.05 mol/dm^3) and BTMPTPA (0.1 mol/dm^3) from hydrochloric acid solutions (1.0 mol/dm^3 for EHEHPA and BTMPTPA and 0.18 mol/dm^3 in the case of BTMPPA). In all the systems, the extraction of titanium(IV) was found to be independent of metal ion

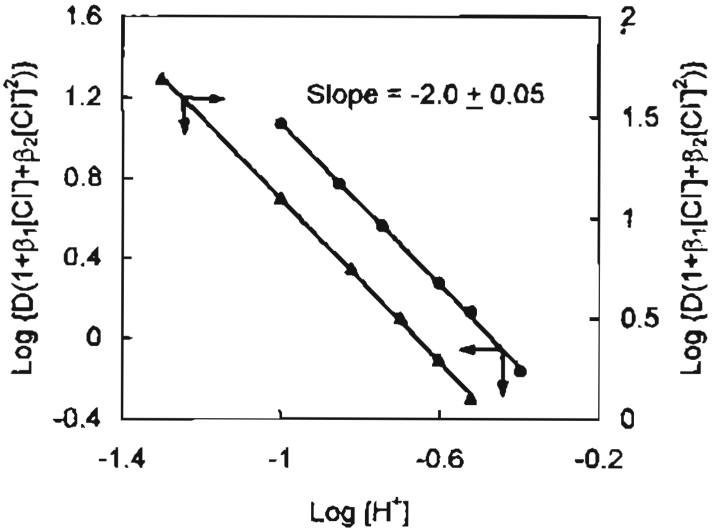
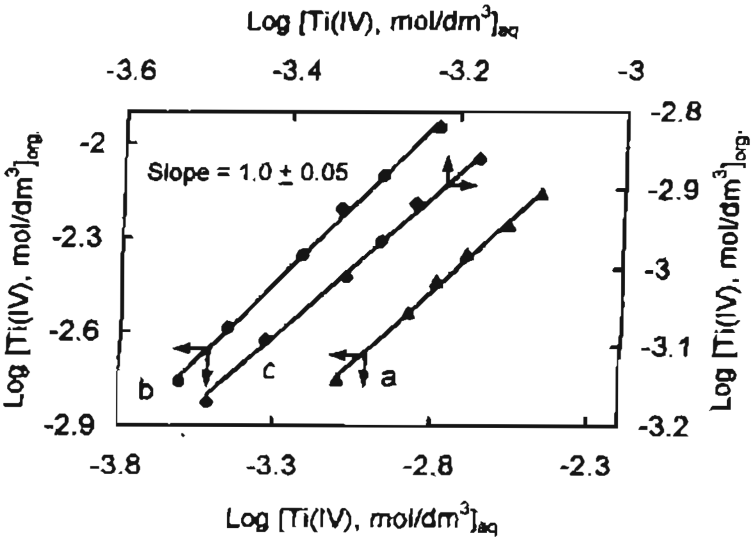


Figure 3.6 Effect of hydrogen ion concentration on the extraction of titanium(IV). (a) [BTMPPA] = 0.05 mol/dm^3, [Ti(IV)] = 2.5×10^{-3} mol/dm^3 (b) [BTMPTPA] = 0.2 mol/dm^3, [Ti(IV)] = 1.0×10^{-3} mol/dm^3.



igure 3.7 Effect of metal ion concentration on the extraction of titanium(IV). (a) EHEHPA] = 0.1 mol/dm^3, [HCl] = 1.0 mol/dm^3 (b) [BTMPPA] = 0.05 mol/dm^3, Cl] = 0.18 mol/dm^3 (c) [BTMPTPA] = 0.1 mol/dm^3, [HCl] = 0.1 mol/dm^3.

concentration in the aqueous phase. The log-log plots (Fig. 3.7) of equilibrium organic phase metal concentration against aqueous phase metal concentration is linear with a slope of unity indicating the extraction of mononuclear species into the organic phase.

Based on the preceding studies, the extraction equilibrium for titanium(IV) from hydrochloric acid solutions using EHEHPA or BTMPPA or BTMPTPA as an extractant can be represented as :

$$\mathrm{TiO}^{2+}_{aq} + 2(\mathrm{HX})_{2_{org}} \overset{K_{ex}}{\Leftrightarrow} \mathrm{TiO}(\mathrm{HX}_2)_{2_{org}} + 2\mathrm{H}^{+}_{aq} \qquad (38)$$

Biswas and Begum [39] have also reported the usual cation exchange mechanism for the extraction of titanium(IV) from hydrochloric acid solutions using DEHPA as an extractant.

The formation of the above extracted complex was further confirmed by analysing the equilibrium data presented in Figs. 3.3 - 3.7 using Eq. (36) with the aid of suitable chemically based model developed by taking into account complexation of chloride ions with titanium(IV) in the aqueous phase and all plausible complexes extracted into the organic phase. The best fit between the experimental and calculated D values was obtained only when the formation of the complex $\mathrm{TiO(HX_2)_2}$ was assumed. The equilibrium constants for the extracted complexes were determined by non-linear regression analysis using the procedure described earlier. The equilibrium constants thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the experimental conditions.

Table 3.1 gives the equilibrium constant values for various acidic organophosphorus extractants along with their pK_a values for the extraction of titanium(IV) from acidic aqueous solutions. It can be concluded from these comparisons that the extraction efficiency of titanium(IV) with various acidic organophosphorus extractants increases in the order : BTMPTPA (Cyanex 302) <

Table 3.1 Two phase equilibrium constants of titanium(IV) with various acidic organophosphorus extractants.

Extractant	pK_a	Log K_{ex}
DEHPA	1.72	5.42 [49]
EHEHPA	3.42	4.09 ± 0.03
BTMPPA	6.37	2.27 ± 0.02
BTMPTPA	5.63	1.08 ± 0.02

BTMPPA (Cyanex 272) < EHEHPA < DEHPA. Further, it is clear from these comparisons that log K_{ex} values increases as pK_a value decreases. In the case of BTMPTPA, by substituting the oxygen atom of P = O group of BTMPPA molecule with a sulfur atom, the pK_a value (5.63 [169]) becomes lower than that of BTMPPA ($pK_a = 6.37$ [169]). This means that BTMPTPA would have a higher affinity towards metal ions than BTMPPA in the cationic exchange reaction since P-OH group plays a dominant role in such a reaction. However, contrary to the above expectations, in the present study, BTMPTPA gives significantly lesser extraction for titanium(IV) than that of BTMPPA. This can be attributed to the fact that the P=S group of BTMPTPA forms a weaker complex with titanium(IV) than the P=O group of BTMPPA. This is in good agreement with the principle of Hard-Soft-Acid-Base (HSAB) concept, which indicates that sulphur is a weaker ligand than oxygen for hard lewis acid like titanium.

3.3.3 *IR spectral studies of the extracted complexes*

The IR spectra of titanium complexes with EHEHPA and BTMPPA are shown in Figs. 3.8 and 3.9. For comparison, the spectra of pure extractant is also shown in the figures. In the IR spectra of EHEHPA, the bands in the region 2700-1700 cm^{-1} are due to aggregative P-OH vibrations between intermolecular hydrogen

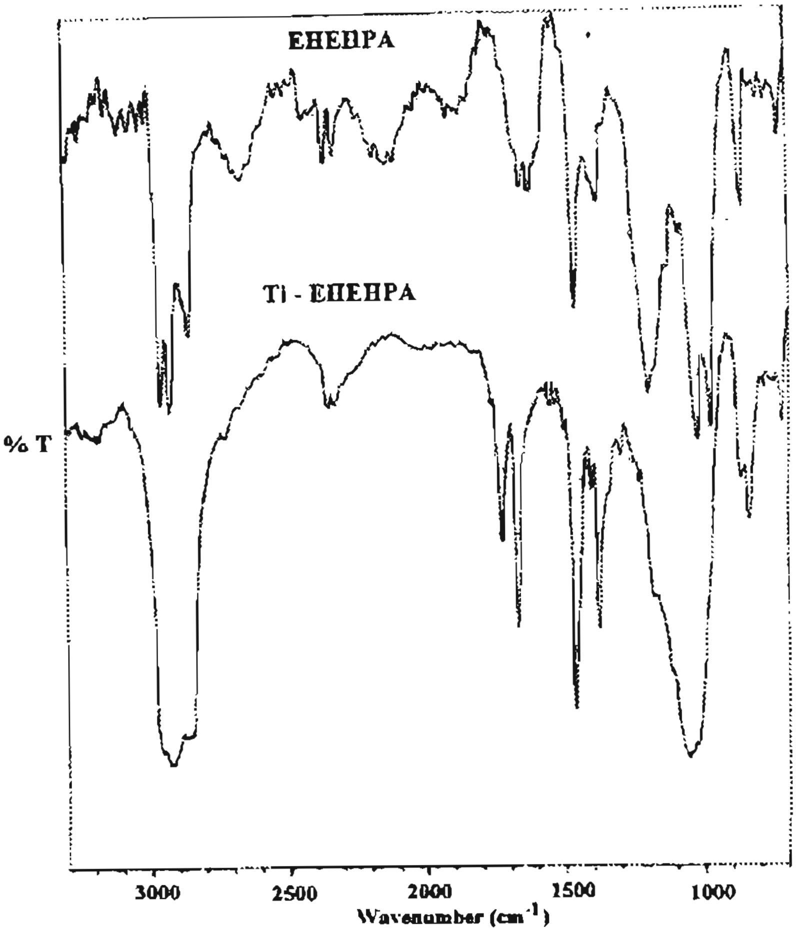


Figure 3.8 IR spectra of EHEHPA and Ti-EHEHPA complex.

bonding in the dimeric form. The band at 1195 cm^{-1} is due to P=O stretching and the band at 1038 cm^{-1} is assigned to P-O-H stretch. In the spectra of Ti-EHEHPA complex, the bands due to the aggregative P-OH vibrations in the region 2700-1700cm^{-1} are absent. The band due to the P-O-H stretching is also absent. These results suggest that when the dimeric EHEHPA molecule forms a complex with titanium(IV), the hydrogen atom of P-O-H is displaced by Ti thus confirming the cation exchange mechanism proposed. Further the shift in the P=O stretching band from *1195 cm^{-1} to 1065 cm^{-1} is indicative of the participation of oxygen of* P=O

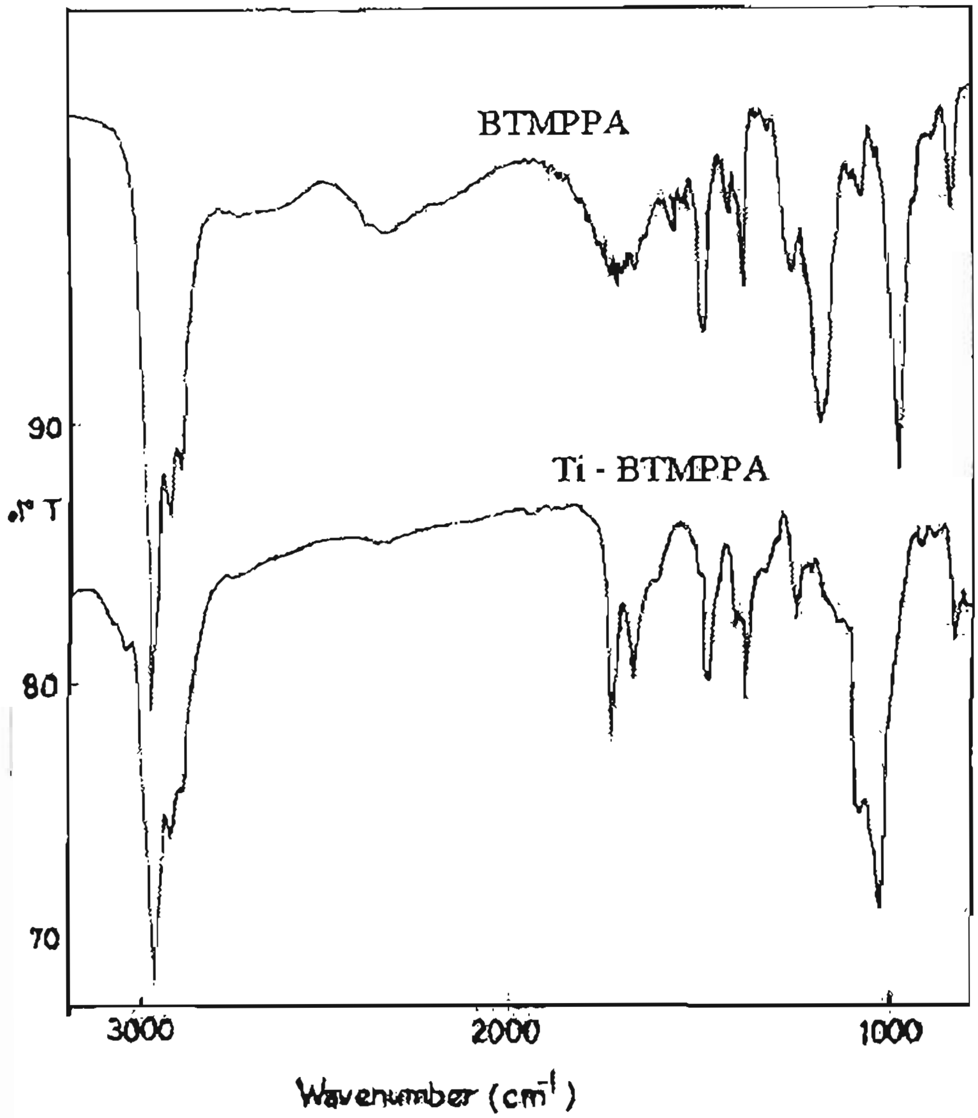


Figure 3.9 IR spectra of BTMPPA and Ti-BTMPPA complex.

group in the complex formation through coordination. Similarly in the IR spectra of Ti-BTMPPA complex, the band due to P-OH stretching in the BTMPPA at 958 cm^{-1} is absent. Further, the shift in P=O stretching band from 1170 cm^{-1} to 1014 cm^{-1} confirms the complex formation involving the coordination of oxygen of P=O group in BTMPPA with titanium.

.3.4 *Effect of nature of diluent on the extraction of titanium*

The extraction of titanium(IV) from hydrochloric acid solutions (1.0 mol/dm^3 r EHEHPA and 0.14 mol/dm^3 for BTMPPA) using EHEHPA (0.1 mol/dm^3) and TMPPA (0.05 mol/dm^3) in various diluents has been investigated and the results re given in Table 3.2. The results clearly demonstrate that the extraction of itanium(IV) varies with the nature of diluent. Diluents such as benzene, xylene, oluene and kerosene having low dielectric constants show higher extraction fficiency for titanium(IV). On the other hand, diluents having high dielectric onstant such as chloroform, gave poor extraction. This may be due to the strong nteraction between the extractant and chloroform through hydrogen bonding. Among aromatic hydrocarbons, the extraction efficiency of titanium varies in the rder: benzene ≈ toluene < xylene. However, in the present study, methylisobutyl etone, having high dielectric constant, shows high extraction of titanium. This can e attributed to the synergistic effect of the mixed-ligand system. Due to high xtraction efficiency and cheap availability, in the subsequent studies, kerosene has een used as the diluent.

Table 3.3 Dependence of the nature of diluent on the extraction of titanium(IV) sing acidic organophosphorus extractants.

Diluent	Dielectric constant [166]	D	
		EHEHPA	BTMPPA
Methylisobutyl ketone	13.11	2.36	10.11
Chloroform	4.90	1.15	1.94
Benzene	2.28	1.32	3.65
Xylene	2.26	1.59	3.92
Toluene	2.24	1.32	3.75
Kerosene	2.00	5.27	7.33

3.3.5 *Loading capacity of the extractants*

Aliquot of 10 cm^3 of 1.0 mol/dm^3 EHEHPA was repeatedly contacted at 303 ± 1 K for 2h with the same volume of aqueous solutions containing 0.48 g/dm^3 of titanium and 2.0 mol/dm^3 HCl. After equilibration, the phases were analysed for titanium content. The amount of titanium transferred into the organic phase in each contact was calculated by difference and the cumulative concentration of titanium in the organic phase after each stage of contact was determined. The plot of cumulative $[Ti(IV)]_{org}$ per 100g of EHEHPA versus contact number is given in Fig. 3.10. It is clear that most of the titanium existing in the aqueous phase is extracted into the organic phase upto 40th contact. It has been calculated that 10 cm^3 portion of 1.0 mol/dm^3 EHEHPA solution can extract as much as 0.182 g Ti^{4+} which indicated that the loading capacity of EHEHPA for titanium is 5.92 g of Ti^{4+} per 100g of EHEHPA.

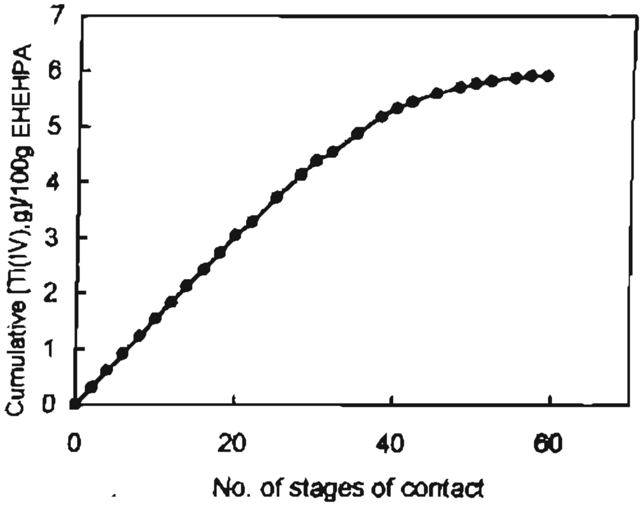


Figure 3.10 Loading of EHEHPA by titanium(IV). [EHEHPA] = 1.0 mol/dm^3, [HCl] = 2.0 mol/dm^3.

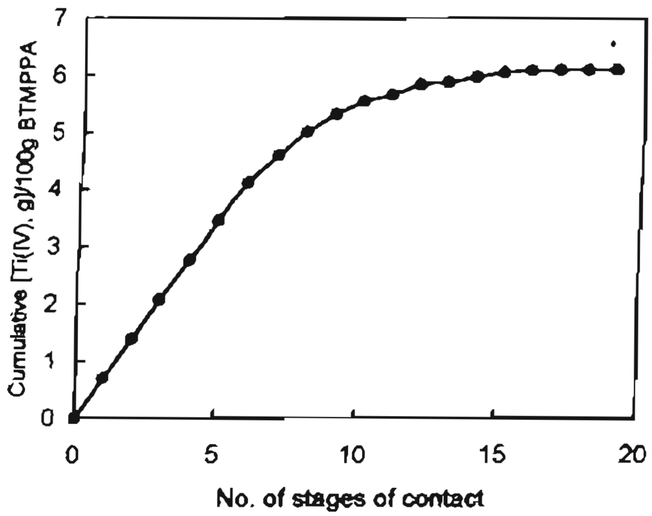


Figure 3.11 Loading of BTMPPA by titanium(IV). [BTMPPA] = 0.2 mol/dm^3, [HCl] = 0.25 mol/dm^3.

The loading capacity of BTMPPA was studied by contacting 10 cm^3 of 0.2 mol/dm^3 BTMPPA in xylene diluent with equal volume of aqueous phases containing 0.12 g/dm^3 of titanium in 0.25 mol/dm^3 HCl. The plot of cumulative $[Ti(IV)]_{org}$ per 100 g BTMPPA versus number of stages of contact is presented in Fig. 3.11. It is clear from the figure that the loading capacity of BTMPPA in xylene for extraction of titanium from hydrochloric acid solutions is 6.10g Ti^{4+} per 100g of BTMPPA. The loading capacities for EHEHPA and BTMPPA were comparable to that of DEHPA for the extraction of titanium (7.31 g of Ti^{4+} per 100g of DEHPA [39]).

3.3.6 *Stripping studies*

In any commercial extraction process it becomes imperative to back extract the metal from the loaded organic phase. Titanium stripping from a loaded organic solvent system, EHEHPA (0.2 mol/dm^3) containing 0.01 mol/dm^3 titanium(IV) has been investigated using various stripping agents and the results are shown in

Table 3.3 Stripping of titanium(IV) from loaded EHEHPA (0.2 mol/dm^3) phase.

Stripping agent	% Ti recovery
1 mol/dm^3 HCl	0.5
2 mol/dm^3 HCl	3.0
3 mol/dm^3 HCl	10.0
4 mol/dm^3 HCl	11.7
2 mol/dm^3 HCl + 1 % H_2O_2	61.2
2 mol/dm^3 HCl + 2 % H_2O_2	95.5
2 mol/dm^3 H_2SO_4 + 1 % H_2O_2	68.2
2 mol/dm^3 H_2SO_4 + 2 % H_2O_2	> 99.9

Table 3.4 Stripping of titanium(IV) from loaded BTMPPA (0.2 mol/dm^3) phase.

Stripping agent	% Ti recovery
1 mol/dm^3 HCl	21.0
2 mol/dm^3 HCl	38.6
3 mol/dm^3 HCl	39.7
1 mol/dm^3 H_2SO_4	38.6
2 mol/dm^3 H_2SO_4	45.4
3 mol/dm^3 H_2SO_4	56.8
1 mol/dm^3 HNO_3	15.9
2 mol/dm^3 HNO_3	22.7
3 mol/dm^3 HNO_3	22.7
1 mol/dm^3 H_2SO_4 + 1 % H_2O_2	94.0
2 mol/dm^3 H_2SO_4 + 2 % H_2O_2	> 99.9

Table 3.3. As the distribution ratio values of titanium(IV) were found to be high in the range of 0.5 to 2.0 mol/dm^3 HCl, stripping was impractical with hydrochloric acid alone. Among the many strippants tried, a mixture of 2.0 mol/dm^3 H_2SO_4 and 2% H_2O_2 was found to be an effective stripping agent (>99.9%) for the recovery of titanium from the loaded EHEHPA phase in a single stage with a phase ratio of unity.

A similar stripping behaviour was observed for titanium(IV) from a loaded BTMPPA (0.2 mol/dm^3) extractant system containing 8.8×10^{-3} mol/dm^3 titanium(IV) (Table 3.4). Stripping of titanium(IV) from loaded organic BTMPPA phase is not quantitative even at high mineral acid concentrations (20 to 50 % with 3.0 mol/dm^3 $HCl/HNO_3/H_2SO_4$). On the other hand, a mixture of hydrochloric acid and H_2O_2 as stripping agent gave better stripping efficiency.

3.3.7 *Recycling capacity of EHEHPA or BTMPPA*

Studies on the recycling capacity of EHEHPA or BTMPPA for the extraction of titanium(IV) were carried out by first loading them with titanium(IV) and then

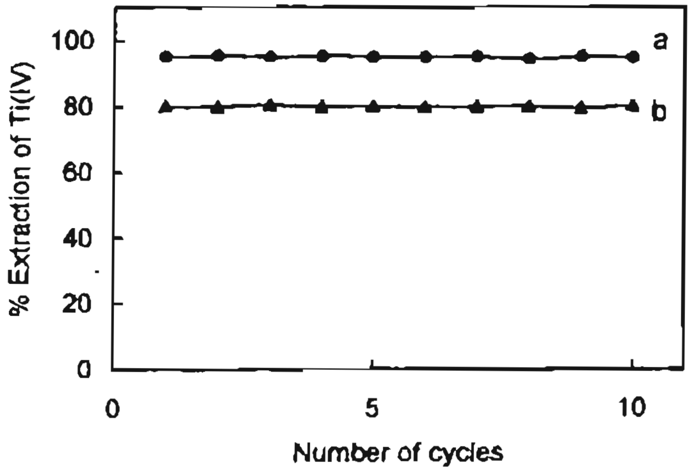


Figure 3.12 Recycling capacity of extractants. (a) [EHEHPA] = 0.2 mol/dm^3, [Ti(IV)] = 0.01 mol/dm^3, [HCl] = 1.0 mol/dm^3. (b) [BTMPPA] = 0.05 mol/dm^3, [Ti(IV)] = 2.5×10^{-3} mol/dm^3, [HCl] = 0.14 mol/dm^3.

stripping with a mixture of 2.0 mol/dm^3 H_2SO_4 and 2% H_2O_2. The stripped organic phase was then used for extraction. The results revealed practically insignificant change in the extraction efficiency of these extractants upto ten cycles of extraction (Fig. 3.12).

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*

The extraction behaviour of magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II) and iron(III) (0.01 mol/dm^3 each) has been investigated as a function of hydrochloric acid concentration using 0.2 mol/dm^3 EHEHPA in kerosene as an extractant and the results are presented in Fig. 3.13. It is clear from these results that the percentage extraction of titanium(IV), iron(III) and vanadium(V) decreases with increasing hydrochloric acid concentration. On the other hand, the extraction of magnesium(II), aluminium(III), chromium(III) and

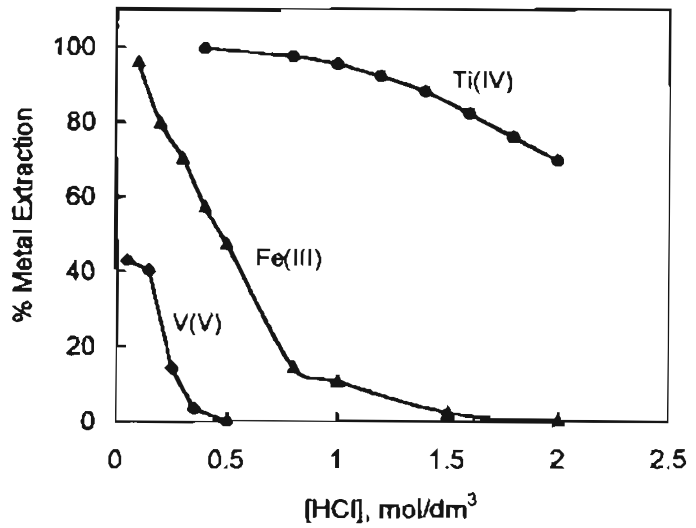


Figure 3.13 Effect of HCl concentration on the extraction of titanium(IV) (0.01 mol/dm^3), iron(III) (0.01 mol/dm^3) and vanadium(V) (0.01 mol/dm^3) using EHEHPA (0.2 mol/dm^3).

manganese(II) were found to be negligible under the present experimental conditions. Further, it is also clear from the results that the extraction of vanadium(V) and iron(III) is also negligible at about 2.0 mol/dm^3 HCl concentration. Thus, these results clearly indicate that it is possible to separate titanium(IV) from other associated multivalent metal ions such as magnesium(II), aluminium(III), vanadium(V) chromium(III), manganese(II) and iron(III) using 0.2 mol/dm^3 EHEHPA in kerosene as an extractant at an aqueous phase acidity of 2.0 mol/dm^3 HCl.

Based on the preceding studies, a simulated waste chloride liquor consisting of magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II) and iron(III) in 2.0 mol/dm^3 HCl has been prepared and subjected to extraction using 0.5 mol/dm^3 EHEHPA in kerosene as an extractant (aq. : org. = 1:1) with a view to develop a selective extraction and separation method for the recovery of titanium from the waste chloride liquors from titanium mineral processing industry and the results are shown in Table 3.4. It is clear from the table that titanium

Table 3.5 Separation of titanium(IV) from multivalent metal chloride mixtures. [EHEHPA] = 0.5 mol/dm^3, [HCl] = 2.0 mol/dm^3.

Metal ion	Amount of metal ion (× 10^{-2} mol/dm^3)		
	Feed	Raffinate	Strip liquor
Ti(IV)	0.80	0.01	0.79
Mg(II)	7.60	7.60	N.D
Al(III)	1.30	1.30	N.D.
V(V)	0.90	0.90	N.D
Cr(III)	0.20	0.20	N.D.
Mn(II)	3.10	3.10	N.D.
Fe(III)	0.80	0.80	N.D.

can be selectively separated from multivalent metal chloride solutions when extracted from 2.0 mol/dm^3 hydrochloric acid solutions with 0.5 mol/dm^3 EHEHPA in kerosene as an extractant in a single stage of extraction (aq. : org. = 1:1). Subsequently, titanium(IV) can be quantitatively recovered from the loaded organic phase in a single stage of stripping (org. : aq.= 1:1) using a mixture consisting of 2 mol/dm^3 H_2SO_4 and 2% H_2O_2 as stripping agent.

Separation of titanium(IV) from various synthetic binary and ternary multivalent metal chloride mixtures has also been studied by extracting with 0.2 mol/dm^3 BTMPPA in xylene from 0.3 mol/dm^3 hydrochloric acid solution (aq. : org. = 1:1, number of stages = 1) and the results are given in Table 3.6. The results clearly demonstrate that selective extraction and recovery of titanium(IV) is possible from binary and ternary mixtures of multivalent metal ions which are associated with titanium in the waste chloride liquors of titanium minerals processing industry.

The above results show that titanium(IV) can be selectively extracted from waste chloride liquors of titanium minerals processing industry using EHEHPA or BTMPPA as an extractant by controlling the hydrochloric acid concentration in the aqueous phase. However, EHEHPA provides selectivity for titanium(IV) over other associated multivalent metal ions at a higher hydrochloric acid concentration (2.0 mol/dm^3) than BTMPPA. Further, the extraction efficiency of EHEHPA for titanium(IV) was found to be significantly higher than that of BTMPPA.

Table 3.6 Separation of titanium(IV) from binary/multicomponent mixtures. [BTMPPA] = 0.2 mol/dm^3, [HCl] = 0.3 mol/dm^3.

Sample No.	Mixture	Amount of metal ion ($\times 10^{-3}$ mol/dm^3)	Extraction (%)	Recovery (%)
1	Ti(IV)	2.5	>99.9	99.9
	Mg(II)	1.0	unextracted	-
2	Ti(IV)	2.5	>99.9	99.9
	Al(III)	1.0	unextracted	-
3	Ti(IV)	2.5	>99.9	99.9
	V(V)	1.0	unextracted	-
4	Ti(IV)	2.5	>99.9	99.9
	Cr(III)	1.0	unextracted	-
5	Ti(IV)	2.5	>99.9	99.9
	Mn(II)	1.0	unextracted	-
6	Ti(IV)	2.5	>99.9	99.9
	Fe(III)	0.5	unextracted	-
7	Ti(V)	2.5	>99.9	99.9
	Mg(II)	1.0	unextracted	-
	Al(III)	1.0	unextracted	-
	V(V)	1.0	unextracted	-
	Cr(III)	1.0	unextracted	-
	Fe(III)	1.0	unextracted	-
	Mn(II)	1.0	unextracted	-

Chapter 4

Liquid-liquid extraction separation of vanadium(V) from acidic chloride solutions using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester

Vanadium is commercially important as a constituent of several alloys and catalysts. Nowadays, vanadium production is limited to the recovery from industrial wastes or low grade ores such as vanadium bearing ferrophosphorus slag, iron slag, fly ash, spent catalysts and titaniferrous magnetite ore. Mineral acid leaching followed by liquid-liquid extraction is one of the techniques being used industrially for the production of high purity vanadium compounds. Selective extraction and separation of vanadium from industrial waste streams is of paramount importance in view of the depleting resources of vanadium. Hence in the present work, an attempt has been made to recover vanadium through solvent extraction process from the waste chloride liquors of titanium minerals processing industry.

A survey of literature showed that di-(2-ethylhexyl) phosphoric acid (DEHPA) has been widely used for the extraction of vanadium from acidic aqueous solutions [54,171,172]. DEHPA has also been used commercially for the recovery of vanadium from uranium circuits [58]. Biswas *et al.* [173] have reported a solvent extraction method for the recovery of vanadium from heavy oil desulphurisation catalyst using DEHPA as an extractant. However, as compared to dialkyl phosphoric acids, studies on the extraction of vanadium(V) from hydrochloric acid solutions using dialkyl phosphonic or dialkyl phosphinic acids are lacking. Hence in the present study, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) has been explored for the extraction of vanadium(V) from acidic chloride solutions with a view to elucidate the nature of complexes extracted into the organic phase and also to investigate the selectivity between vanadium(V) and other associated multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry. For comparison, the extraction behaviour of vanadium(V) from hydrochloric acid solutions has also been studied using bis(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA) in kerosene as an extractant.

4.1 Experimental

Reagents

2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (Ionquest 801 ≡ EHEHPA), supplied by Albright and Wilson, USA and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272 ≡ BTMPPA) supplied by Cytec, Canada were used as extractants after purification by following the methods described in Chapter 3. Purified kerosene was used as a diluent in the present work.

The preparation of stock solutions of metal ions were described in chapter 2. Freshly prepared solutions of vanadium(V) were used in all the experimental studies to prevent partial reduction to tetravalent vanadium in HCl solutions with respect to time [107]. The initial vanadium concentration was maintained at 1.0×10^{-2} mol/dm^3 in all the extraction studies. All organic phase solutions were prepared by dissolving weighed amounts of EHEHPA or BTMPPA in kerosene, which were then diluted to required volume.

Liquid-liquid extraction procedure

The liquid-liquid extraction and analytical procedures for the determination of metal ions were the same as described in chapter 2. The vanadium-EHEHPA complex was prepared by the procedure described in chapter 3.

4.2 Results and discussion

4.2.1 *Extraction of vanadium(V) from acidic chloride solutions using dialkylphosphonic or phosphinic acids*

Extraction equilibrium

Preliminary experiments showed that the extraction equilibrium of vanadium(V) from hydrochloric acid solutions with EHEHPA or BTMPPA in kerosene as an extractant was attained within 5 min. (Table 4.1). The effect of concentration of EHEHPA (0.05 to 0.4 mol/dm^3) and BTMPPA (0.1 to 0.7 mol/dm^3) on the extraction of vanadium(V) has been studied by keeping the metal ion (0.01 mol/dm^3) and acid (0.1 mol/dm^3) concentrations constant and the results are shown in Fig. 4.1. It is clear from the figure that the extraction of vanadium(V) increases with increase in extractant concentrations. From the slope of plots, log D versus log $[(HX)_2]$, it is inferred that one dimeric molecule of the extractant (HX ≡ EHEHPA or BTMPPA) is involved in the extracted complexes of vanadium(V).

Table 4.1 Effect of phase contact time on the extraction of vanadium(V) (0.01 mol/dm^3). [EHEHPA] = [BTMPPA] = 0.4 mol/dm^3, [HCl] = 0.1 mol/dm^3.

Time, min.	D	
	EHEHPA	BTMPPA
5	6.16	2.14
10	6.15	2.16
15	6.16	2.15
30	6.15	2.15
45	6.17	2.16
60	6.17	2.16

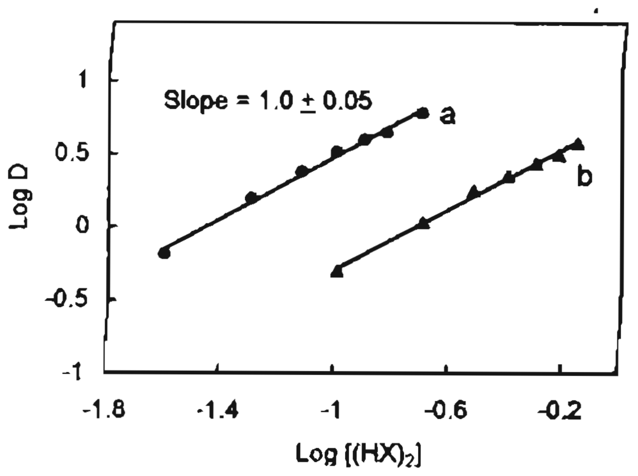


Figure 4.1 Effect of extractant concentration on the extraction of vanadium(V). [V(V)] = 0.01 mol/dm^3, [HCl] = 0.1 mol/dm^3. (a) EHEHPA (b) BTMPPA.

The extraction of vanadium(V) (0.01 mol/dm^3) with EHEHPA (0.4 mol/dm^3) or BTMPPA (0.4 mol/dm^3) as a function of hydrochloric acid concentration and has been studied and the results are depicted in Fig. 4.2. In both the extraction systems, the extraction behaviour showed an inverse dependence with acidity. The plots of log D versus log [H$^+$] gave a slope of -1.0, confirming the formation of the complex, $VO_2X{\cdot}HX$. Nishihama *et al.* [171] and Brunette *et al.* [174] have also reported a cation exchange mechanism for the extraction of vanadium(V) using DEHPA from acidic aqueous solutions.

The effect of metal ion concentration (0.01 to 0.05 mol/dm^3) on the extraction process of vanadium(V) has been investigated using EHEHPA (0.4 mol/dm^3) and BTMPPA (0.4 mol/dm^3) in kerosene as an extractant from 0.5 mol/dm^3 and 0.2 mol/dm^3 hydrochloric acid solutions, respectively. In both the systems, the extraction of vanadium(V) was found to be independent of initial metal ion concentration in the aqueous phase. The log-log plots (Fig. 4.3) of the

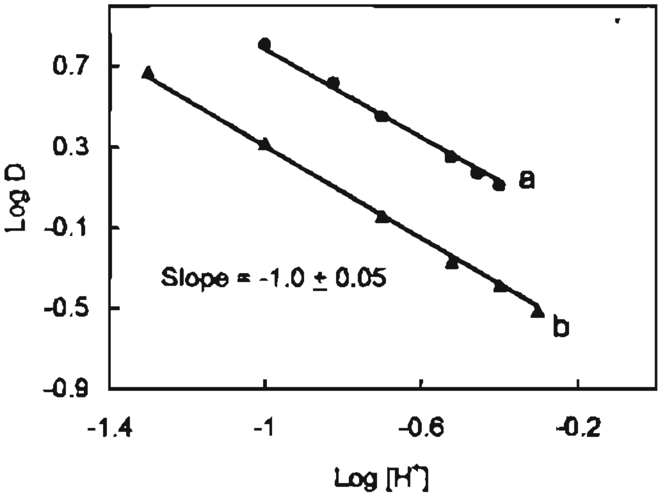


Figure 4.2 Effect of hydrogen ion concentration on the extraction of vanadium(V) (0.01 mol/dm^3) (a) [EHEHPA] = 0.4 mol/dm^3 (b) [BTMPPA] = 0.4 mol/dm^3.

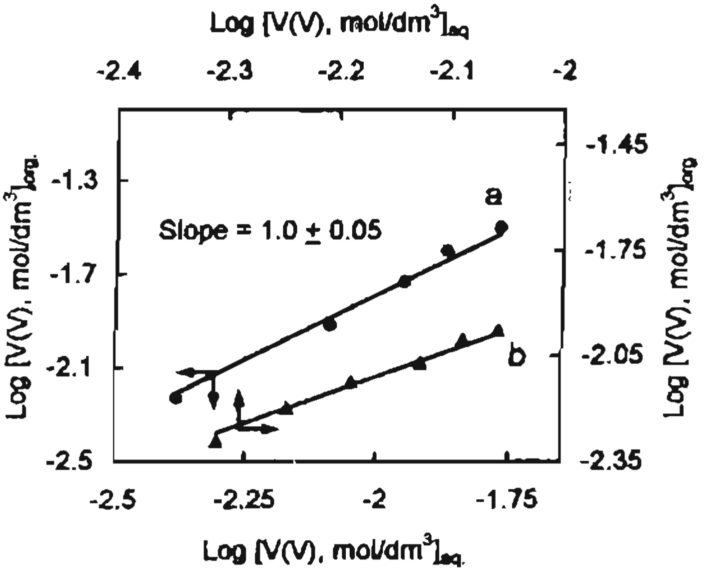


Figure 4.3 Effect of metal ion concentration on the extraction of vanadium(V) (a) [EHEHPA] = 0.4 mol/dm^3, [HCl] = 0.5 mol/dm^3 (b) [BTMPPA] = 0.4 mol/dm^3, [HCl] = 0.2 mol/dm^3.

equilibrium organic phase metal concentration against the aqueous phase metal concentration is linear with a slope of unity indicating the extraction of mononuclear species into the organic phase.

Based on the preceding studies, the extraction for vanadium(V) from hydrochloric acid solutions using EHEHPA or BTMPPA in kerosene as an extractant can be represented as :

$$VO^{+}_{2\,aq} + (HX)_{2\,org} \overset{K_{ex}}{\Leftrightarrow} VO_2X \cdot HX_{org} + H^{+}{}_{aq} \qquad (39)$$

where $(HX)_2$ refers to the dimeric form of EHEHPA or BTMPPA and K_{ex} denotes the equilibrium constant. The equilibrium constants for the extraction of vanadium(V) were calculated from the distribution data and were found to be $K_{ex,EHEHPA} = 3.14$ and $K_{ex,BTMPPA} = 1.01$ for EHEHPA and BTMPPA, respectively. It is clear from these results that the extraction efficiency of vanadium(V) with EHEHPA ($pK_a = 3.42$) is higher than that of BTMPPA ($pK_a = 6.37$), which is in accordance with their pK_a values. Hence, in the subsequent studies, EHEHPA has been chosen as an extractant to investigate the selectivity of vanadium(V) over other associated multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry.

4.2.2 *IR spectra of V(V) - EHEHPA complex*

The IR spectra of EHEHPA and V(V)-EHEHPA complex are shown in Fig. 4.4. In the IR spectra of EHEHPA, the band at 1195 cm^{-1} is due to P=O stretching and the band at 986 cm^{-1} is assigned to P-OH stretch . The absorption bands in the region 1700 - 2700 cm^{-1} correspond to the aggregative P-OH vibrations in the intermolecular hydrogen bonding of EHEHPA in the dimeric form. In the spectra of V(V)-EHEHPA complex, the P=O absorption band at 1195 cm^{-1} shifts by 30 cm^{-1} to a lower frequency; P-OH stretching band at 986 cm^{-1} becomes significantly weaker;

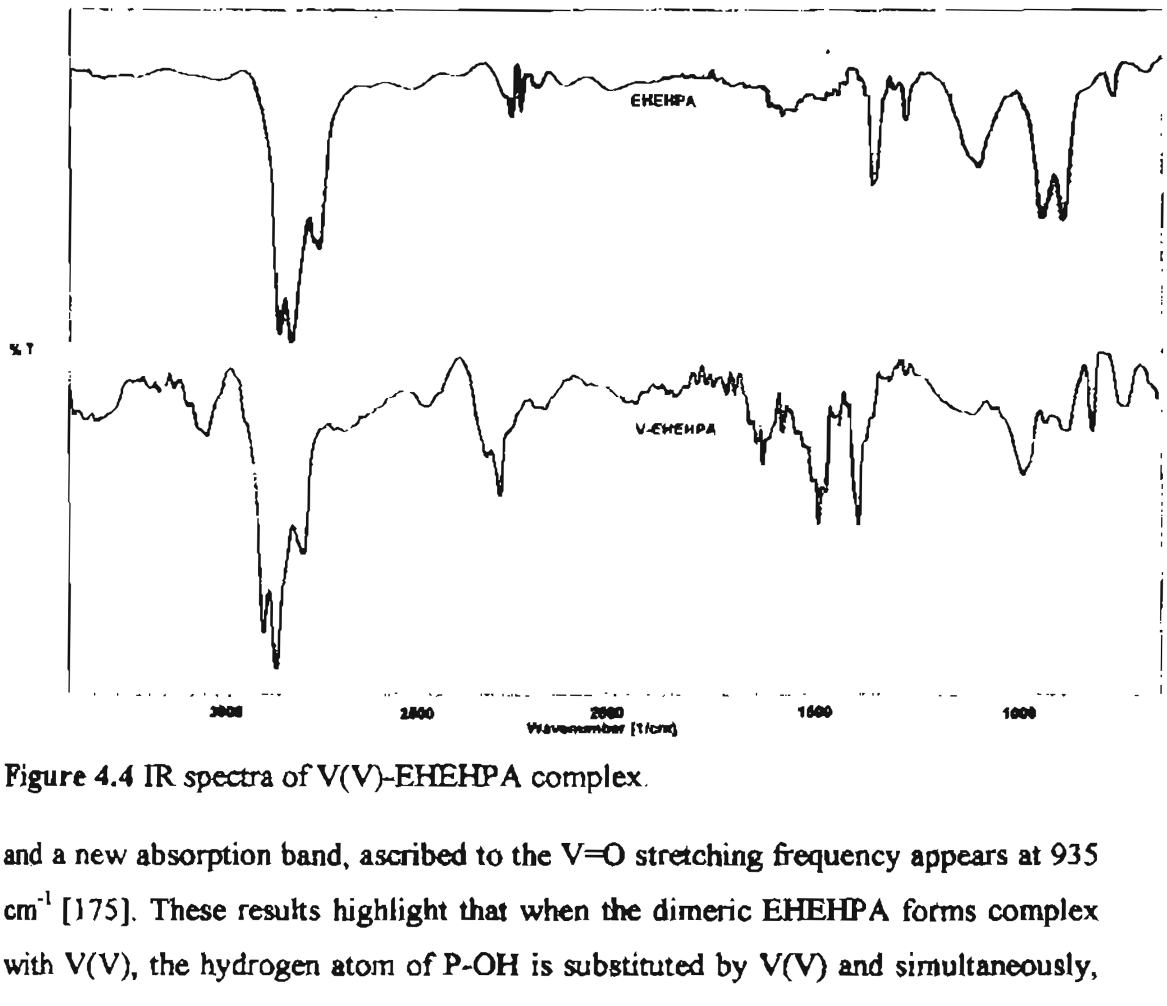


Figure 4.4 IR spectra of V(V)-EHEHPA complex.

and a new absorption band, ascribed to the V=O stretching frequency appears at 935 cm^{-1} [175]. These results highlight that when the dimeric EHEHPA forms complex with V(V), the hydrogen atom of P-OH is substituted by V(V) and simultaneously, the oxygen atom in P=O group takes part in the coordination with V(V). These spectral changes further confirm the cation exchange mechanism as described previously.

4.2.3 *Effect of the nature of diluent on the extraction of vanadium(V)*

The extraction of vanadium(V) from 0.1 mol/dm^3 hydrochloric acid solutions has been studied using 0.4 mol/dm^3 EHEHPA in various diluents (Table 4.2). The results clearly demonstrate that diluents such as benzene, xylene, toluene and kerosene having low dielectric constants shows higher extraction efficiency for vanadium(V). On the other hand, lower extraction was observed with diluents having higher dielectric constant such as methylisobutyl ketone and chloroform. Strong

Table 4.2 Effect of nature of diluent on the extraction of vanadium(V) (0.01 *mol/dm^3). [HCl] = 0.1 mol/dm^3, [EHEHPA] = 0.4 mol/dm^3.*

Diluent	Dielectric constant [166]	D
Methylisobutyl ketone	13.11	1.61
Chloroform	4.90	2.53
Benzene	2.28	3.90
Xylene	2.26	4.22
Toluene	2.24	4.21
Cyclohexane	2.02	5.67
Kerosene	2.00	5.76

interactions of diluent with the extractant can result in lower extraction of metal ions. The interactions of aromatic hydrocarbons with the extractant are stronger than those of non-aromatic hydrocarbons such as cyclohexane. Hence in the present study, the use of diluents such as cyclohexane resulted in higher extraction efficiency for vanadium(V). In view of the commercial availability and high extraction efficiency, in subsequent studies, kerosene has been chosen as the diluent.

4.2.4 *Loading capacity of EHEHPA by vanadium*

Aliquot of 10 cm^3 of 0.4 mol/dm^3 EHEHPA in kerosene was repeatedly extracted at 303 ± 1K for 10 min. with equal volumes of the aqueous phase containing 0.51 g/dm^3 of vanadium(V) in 0.1 mol/dm^3 HCl. The aqueous phases were analysed for vanadium after each stage of extraction and the cumulative vanadium content transferred into the organic phase was calculated. The plot of cumulative vanadium(V) in organic phase per 100 g of EHEHPA versus number of contact stages is presented in Fig. 4.5. It is clear from the figure that the loading capacity of EHEHPA in kerosene for the extraction of vanadium from hydrochloric acid solutions is 2.01g of vanadium(V) per 100 g of EHEHPA.

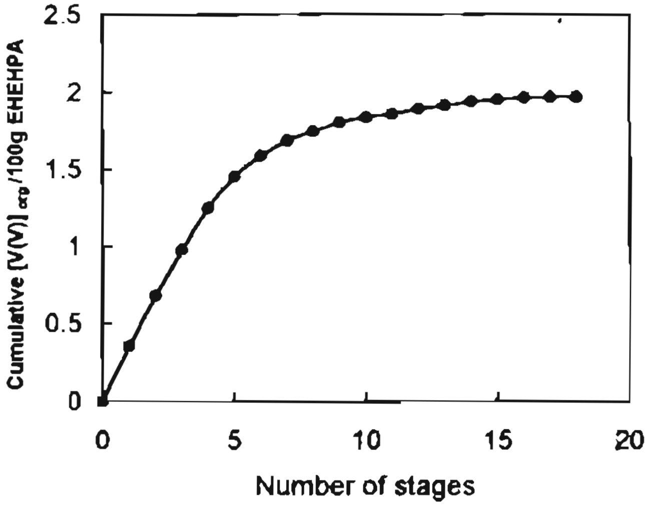


Figure 4.5 Loading capacity of EHEHPA (0.4 mol/dm^3) by vanadium(V). [HCl] = 0.1 mol/dm^3.

4.2.5 ***Extraction and stripping isotherms***

The extraction isotherm for a typical feed solution containing 0.51 g/dm^3 of vanadium(V) and 0.1 mol/dm^3 HCl using 0.5 mol/dm^3 EHEHPA in kerosene as an extractant has been studied and the result is shown in Fig. 4.6. The McCabe-Thiele plot for a feed solution containing 0.51 g/dm^3 of vanadium(V) showed almost quantitative extraction of vanadium(V) in two counter-current stages at an aq. : org. phase ratio of 1:1.

Vanadium(V) stripping from the loaded organic solvent system of 0.4 mol/dm^3 EHEHPA in kerosene containing 0.51 g/dm^3 V(V) has been investigated using various concentrations of HCl and H_2SO_4 as stripping agents (Fig. 4.7). It is clear from the results that H_2SO_4 is a better stripping agent for vanadium(V) than HCl. A McCabe-Thiele plot (Fig. 4.8) for a loaded organic phase (0.5 mol/dm^3 EHEHPA) containing 0.51 g/dm^3 of vanadium(V) showed that quantitative stripping is possible using 0.4 mol/dm^3 H_2SO_4 as a stripping agent in four counter-current stages with an org. : aq. phase ratio of 1:2.

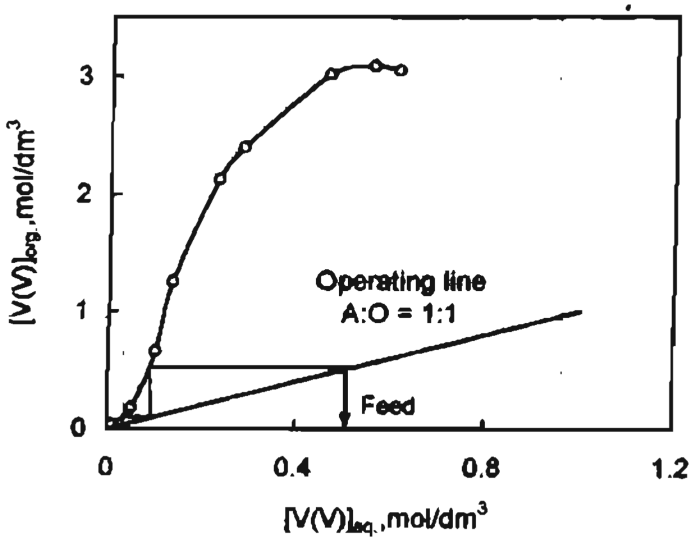


Figure 4.6 McCabe-Thiele plot for vanadium(V) extraction. [V(V)] = 0.51 g/dm^3, HCl = 0.1 mol/dm^3, EHEHPA = 0.5 mol/dm^3.

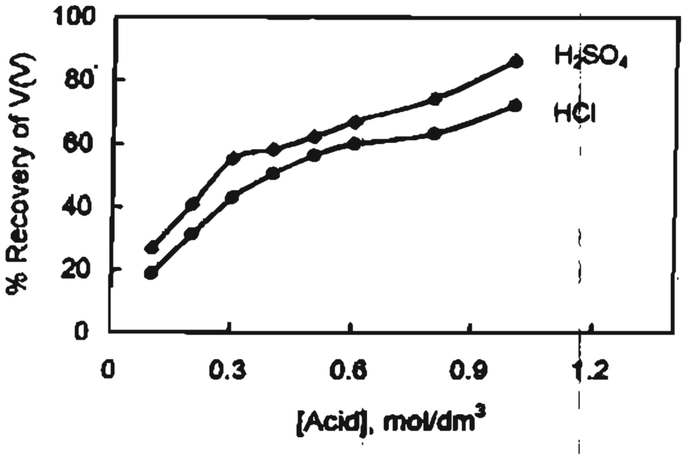


Figure 4.7 Stripping of vanadium(V) from loaded EHEHPA (0.4 mol/dm^3) with H_2SO_4 and HCl.

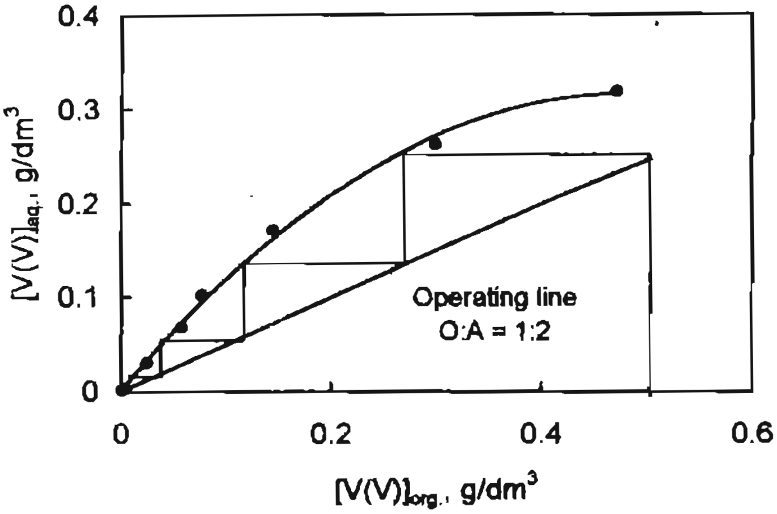


Figure 4.8 McCabe-Thiele plot for vanadium(V) stripping. $[V(V)]_{org}$ = 0.51 g/dm^3, $[H_2SO_4]$ = 0.4 mol/dm^3.

4.2.6 *Recycling capacity of EHEHPA*

Studies on the recycling capacity of EHEHPA for the extraction of vanadium(V) were carried out by first loading the organic phase with vanadium(V) and then stripping with 0.4 mol/dm^3 H_2SO_4. The stripped organic phase was then used for extraction. The results revealed practically insignificant change in the efficiency of the extractant upto ten cycles of extraction (Fig. 4.9).

4.2.7 *Selective separation of vanadium(V) from multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry*

The extraction of vanadium(V) (0.01 mol/dm^3) and other associated metal ions *viz.*, magnesium(II) (0.01 mol/dm^3), aluminium(III) (0.01 mol/dm^3), titanium(IV) (0.01 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.01 mol/dm^3) and iron(III) (0.01 mol/dm^3) present in the waste chloride liquors of titanium minerals processing industry has been investigated as a function of hydrochloric acid concentration using 0.5 mol/dm^3 EHEHPA in kerosene (Fig. 4.10).

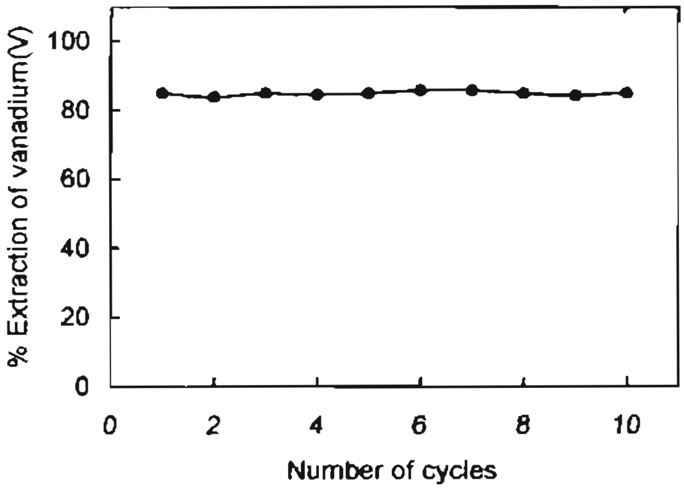


Figure 4.9 Recycling capacity of EHEHPA. [EHEHPA] = 0.4 mol/dm^3, [HCl] = 0.1 mol/dm^3.

It is clear from the figure that titanium(IV) and iron(III) are co-extracted with vanadium(V). On the other hand, magnesium(II), aluminium(III) chromium(III) and manganese(II) are not extracted under the present experimental conditions.

To develop a selective separation method for the recovery of vanadium(V) from the loaded organic phase, the stripping behaviour of vanadium(V), titanium(IV) and iron(III) (0.5 mol/dm^3 EHEHPA loaded with 0.01 mol/dm^3 metal ion) has been investigated using H_2SO_4 as a stripping agent (Fig. 4.11). These results show that vanadium(V) can be easily recovered from the loaded organic phase using dilute H_2SO_4 (0.1 - 1.0 mol/dm^3) whereas the stripping of iron(III) requires higher concentrations of H_2SO_4 (1.0 - 4.0 mol/dm^3). On the other hand, the stripping of titanium(IV) was found to be negligible under these conditions. Thus, vanadium(V) can be selectively separated from a loaded organic phase containing iron(III) and titanium(IV) with 0.4 mol/dm^3 H_2SO_4 as a stripping agent in four stages. Subsequently, the iron(III) can be recovered using 4 mol/dm^3 H_2SO_4 in two stages.

Finally, titanium(IV) can be quantitatively stripped from the loaded phase using a mixture of 2 mol/dm^3 H_2SO_4 and 2 % H_2O_2 in two stages.

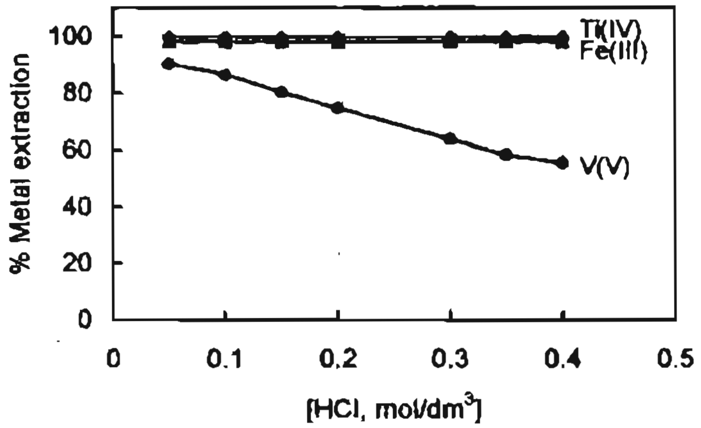


Figure 4.10 Extraction behaviour of titanium(IV), vanadium(V), and iron(III) using EHEHPA (0.5 mol/dm^3) in kerosene from hydrochloric acid solutions. [Metal ion] = 0.01 mol/dm^3.

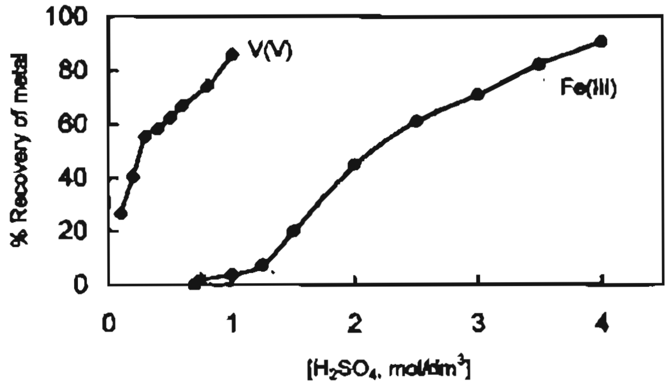


Figure 4.11 Stripping behaviour of vanadium(V), iron(III) and titanium(IV) from loaded EHEHPA (0.5 mol/dm^3) phase using H_2SO_4.

Based on the above results a simulated waste chloride liquor consisting of magnesium(II) (0.01 mol/dm^3), aluminium(III) (0.01 mol/dm^3), titanium(IV) (0.01 mol/dm^3), vanadium(V) (0.01 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.01 mol/dm^3) and iron(III) (0.01 mol/dm^3) present in the waste chloride liquors of titanium minerals processing has been prepared and subjected to two stages of solvent extraction using 0.5 mol/dm^3 EHEHPA in kerosene as an extractant (aq. : org. = 1:1). The schematic diagram of the process and typical results are shown in Fig 4.12 and Table 4.3, respectively. It is clear from the results that vanadium(V) can be selectively recovered from a multivalent metal chloride waste generated during the manufacture of titanium dioxide by the chloride route using 0.5 mol/dm^3 EHEHPA in kerosene as an extractant.

Table 4.3 Extraction of vanadium(V) using 0.5 mol/dm^3 EHEHPA from simulated waste chloride liquor.

Metal Ion	Amount of metal ion (mol/dm^3)		Stripping agent (no. of stages)	Recovery (%)
	Feed	Raffinate		
Fe(III)	0.01	N.D.*	4 mol/dm^3 H_2SO_4 (2 stages, O:A=1:1)	99.9
Mg(II)	0.01	0.01	-	-
Al(III)	0.01	0.01	-	-
Ti(IV)	0.01	N.D.	2 mol/dm^3 H_2SO_4+2% H_2O_2 (2 stages,O:A=1:1)	99.9
V(V)	0.01	N.D.	0.4 mol/dm^3 H_2SO_4 (4 stages, O:A=1:2)	99.9
Cr(III)	0.01	0.01	-	-
Mn(II)	0.01	0.01	-	-

*N.D. - not detectable

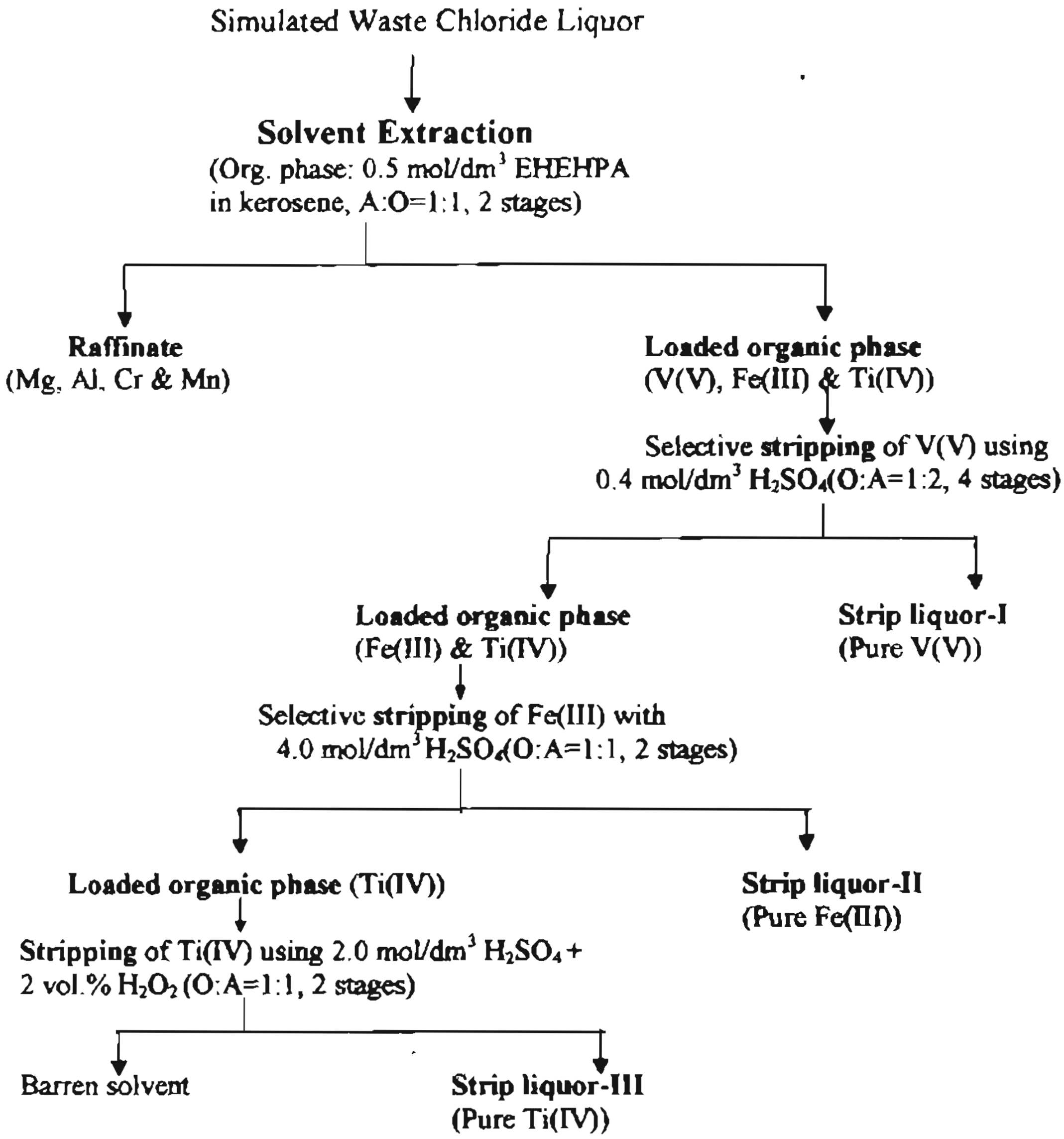


Figure 4.12 Separation scheme for the recovery of vanadium(V) from simulated titania waste chloride liquor.

Conclusions

The management of the waste acidic chloride liquors from the titanium minerals processing industry containing heavy metals represents a major environmental issue in many industrialised countries. Pyrohydrolysis of the spent acid used to recover the mineral acid generates impure iron oxide containing several other metallic oxides which is not marketable and hence resulting as a solid waste. Further, many valuable metal species have not been recovered for potential use. Selective separation and recovery of valuable metal ions from these wastes is important in the context of increasing demand for high purity products and also due to environmental concerns. 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. This thesis embodies the results of the investigation carried out with an objective to develop selective solvent extraction procedures by employing various commercially available extractants for the recovery of metal ions such as iron(III), titanium(IV) and vanadium(V), based on their value and concentrations in the waste chloride liquor.

The solvent extraction behaviour of iron(III), magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III) and manganese(II) has been investigated from hydrochloric acid solutions using a mixed solvent system consisting of tributylphosphate (TBP) and methylisobutyl ketone (MIBK). The results demonstrate that iron(III) is extracted as $HFeCl_4$ with 2 moles of the solvent. On the other hand, magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III) and manganese(II) were found to be not extracted with 70 vol.% TBP and 30 vol.% MIBK from 2 mol/dm^3 hydrochloric acid solutions. The present investigations clearly indicate that high purity iron(III) chloride can be selectively recovered from titania waste chloride liquor through a solvent extraction process using a mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK. Further, the problems associated with TBP and MIBK (third phase formation, poor phase disengagement etc.) when used individually for the extraction of iron(III) could be overcome by employing the mixed solvent system. The two solvents, when used together were also found to exert a small synergistic enhancement in the extraction of iron(III). The developed solvent extraction procedure using the mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK was applied to the recovery of high purity iron(III) chloride from the waste chloride liquors obtained from titanium minerals processing industry. The extraction process comprises the steps of (i) chlorination of the waste chloride liquor and adjustment of feed acidity, (ii) selective extraction of high purity iron(III) chloride from the chlorinated waste chloride liquor in three stages of countercurrent extraction (aq. : org. = 1:2) using the mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK and (iii) stripping of the loaded organic phase using distilled water of pH = 2.0 in three stages (aq. : org. = 3:2) to recover high purity iron(III) chloride. The present study reveals that the above mixed solvent system can be used for the recovery of iron(III) chloride (99.9% purity) with an yield of >99% from the waste chloride liquors of titanium minerals processing industry. By converting ferric chloride into iron oxides of various purities by known methods such as pyrohydrolysis/spray roaster process, applications will be found in the pigment and electronic industries. Further, ferric chloride may also find potential application as a flocculating agent in the water purification.

Cyanex 923 (TRPO), a mixture of four trialkylphosphine oxides has also been explored as an extractant for iron(III) from acidic chloride solutions with a view to elucidate the nature of the complexes extracted into the organic phase and also to investigate the selectivity of iron(III) over other associated multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry. The species extracted into the organic phase appears to be as $HFeCl_4 \cdot 2TRPO$. For comparison, extraction of iron(III) has also been investigated from hydrochloric acid solutions using trioctylphosphine oxide (TOPO) in xylene as an extractant and observed a similar extraction behaviour for iron(III). Further, it is clear from the results that the extraction efficiency of iron(III) with TRPO is almost equal to that of TOPO, which is in accordance with their basicity values (K_H = nitric acid uptake constant, $K_{H,TRPO} = 8.5$, $K_{H,TOPO} = 8.9$). The extraction behaviour of iron(III) has also been compared with that of other associated metal ions *viz.*, magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II) and iron(II) present in the waste chloride liquors of titanium minerals processing industry. The results demonstrate that metal ions such as titanium(IV) and iron(II) were found to be co-extracted with iron(III). On the other hand, magnesium(II), aluminium(III), chromium(III), vanadium(V) and manganese(II) were found to be not extracted under the present experimental conditions. From the above studies, it can be concluded that TRPO provides poor selectivity for iron(III) due to the co-extraction of titanium(IV).

The extraction behaviour of titanium(IV) from hydrochloric acid solutions has been investigated using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) in kerosene as an extractant. For comparison, extraction studies have also been performed with dialkylphosphinic acids namely, bis(2,4,4-trimethyl pentyl)phosphinic acid (BTMPPA) and bis(2,4,4-trimethylpentyl) monothiophosphinic acid (BTMPTPA). The extraction data have been analysed by both graphical and theoretical methods by taking into account complexation of metal ion in the aqueous phase with inorganic ligands and all plausible complexes extracted into the organic phase. The results demonstrate that the extraction of titanium(IV) follows the usual cation exchange mechanism (HX ≡ EHEHPA or BTMPPA or BTMPTPA):

$$TiO^{2+}_{aq} + 2(HX)_{2_{org}} \overset{K_{ex}}{\Leftrightarrow} TiO(HX_2)_{2_{org}} + 2H^{+}_{aq}$$

The nature of the extracted complexes were further confirmed by IR spectral studies. The equilibrium constant of the extracted complexes has been deduced by non-linear regression analysis with the aid of suitable chemically based models developed. The equilibrium constant values for the extraction of titanium(IV) with various acidic organophosphorus extractants have been compared with their pK_a values. It can be concluded from these comparisons that the extraction efficiency of titanium(IV) with various acidic organophosphorus extractants increases in the order : BTMPTPA (pK_a = 5.63) < BTMPPA (pK_a = 6.37) < EHEHPA (pK_a = 3.42) < DEHPA (pK_a = 1.72). Further, it is also clear from these comparisons that log K_{ex} values increases as pK_a value decreases with an exception in the case of BTMPTPA. This means that BTMPTPA would have a higher affinity towards metal ions than BTMPPA in the cationic exchange reaction since P-OH group plays a dominant role in such a reaction. However, contrary to the above expectation, in the present study, BTMPTPA gives significantly lesser extraction for titanium(IV) than that of BTMPPA. This can be attributed to the fact that the P=S group of BTMPTPA forms a weaker complex with titanium(IV) than the P=O group of BTMPPA. This is in good agreement with the principle of HSAB concept, which indicates that sulphur is a weaker ligand than oxygen for hard lewis acid like titanium. The loading capacitites of the extractants have been determined and found to be 5.92 g of titanium per 100 g of EHEHPA and 6.1 g of titanium per 100 g of BTMPPA. These loading capacities are comparable to that of DEHPA (7.31 g of titanium per 100 g of

DEHPA). The effect of the nature of diluent on the extraction process of titanium(IV) has also been investigated and correlated with their dielectric constants. The results clearly demonstrate that the extraction of titanium(IV) varies with the nature of the diluent. Diluents such as kerosene having low dielectric constant show higher extraction efficiency for titanium(IV). The extraction behaviour of titanium(IV) and other associated multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry has also been investigated as a function of hydrochloric acid concentration using EHEHPA or BTMPPA as an extractant. The results clearly show that none of the associated metal ions were found to be co-extracted with titanium(IV) into the organic phase at about 2.0 mol/dm^3 HCl. Based on these results, a simulated waste chloride liquor consisting of magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II) and iron(III) in 2.0 mol/dm^3 HCl has been prepared and subjected to solvent extraction using 0.5 mol/dm^3 EHEHPA in kerosene as an extractant. It is clear from the results that titanium(IV) can be selectively separated from multivalent metal chloride solutions in a single stage leaving behind all the other metal ions in the raffinate stream. Subsequently, titanium(IV) can be recovered quantitatively from the loaded organic phase in a single stage of stripping using a mixture consisting of 2 mol/dm^3 H_2SO_4 and 2% H_2O_2 as a stripping agent. Thus, it can be concluded from these investigations that EHEHPA can be used as a potential extractant for the selective recovery of titanium(IV) from the waste chloride liquors of titanium minerals processing industry.

The extraction equilibrium of vanadium(V) from acidic chloride solutions has been investigated using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) in kerosene as an extractant. The extraction of vanadium(V) follows the usual cation exchange mechanism and this has been further confirmed with the aid of IR spectral studies. For comparison, the extraction studies have also been performed with bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA). It is clear from these results that the extraction efficiency of vanadium(V) with EHEHPA is higher than that of BTMPPA, which is in accordance with their pK_a values. The effect of the nature of diluent on the extraction of vanadium(V) from hydrochloric acid solutions has been studied and correlated with their dielectric constants. The results clearly highlight that diluents such as benzene, xylene, toluene and kerosene having low dielectric constant show higher extraction efficiency for vanadium(V). On the other hand, lower extraction efficiency has been observed with diluents having higher dielectric constants such as methylisobutyl ketone and chloroform. The loading capacity studies indicate that 2.0 g of vanadium can be loaded to 100 g of EHEHPA. The results on the recycling capacity experiment of EHEHPA reveal practically insignificant change in the efficiency of the extractant even after ten cycles of extraction. The McCabe-Thiele plot for a feed solution containing 0.51 g/dm^3 of vanadium(V) and 0.5 mol/dm^3 HCl showed almost quantitative extraction of vanadium(V) in two counter current stages at an aq. : org. phase ratio of 1:1 using 0.5 mol/dm^3 EHEHPA in kerosene as an extractant. The stripping isotherm highlights that 0.51 g of vanadium in the loaded organic phase can be recovered quantitatively in four counter current stages with an org. : aq. phase ratio of 1:2 using 0.4 mol/dm^3 H_2SO_4 as a stripping agent.

The extraction behaviour of vanadium(V) and other associated metal ions *viz.*, magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II) and iron(III) present in the waste chloride liquors of titanium minerals processing industry has also been studied and found that titanium(IV) and iron(III) are co-extracted with vanadium(V). On the other hand, magnesium(II), aluminium(III), chromium(III) and manganese(II) were found to be not extracted under the present experimental conditions. To develop a selective separation method for the recovery of vanadium from the loaded organic phase, the stripping behaviour of vanadium(V), titanium(IV) and iron(III) has been investigated using H_2SO_4 as a stripping agent. The results show that vanadium(V) can be easily recovered from the loaded organic phase using dil. H_2SO_4 (0.1 to 1.0 mol/dm^3), whereas the stripping of iron(III) requires higher concentration of H_2SO_4 (1.0-4.0 mol/dm^3). On the other hand, the stripping of titanium(IV) has been found to be negligible under these conditions. Thus, this study clearly demonstrate that 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester can be used as an extractant for the extraction and separation of vanadium(V) from multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry.

Based on the above investigations, a separation scheme has been proposed for the recovery of iron(III), titanium(IV) and vanadium(V) from the waste liquors of titanium minerals processing industry in a two step solvent extraction process (Fig. 5.1). In the solvent extraction process I, iron(III) chloride can be selectively recovered using the mixed solvent system consisting of 70 vol.% TBP and 30 vol.% MIBK leaving behind all other multivalent metal ions in the raffinate (no. of stages of extraction = 3, aq. : org.=1:2, no. of stages of stripping = 3, org. : aq.=2:3). The raffinate from the solvent extraction process I, after selective recovery of iron(III) chloride can be subjected to solvent extraction process II to recover titanium(IV) and vanadium(V) using 0.5 mol/dm^3 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester in kerosene as an extractant (0.1 mol/dm^3 HCl, no. of stages = 2, aq. : org.=1:1). Titanium(IV) and vanadium(V) were found to be co-extracted into the organic phase leaving behind magnesium(II), aluminium(III), chromium(III) and manganese(II) in the raffinate stream of solvent extraction process II. Vanadium(V) can be selectively stripped from the loaded organic phase using 0.4 mol/dm^3 H_2SO_4 as a stripping agent leaving behind titanium(IV) in the organic phase (no. of stages = 4, org. : aq.=1:2). Subsequently, titanium(IV) can be removed from the loaded organic phase using a mixture of H_2SO_4 and H_2O_2 as stripping agent (no. of stages =

2, org. : aq. =1:1). Thus, this study clearly demonstrate that iron(III), titanium(IV) and vanadium(V) can be selectively recovered from the waste liquors obtained from titanium minerals processing industry in a two step solvent extraction process.

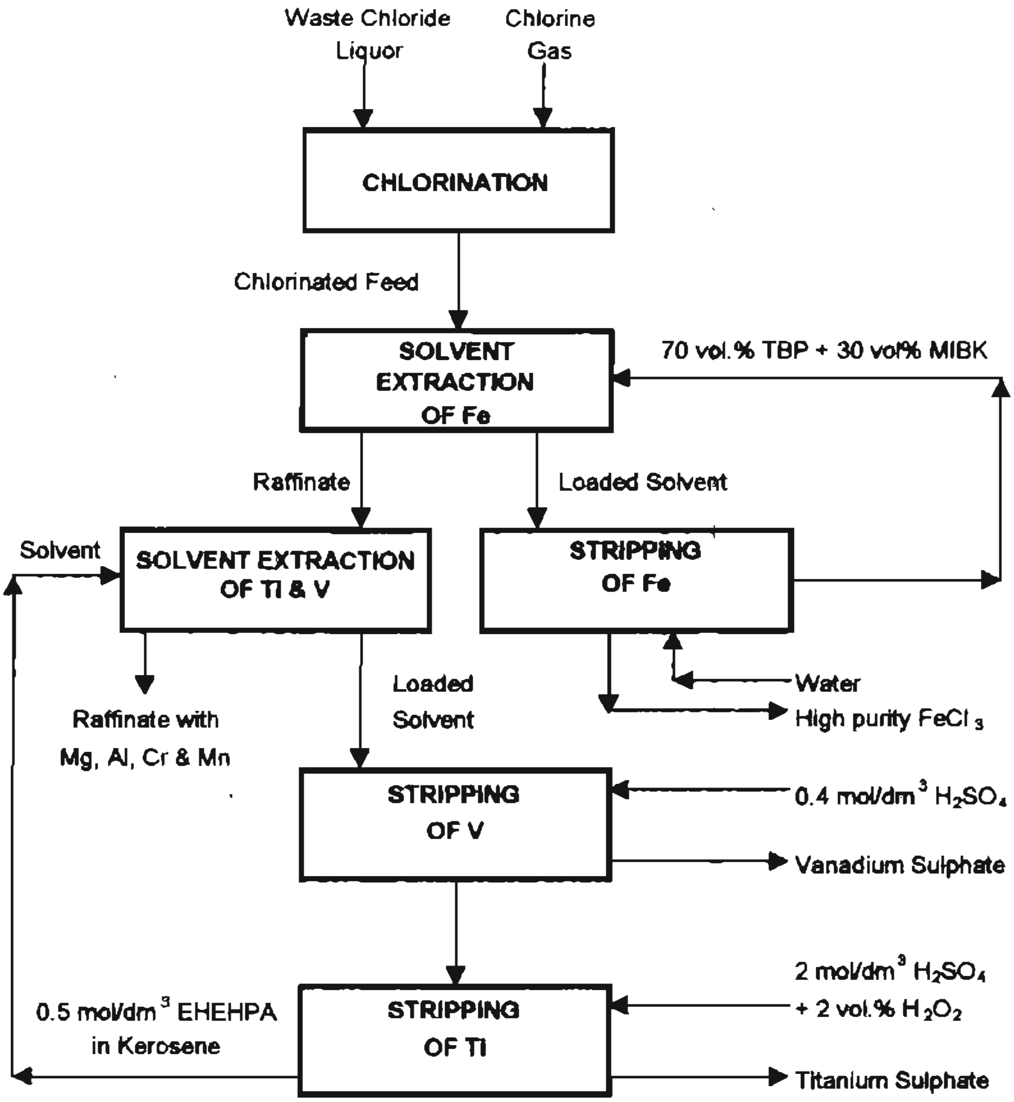


Figure 5.1 Schematic flow diagram for the two step solvent extraction process.

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