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/dm³) 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 FeCl₃·H₂O in concentrated hydrochloric acid and diluted to 1 dm³ with distilled water. Titanium(IV) solutions were prepared from TiCl₄ (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 dm³ with distilled water. Stock solutions of magnesium(II), aluminium(III), chromium(III) and manganese(II) were prepared by dissolving 12.32 g of MgSO₄·7H₂O, 18.75 g of Al(NO₃)₃·9H₂O, 25 g of CrK(SO₄)₃·12H₂O and 8.45 g of MnSO₄·H₂O in 1 dm³ 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 SnCl₂ reduction–K₂Cr₂O₇ titration method [154]. Iron(III) in the analyte is reduced to iron(II) by the addition of 5% SnCl₂ solution at 90°C. The excess SnCl₂ was removed by adding 10% HgCl₂ and the ferrous iron was estimated by titrating with standard K₂Cr₂O₇ (0.1 N) solution using diphenylamine-4-sulphonic acid (0.01% in conc. H₂SO₄) 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% hydroxyl ammonium chloride and complexed with 1,10-phenanthroline (0.25%) in sodium acetate buffer (0.2 mol/dm³) 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 H₂O₂ complexes in 1.0 mol/dm³ 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/dm³ H₂SO₄ 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 ZnSO₄ 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/dm³ iron(III) chloride and 2 mol/dm³ 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. $[\text{FeCl}_3] = 1.0 \text{ mol/dm}^3$, $[\text{HCl}] = 2.0 \text{ mol/dm}^3$.

<table>
<thead>
<tr>
<th>Concentration of solvent (volume %)</th>
<th>Distribution ratio for iron(III) extraction (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.72</td>
</tr>
<tr>
<td>70</td>
<td>0.88</td>
</tr>
<tr>
<td>80</td>
<td>1.07</td>
</tr>
<tr>
<td>90</td>
<td>1.40</td>
</tr>
<tr>
<td>100</td>
<td>1.73</td>
</tr>
<tr>
<td>MIBK</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>negligible</td>
</tr>
<tr>
<td>20</td>
<td>negligible</td>
</tr>
<tr>
<td>30</td>
<td>negligible</td>
</tr>
<tr>
<td>40</td>
<td>negligible</td>
</tr>
<tr>
<td>TBP:MIBK (mixture)</td>
<td></td>
</tr>
<tr>
<td>70:30</td>
<td>1.18</td>
</tr>
<tr>
<td>75:25</td>
<td>1.33</td>
</tr>
<tr>
<td>80:20</td>
<td>1.40</td>
</tr>
<tr>
<td>85:15</td>
<td>1.56</td>
</tr>
<tr>
<td>90:10</td>
<td>1.73</td>
</tr>
</tbody>
</table>
Chapter 2

Figure 2.1 Effect of TBP concentration on the extraction of iron(III). (a) TBP-isodecanol-kerosene system (b) TBP + MIBK system. Aq. phase: [FeCl₃] = 1 mol/dm³, [HCl] = 2 mol/dm³.

**Effect of hydrochloric acid concentration**

The extraction behaviour of iron(III) (1 mol/dm³), magnesium(II) (0.05 mol/dm³), aluminium(III) (0.03 mol/dm³), titanium(IV) (0.02 mol/dm³), vanadium(V) (0.01 mol/dm³), chromium(III) (0.002 mol/dm³) and manganese(II) (0.03 mol/dm³) 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/dm³ 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.
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:

$$\text{Fe}^{3+}_{aq} + \text{H}^+_{aq} + 4\text{Cl}^-_{aq} + 2\text{S}_{org} \rightleftharpoons \text{HFeCl}_4\cdot2\text{S}_{org}$$  \hspace{1cm} (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); 
[FeCl₃] = 1 mol/dm³, [Cl⁻] = 5 mol/dm³. (b) Effect of chloride ion concentration on 
the extraction of iron(III); [FeCl₃] = 1 mol/dm³, [H⁺] = 2 mol/dm³.

Reddy and Bhaskara Sarma [116] have reported the extracted complex as 
HFeCl₄·3TBP for the iron(III) extraction from HCl solutions using TBP.

2.2.2 Loading capacity of the mixed solvent system

Aliquot of 10 cm³ of the mixed solvent system consisting of 70 vol.% TBP 
and 30 vol.% MIBK was repeatedly contacted at 303 ± 1 K for 10 min. with equal 
Volumes of aqueous phase containing 55.85 g/dm³ iron(III) in 2.0 mol/dm³ 
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)/dm³ of the solvent.
Figure 2.4 Loading capacity of 70 vol.% TBP + 30 vol.% MIBK solvent system for iron(III) extraction. \([\text{HCl}] = 2.0 \text{ mol/dm}^3\).

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

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

\[ 2\text{FeCl}_2 + \text{Cl}_2 (g) \rightarrow 2\text{FeCl}_3 \]  

(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 TiO₂ industry.**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>g/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₂</td>
<td>215.66</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>48.67</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>13.41</td>
</tr>
<tr>
<td>MnCl₂</td>
<td>5.96</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>13.36</td>
</tr>
<tr>
<td>TiOCl₂</td>
<td>0.22</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>0.78</td>
</tr>
<tr>
<td>VOCl₃</td>
<td>1.16</td>
</tr>
<tr>
<td>HCl</td>
<td>33.32</td>
</tr>
</tbody>
</table>
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.*

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount of metal chloride (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>162.240</td>
</tr>
<tr>
<td>TiOCl₂</td>
<td>0.110</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>6.705</td>
</tr>
<tr>
<td>MnCl₂</td>
<td>2.980</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>6.679</td>
</tr>
<tr>
<td>VCl₃</td>
<td>0.579</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>0.396</td>
</tr>
<tr>
<td>HCl</td>
<td>72.9</td>
</tr>
</tbody>
</table>

*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.

\[
\begin{align*}
R_3P &= O \\
R'R' &= O \\
R' &= \text{octyl} \\
R' &= \text{hexyl}
\end{align*}
\]

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 extractant 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]. Triocetylphosphine 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/dm³) on the extraction of iron(III) (3.6×10⁻⁴ mol/dm³) has been investigated using 0.2 mol/dm³ 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). 
\([Fe(III)] = 3.6 \times 10^{-4} \text{ mol/dm}^3, [Cl^-] = 2.0 \text{ mol/dm}^3. \) (b) Effect of chloride ion concentration on the extraction of iron(III), \([H^+] = 1.0 \text{ mol/dm}^3. \text{ Org. ph. : 0.1 mol/dm}^3 \text{ 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\times10^{-4} \text{ mol/dm}^3, [HCl] = 2.0 \text{ 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:

\[
K_{\text{ex,TRPO}} \quad \frac{\text{Fe}^{3+}_{aq} + a\text{H}^+_{aq} + (3 + a)\text{Cl}^-_{aq} + y\text{TRPO}_{org}}{H_a\text{FeCl}_{3+a} \cdot y\text{TRPO}_{org}} \quad (30)
\]

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} \text{ mol/dm}^3, [HCl] = 1.0 \text{ mol/dm}^3, [TRPO] = 0.2 \text{ mol/dm}^3.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>Dielectric constant(ε) [166]</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylisobutyl ketone</td>
<td>13.11</td>
<td>98</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.90</td>
<td>9</td>
</tr>
<tr>
<td>Xylene</td>
<td>2.26</td>
<td>80</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.24</td>
<td>78</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.28</td>
<td>78</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.02</td>
<td>89</td>
</tr>
<tr>
<td>Kerosene</td>
<td>2.00</td>
<td>87</td>
</tr>
</tbody>
</table>

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)]$_{\text{org}} = 3.6 \times 10^{-4} \text{ mol/dm}^3$) 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. $[\text{Fe(III)}]_{\text{org.}} = 3.6 \times 10^{-4} \text{ mol/dm}^3$, $[\text{TRPO}] = 0.2 \text{ mol/dm}^3$ 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) $(3.6 \times 10^{-4} \text{ mol/dm}^3)$, iron(II) $(3.6 \times 10^{-4} \text{ mol/dm}^3)$, magnesium(II) $(1.0 \times 10^{-3} \text{ mol/dm}^3)$, aluminium(III) $(1.0 \times 10^{-3} \text{ mol/dm}^3)$, titanium(IV) $(1 \times 10^{-3} \text{ mol/dm}^3)$, vanadium(V) $(0.25 \times 10^{-3} \text{ mol/dm}^3)$, chromium(III) $(1.0 \times 10^{-3} \text{ mol/dm}^3)$ and manganese(II) $(1.0 \times 10^{-3} \text{ mol/dm}^3)$ 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) ($3.6 \times 10^{-4}$ mol/dm$^3$), iron(II) ($3.6 \times 10^{-4}$ mol/dm$^3$) and titanium(IV) ($1 \times 10^{-3}$ 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.