Solvent Extraction Separation Study of Fe(III) from Sulphate Medium by CYANEX 272 in kerosene

I.M. Ahmed
Hot Laboratories Centre, Atomic Energy Authority, Post Code 13759, Cairo, Egypt

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ABSTRACT

The extraction of Fe(III) with Bis(2,4,4-trimethylpentyl) phosphinic acid, commonly known as CYANEX 272, in kerosene from aqueous sulphate medium was investigated. The extraction was found to increase with extractant and Fe(III) concentration while it decreases with hydrogen ion and sulphate concentration in the aqueous phase. The stoichiometry of the extracted metal species was found to be Fe(HSO$_4$)$_2$. The equilibrium constant and thermodynamic functions of Fe(III) extraction were calculated. Stripping investigations indicated that H$_2$SO$_4$ of concentration (0.5-5 M) is effective for stripping Fe(III). The experimental obtained capacity of CYANEX 272 was found to be 0.2 M Fe(III) per mole extractant after four stages. Results of the effect of temperature indicate that the Fe(III) extraction in the investigated system is endothermic.

Key words: Solvent Extraction, CYANEX 272, Fe(III), sulphate medium.

INTRODUCTION

With the expansion of industrial activities, the selective separation of iron from undesired impurities is an important issue from environmental point of view. The effective recovery of metal ions is possible only if the separation process is sufficiently selective, especially, in small scale industries operating in communal areas, where there is the need to find easy and reliable methods for waste treatment.

Liquid–liquid extraction is a well-known approach for accomplishing the complex separation of metals from multielement solutions. Its use may be of particular advantage in the partitioning of Fe(III) (1). The extraction of Fe(III) has been carried out with several extractants such as versatic acid (2), tri-n-butyl phosphate (TBP) (3), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) (4), di-2-ethylhexyl phosphoric acid (DEHPA) (5,6), octylphenyl acid phosphate (OPAP) (7). Primary amine, Primene JMT were used for extraction of Fe(III) from neutral solutions as well as from solutions containing sulfuric acid (8-10). CYANEX 923 (a mixture of four trialkylphosphine oxides) (11), N,N'-tetrastubstituted malonamides (12-14), 3-phenyl-4-acyl-5-isoxazolones (15), Bis(2,4,4-trimethylpentyl) mono thiophosphinic acid (CYANEX 302) using hollow fibre membrane modules (16), 1-hydroxy-1-phosphono-hexadecyl (and -1-phosphonododecyl) phosphinic acid (17) and a commercial trialkyl amine (ADOGEN 364) (18) were also extensively investigated for its extraction. Miralles et al. (19) have reported the extraction of Fe(III) from nitrate medium by the active component of CYANEX 272 dissolved in Isopar-H (a commercial hydrocarbon) and showed that the extraction ratio decreases appreciably with the change of the anion existing in the aqueous phase, particularly at lower pH regions.

In the present study, CYANEX 272 has been suggested as a potential extractant for the extraction of Fe(III) from sulfate medium and the effect of the different parameters affecting the extraction process and the possibility of selective separation of Fe(III) from other interfering ions is investigated.
EXPERIMENTAL

1. Materials:

Most of the used chemicals are of analytical grade. Iron (III) sulfate, hydrochloric acid, nitric acid and sulfuric acid were obtained from Prolabo. Sodium sulfate and ammonium thiocyanate were products of Merck. Copper, nickel, cobalt, cadmium, chromium (III), chromium (VI) and lead solutions were prepared by dissolving their corresponding sulfate salts in double distilled water and are products of Sigma. The commercial extractant CYANEX 272 was kindly supplied by Cytec Inc. and used without further purification. Odourless kerosene (non-aromatic) was obtained from Misr Petroleum Company, Egypt.

2. Procedure:

The concentration of iron(III) was determined using a Shimadzu UV–VIS, double beam recording spectrophotometer, Model 160-A, Japan, using the thiocyanate method (20). Copper, nickel, cobalt, cadmium and lead were determined by atomic absorption spectroscopy (Thermo). The hydrogen ion concentration in the solutions was adjusted by using reagent grade sulfuric acid and sodium hydroxide and measured using a digital pH meter of Hanna instruments type at the ambient laboratory temperature degree 25±1°C. Batch experiments were carried out by equilibrating equal volumes of 0.15 M CYANEX 272 in kerosene, represented by HA, with 0.02 M Fe(III) in aqueous solution of pH 2.5 in stoppered glass bottles using a thermostated shaking water bath adjusted at 25±1°C. After equilibration and phase separation, a suitable volume of the aqueous phase was spectrophotometrically measured. The concentration of the metal in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after extraction. The distribution ratio D was calculated as the ratio of the concentration of iron(III) in the organic to that in the aqueous phase.

RESULTS AND DISCUSSION

1. Equilibrium investigations:

The effect of shaking time on the extraction of 0.02 M Fe(III) from 1 M Na₂SO₄ solution using 0.15 M CYANEX 272 in kerosene was investigated over the range 2–30 min. The results showed that equilibrium is reached after 15 min.

1.1. The effect of hydrogen ion, CYANEX 272 and sulphate ion concentration:

The effect of hydrogen ion concentration on the extraction of 0.02 M Fe(III) from 1 M Na₂SO₄ solution using 0.15 M CYANEX 272 in kerosene was investigated in the range 3.16×10⁻³-0.1 M. The extraction was found to decrease with the increase in [H⁺]. When log $D$ are plotted against log [H⁺], a straight line of slope -1.7 is obtained which indicates that during extraction two H⁺ are released in the aqueous medium, Fig. 1. Accordingly, pH 2.5 was selected for further investigations. The effect of CYANEX272 concentration on the extraction of 0.02 M Fe(III) from 1 M Na₂SO₄ solution of pH 2.5 was studied by varying its concentration from 0.05 to 0.25 M. The plot of log$D$ against the corresponding log CYANEX 272 concentrations in the organic medium gives a linear relation of slope 2.83 which indicates that three moles of CYANEX 272 participates in the extracted metal species, Fig. 1.

The effect of sulfate ion on the extraction of 0.02 M Fe(III) of pH 2.5 using 0.15 M CYANEX 272 in kerosene was performed over sulfate ion concentration range 0.2–1.0 M. The plot of log $D$
against the corresponding log sulfate ion concentrations in the aqueous medium gives a linear relation of slope -0.8 which indicates that one mole of sulfate ion is released during the extraction process, Fig. 1.

Based on the above experimental results and considering that the predominant Fe(III) species is Fe(HSO₄)₂⁺ (21) and CYANEX 272 is present as a dimer (H₂A₂) in kerosene (22), the extraction reaction may be represented at equilibrium by

\[ \text{Fe(HSO}₄\text{)}₂⁺ + 3\text{(H₂A₂)} \rightleftharpoons \text{Fe(HSO}₄\text{)A₂.2(H₂A₂)} + 2\text{H}⁺ + \text{HSO}₄⁻ \]  

(1)

Then

\[ K_{ex} = \frac{D[\text{H}⁺]²[\text{HSO}₄⁻]}{[\text{H₂A₂}]³} \]  

(2)

The extraction equilibrium was calculated with respect to CYANEX 272 in the range 0.1-0.25 M and pH range 1.0-2.5 and sulfate ion concentration range 0.2-1.0 M and the average value was found to be \((1.41±0.01)\times10²\).

1.2. The effect of initial Fe(III) concentration:

The effect of initial Fe(III) concentration on its extraction by 0.15 M CYANEX 272 in kerosene was studied over the range 0.02-0.2 M from aqueous 1.0 M Na₂SO₄ solution. The obtained data show that the concentration of Fe(III) in the organic phase increases with the increase in the initial Fe(III) concentration up to 0.03M then becomes constant with further increase in the metal concentration, Fig. 2. The inflection in the isotherm suggests that the loading capacity of the solvent (CYANEX 272) is about 0.2 Fe(III) / 1.0 M extractant.
1.3. Loading capacity:

The loading capacity of CYANEX 272 in kerosene was studied by shaking 0.02 M Fe(III) in aqueous solution of 1 M Na$_2$SO$_4$ solution with 0.15 M CYANEX 272 in kerosene at fixed organic to aqueous phase ratio of 1:1; the two phases were separated, Fe(III) concentration was determined, and the same organic phase was used again for the extraction of fresh Fe(III) solution, Fig. 3. This procedure was repeated till no extraction of Fe(III) was obtained with the organic solvent. The concentration of Fe(III) in the organic phase was found to be 0.03 M after 4 extraction stages. The maximum loading is 0.2 M Fe(III) / 1.0 M extractant.
1.4. Effect of temperature:

The effect of temperature on the extraction of 0.02M Fe(III) from 1 M Na$_2$SO$_4$ solution with 0.15 M CYANEX 272 in kerosene was carried out, in the range 15–50 °C. It was observed that the extraction increases with the increase in temperature throughout the studied temperature range. The results shown in Fig. 4 as a function of log $K_{ex}$ against 1/T gives a linear relation of negative slope. From this slope and applying the Van’t Hoff equations$^{(23)}$ the thermodynamic parameters were calculated:

$$\log K_{ex} = -(\Delta H / 2.303RT) + C \quad (3)$$

$$\Delta G = -RT \ln K_{ex} \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

where R is the universal gas constant (8.314 Jmol$^{-1}$ K$^{-1}$), T is the absolute temperature and C is a constant. The enthalpy change ($\Delta H$) and the free energy ($\Delta G$) were found to be 40.46±1.25 kJ mole$^{-1}$ and 10.56±0.35 kJ mole$^{-1}$, respectively. The positive $\Delta H$ value indicates the endothermic character of the process and the positive value of $\Delta G$ indicates that the process is spontaneous while the entropy change($\Delta S$) was found to be 100.33±2.52 J mole$^{-1}$K$^{-1}$ and indicates that the extraction process is more random in nature.

![Fig. (4): Effect of temperature on the extraction of 0.02 M Fe(III) by 0.15 M CYANEX 272 from 1 M Na$_2$SO$_4$ solution; pH = 2.5; (O/A) = 1](image)

1.5 Effect of phase ratio:

The effect of phase ratio on the extraction of 0.02 M Fe(III) from 1 M Na$_2$SO$_4$ solution by 0.15 M CYANEX 272 in kerosene at pH 2.5 was investigated at different (O/A) phase ratios in the range 0.2 – 1.0. The values of the obtained extraction percentage of Fe(III) plotted against the
corresponding phase ratios and shown in Fig. 5 indicate that the extraction percentage of Fe(III) increases with the phase ratio and reaches 98% at O/A = 2.

![Graph showing the effect of the phase ratio (O/A) on the extraction of Fe(III) by Cyanex 272 from Na₂SO₄ solution.](image)

**Fig. (5):** Effect of the phase ratio (O/A) on the extraction of 0.02 M Fe(III) by 0.3 M Cyanex 272 from 1 M Na₂SO₄ solution; pH = 2.5; (O/A) = 1; T = 25 °C.

1.6. Stripping of Fe(III) from loaded organic phase:

The stripping investigations were carried out using different concentrations of H₂SO₄, HCl and HNO₃ in the range (0.5-5.0 M) to choose a suitable stripping agent that can strip Fe(III) from the loaded CYANEX 272 in kerosene solution. The relation between the strippant concentration and the stripping percent of Fe(III) from the organic phase is tabulated in Table 1. The tabulated data indicate that H₂SO₄ can strip Fe(III) from the loaded CYANEX 272 successfully.

**Table (1):** The relation between the strippant concentration and the stripping Percent after extraction of Fe(III) by Cyanex 272

<table>
<thead>
<tr>
<th>Stripping agent</th>
<th>Stripping Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-5 M H₂SO₄</td>
<td>99</td>
</tr>
<tr>
<td>0.5 M HNO₃</td>
<td>76</td>
</tr>
<tr>
<td>1.0 M HNO₃</td>
<td>70</td>
</tr>
<tr>
<td>3.0 M HNO₃</td>
<td>67</td>
</tr>
<tr>
<td>5.0 M HNO₃</td>
<td>65</td>
</tr>
<tr>
<td>0.5 M HCl</td>
<td>50</td>
</tr>
<tr>
<td>1.0 M HCl</td>
<td>46</td>
</tr>
<tr>
<td>3.0 M HCl</td>
<td>40</td>
</tr>
<tr>
<td>5.0 M HCl</td>
<td>36</td>
</tr>
</tbody>
</table>

1.7. Application studies to electroplating:

In electroplating process, iron(III) beside undesirable impurities (including iron, copper, cadmium, lead, zinc, cobalt, aluminum, organic, etc.) are found with chromium(VI). Such impurities could accumulate during the deposition process and lead to a solution of unacceptable quality;
moreover, these impurities reduce the cathode current efficiency and the bath conductivity and consequently the spent plating solution have to be replaced.

In this respect, preliminary investigations were carried out on the feasibility of recovery of Fe(III) from some metal ions namely, Co(II), Cu(II), Cd(II), Pb(II), Cr(III), Cr(VI) and Ni(II) which may be found as impurities with Cr(VI) in the electroplating process. In this respect, 10 mL Aliquot of the 0.02 M Fe(III) solution containing 5.0×10^{-3} M of Co(II), Cu(II), Cd(II), Pb(II) Cr(III), Cr(VI) and Ni(II) at pH 2.5 were shaken with 10 mL of 0.15 M CYANEX 272 in kerosene. After equilibration and phase separation, the concentration of the cations was determined by atomic absorption spectrophotometry. The extraction percent of Fe (III) decreased from 82% to 75% while the extraction percent of Co(II), Cu(II), Cd(II), Pb(II), Cr(III), Cr(VI) and Ni(II) was less than 3% giving separation factors for Fe(III) from these ions of 200, 240, 150, 290, 270, 250, 285 and 300 respectively.

Table 2 compares the data between some studies on the extraction of Fe(III) from sulfate solutions reported in literature and the results obtained in this study. It is clear that the extraction of Fe(III) by neutral and basic extractants at high acid concentration gives higher loading capacity compared with acidic extractants. The present work has higher loading capacity at higher pH.

Table (2). Comparison between some studies and this work.

<table>
<thead>
<tr>
<th>Work</th>
<th>Extractant</th>
<th>[H+]</th>
<th>Media</th>
<th>Loading capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y. El-Nadi, N. El-Hefny</td>
<td>HDEHP</td>
<td>pH =1.0</td>
<td>H_2SO_4</td>
<td>0.016M</td>
</tr>
<tr>
<td>F. Principe, G. Demopoulos</td>
<td>OPAP</td>
<td>0.5M</td>
<td>H_2SO_4</td>
<td>0.30M</td>
</tr>
<tr>
<td>A. Agrawal et al.,(24)*</td>
<td>Trialalklyphosphine oxide (CYANEX 923)</td>
<td>0.5M</td>
<td>H_2SO_4</td>
<td>0.93M</td>
</tr>
<tr>
<td>P. Nekovar et al.,(25)</td>
<td>Primene JMT</td>
<td>1.8M</td>
<td>H_2SO_4</td>
<td>0.50M</td>
</tr>
<tr>
<td>F.J.Alguacil and S. Amer (26)</td>
<td>Primene81R</td>
<td>0.2M</td>
<td>H_2SO_4</td>
<td>0.12M</td>
</tr>
<tr>
<td>Present work</td>
<td>CYANEX 272</td>
<td>pH=2.5</td>
<td>H_2SO_4</td>
<td>0.20M</td>
</tr>
</tbody>
</table>

* The composition of the aqueous feed used was 60.88 g/L Fe(III), 53 g/L acid, 40% CYANEX923. Extraction was carried in four contacts at O/A ratio = 1

Further, a synthetic electroplating solution containing 1.25g/L iron(III) and 95.4 g/L chromium(VI) in 0.1M sulphuric acid (27) was used as feed solution and the pH of this solution was adjusted to 2.5, shaken with 0.3M CYANEX 272 in kerosene at phase ratio (O/A) = 1 for 15 min. After separating the phases, the extraction step was repeated twice. The organic phase containing iron(III) was stripped with 0.5 M H_2SO_4 solution in one stage. It is worth to mention that chromium(VI) at pH 2.0-6.0 is found as bichromate and dichromate(28) which are poorly extracted by CYANEX 272(29) (its extraction reaches 1.5%). The electroplating solution containing chromium was highly purified from Fe(III) by the proposed system with a purification percent not less than 99.9%.

CONCLUSION

The method described herein brings forth the potential use of CYANEX 272 as extractant for the extraction of Fe(III). The extraction was found to increase with extractant and Fe(III) concentration and temperature while it decreases with hydrogen ion and sulfate concentration of the aqueous phase. The extraction process was found to be endothermic and stripping investigations indicate that H_2SO_4 concentration (0.5-5 M) are effective for stripping Fe(III) from the loaded organic solution. The loading capacity of CYANEX 272 was found to be 0.2 M Fe(III) per mole extractant.
The investigation shows the feasibility of recovery of Fe(III) from some metal ions namely Co(II), Cu(II), Cd(II), Pb(II) and Ni(II). The data obtained shows the feasibility of using CYANEX272 in purification of electroplating solution.

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