# STUDIES ON EXTRACTION OF IRON(III) USING PHOSPHONIUM AND AMMONIUM IONIC LIQUIDS AS EXTRACTANTS OF METALS

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## Abstract

In this work the solvent extraction has been carried out for the removal of iron(III) from hydrochloric acid solutions. Tricaprylmethylammonium thiosalicylate [A336][TS] and trihexyl(tetradecyl)phosphonium thiosalicylate, [$PR_4$][TS], a thiol-containing task specific ionic liquids (TSIL) were used as extractants in this process. Effect of hydrochloric acid concentration in aqueous phase on iron(III) extraction and separation has been investigated. Fe(III) ions were effectively removed from the aqueous phase by the phosphonium and ammonium ionic liquids and extraction efficiency increased with hydrochloric acid concentration increase. Also separation of Fe(III) was carried out from hydrochloric solution containing Cu(II) and the separation coefficients with [A336][TS] and [$PR_4$][TS] were found. Highly selective extraction of Fe(III) over Cu(II) from hydrochloric acid has been achieved with 0.1 M [A336][TS] in toluene.

**Keywords:** Iron(III), solvent extraction, trihexyl(tetradecyl)phosphonium thiosalicylate, tricaprylmethylammonium thiosalicylate, ionic liquids

## 1. INTRODUCTION

Iron and metal alloys are very important in electronic and electrical industry. Pyrometallurgical and hydrometallurgical processes are very often used in recycling of metals from waste electric and electronic equipment (WEEE), electronic waste (e-waste) and printed circuit boards (PCBs) [1]. Removal of iron(III) from aqueous solutions after leaching of metallic wastes is very important stage in hydrometallurgical technologies. Spent metallic materials contain usually iron and other metals. Selective extraction of iron(III) from leach liquor is necessary in order to recovery of other important metals. We know various separation methods of metal ions from aqueous solutions such as precipitation, cementation, adsorption, ion exchange, solvent extraction as well as membrane processes. Several extractants were used in hydrometallurgical technologies for extraction of Fe(III) from aqueous solutions such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) [2], tributyl phosphate (TBP) [3], trioctylphosphine oxide (TOPO) [2], bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) [3], tricaprylmethylammonium chloride (Aliquat 336)[4].Recently, we can observe that ionic liquids (ILs) are very often used as extractants of heavy metal cations from aqueous solutions [5]. The most important advantages of ILs are the following: insignificant vaporpressure, excellent thermal stability up to 300 °C, non-flammability, tunable viscosity as well as good extractability for metal ions [7].

In this work, task specific ionic liquids (TSILs) have been used as extractants of iron(III) form aqueous chloride solutions. Effect of hydrochloric acid concentration in aqueous phase on the efficiency of iron(III) extraction by trihexyl(tetradecyl)phosphonium thiosalicylate, [$PR_4$][TS] and tricaprylmethylammonium thiosalicylate [A336][TS] in toluene has been investigated.

## 2. EXPERIMENTAL PART

### 2.1. Reagents

Inorganic chemicals, i.e. iron(III) chloride ($FeCl_3$, purity=98%), copper(II) chloride ($CuCl_2 \cdot 2H_2O$, purity=99%), hydrochloric acid (HCl), were of analytical grade and were purchased from POCh (Gliwice, *Poland).* Aqueous solutions were prepared with deionized water.Organic reagents, i.e. tricaprylmethylammonium thiosalicylate [A336][TS], trihexyl(tetradecyl)phosphonium thiosalicylate, [$PR_4$][TS] (purity≥97%) were purchased from Aldrich.

## 2.2. Solvent extraction

The procedure of solvent extraction was reported in the earlier paper [2]. Equal volumes of organic and aqueous phases (phase volume ratio O/A=1) were mechanically shaken for 20 minutes at 22±2 °C. 0.1 M [$PR_4$][TS] and [A336][TS] in toluene were used as the organic phase. After establishing equilibrium, the aqueous phase was separated from the organic phase. Metal ions concentrations in aqueous phases were analyzed with plasma emission spectrometer (the **Agilent 4200 MP-AES)**. The concentrations of metal ions in aqueous phases were determined before and after solvent extraction for calculating extraction efficiency and after stripping for calculating stripping efficiency. The concentrations of metals in organic phases were deduced by mass balance. Distribution ratio (D) and extraction percent (%E) were calculated as follows:

$$D = \frac{[M]_{org}}{[M]_{aq}} \qquad (1)$$

$$\% E = \frac{D}{D+1} \cdot 100\ \% \qquad (2)$$

where $[M]_{org}$ and $[M]_{aq}$ denote metal concentrations in the organic and aqueous phases after solvent extraction, respectively. Selectivity coefficient ($S_{M1/M2}$) for $M_1$ over $M_2$ was calculated as follows:

$$S_{M1/M2} = \frac{D_{M1}}{D_{M2}} \qquad (3)$$

## 3. RESULTS AND DISSCUSION

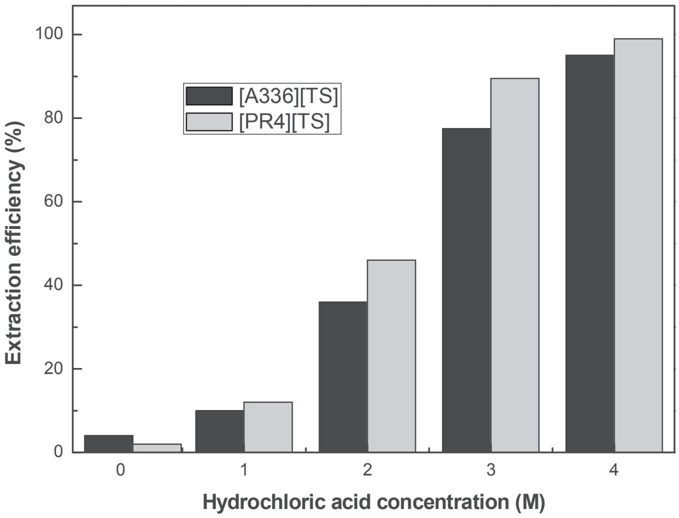

**Figure 1** Effect of hydrochloric acid concentration on the extraction efficiency of Fe(III) with 0.1 M [A336][TS] in toluene and 0.1 M [$PR_4$][TS] in toluene, respectively. The aqueous phase: 0.01 M Fe(III) in HCl solutions

The extraction of Fe(III) with [A336][TS] and [$PR_4$][TS] in toluene was carried out from 0.1 to 4 M HCl. **Figure1** shows the extraction efficiency of Fe(III) depending on HCl concentration in the aqueous phase. As can be seen from this figure, the increase in acid concentration in the range 0.1-4 M HCl caused the increase of the extraction efficiency of this metal ions likely due to the increase of the concentration of anionic species, specially such as $FeCl_4^-$.

The distribution ratios obtained in the extraction of Fe(III) are given in **Table 1**. As can be seen from this Table, distribution ratios of Fe(III) increased within the hydrochloric acid concentration range from 0.1 M to 4 M in extraction process by ILs.

**Table 1** Distribution ratio (D) of Fe(III) with 0.1 M [A336][TS] and [PR4][TS] in toluene

| [HCl], mol/dm$^3$ | $D_{Fe(III)}$ | |
|---|---|---|
| | [A336][TS] | [$PR_4$][TS] |
| 0.1 | 0.05 | 0.02 |
| 1.0 | 0.13 | 0.24 |
| 2.0 | 0.58 | 0.83 |
| 3.0 | 3.38 | 12.6 |
| 4.0 | 17.4 | 18.4 |

In the next part of investigation the selectivity of Fe(III) extraction over Cu(II) from HCl solutions has been studied. **Figures 2 and 3** show the extraction efficiency (%E) of metal ions with 0.1 M [A336][TS] and [$PR_4$][TS] in toluene, respectively. Hydrochloric acid concentration in the aqueous phase was varied from 0.1 M to 4 M. As can be observed from **Figure 2**, the highest extraction percent of Fe(III) was obtained with 0.1 M [A336][TS] in toluene at 4 M HCl in the aqueous phase. Extraction efficiency of Cu(II) in this process was very low ( 2.5% at 0.1 M HCl and 6.5% at 4 M HCl).On the other hand, as can be seen from **Figure 3**, extraction percent of Cu(II) with 0.1 M [$PR_4$][TS] in toluene was very high at low as well as high HCl concentration. The increase of hydrochloric acid concentration was responsible for an increase of Fe(III) extraction when [$PR_4$][TS] was used as extractant. Extraction of Fe(IIII) increased with HCl concentration increase.

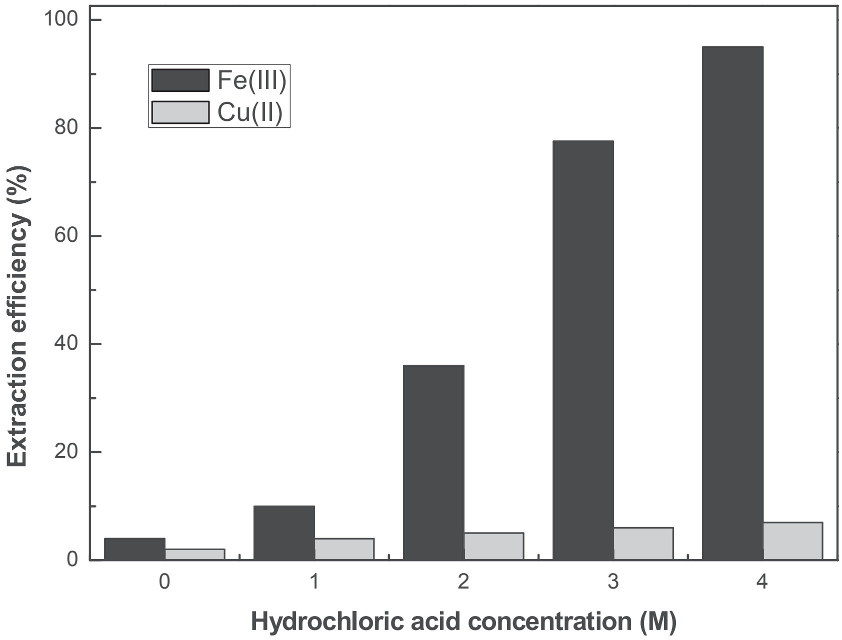

**Figure 2** Effect of hydrochloric acid concentration on the extraction efficiency of Fe(III) and Cu(II) with 0.1 M [A336][TS] in toluene. The aqueous phase: 0.01 M Fe(III) and 0.1 M Cu(II) in HCl solutions

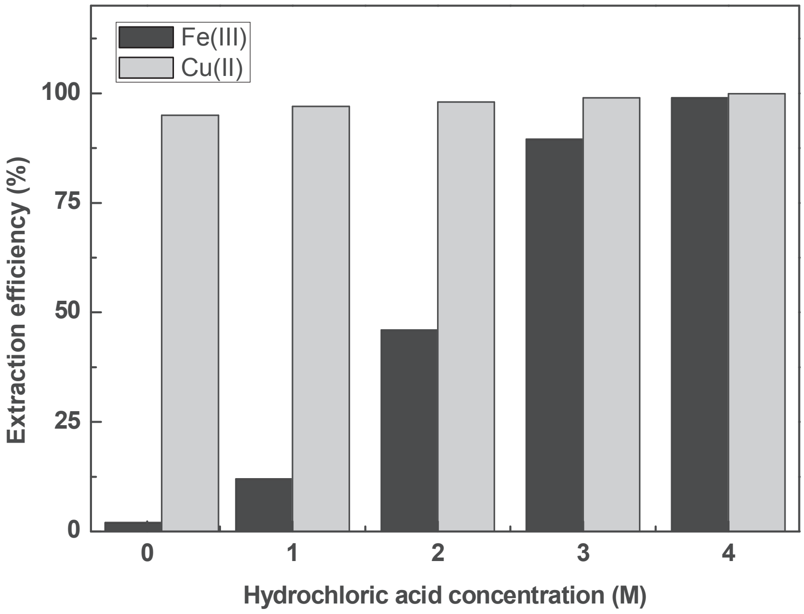

**Figure 3** Effect of hydrochloric acid concentration on the extraction efficiency of Fe(III) and Cu(II) with 0.1 M $[PR_4][TS]$ in toluene. The aqueous phase: 0.01 M Fe(III) and 0.01 M Cu(II) in HCl solutions

The log of selectivity coefficients Fe(III) over Cu(II) was plotted against hydrochloric acid concentration in **Figure 4 and Figure 5**, which indicated an increase in selectivity process with increase of HCl concentration from 0.1 to 4 M with [A336][TS]. On the other hand, with increase of acid concentration in the aqueous phase, the selectivity coefficients of metal ions with [PR4][TS] decreased. In this case, extraction efficiency of Cu(II) was very high and extraction percent of Fe(III) increased with the acid concentration increase. The highest selectivity coefficient of Cu(II) over Fe(III) was obtained for 0.1 M HCl.

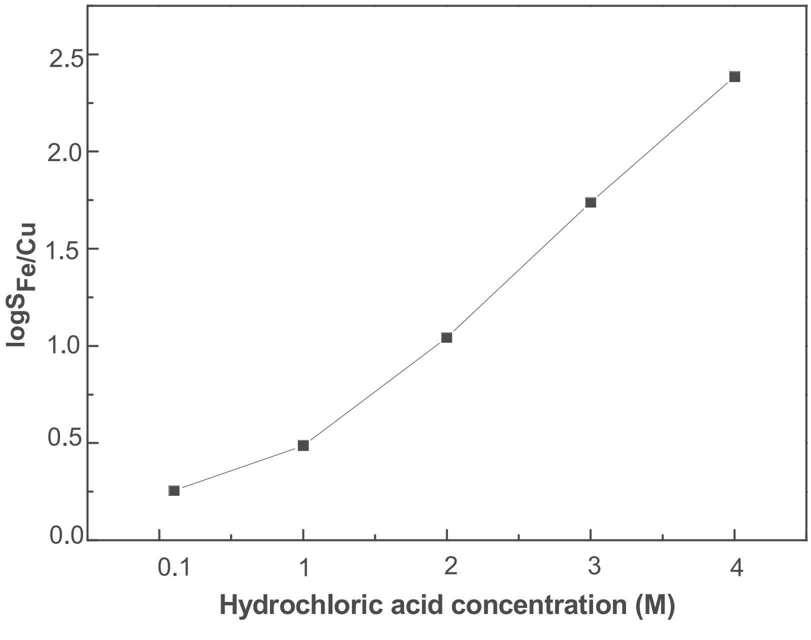

**Figure 4** Logarithm of the selectivity coefficient of Fe(III) over Cu(II) ($\log S_{Fe/Cu}$) with 0.1 M [A336][TS] in toluene vs. HCl concentration under the same experimental conditions as in Figure 2

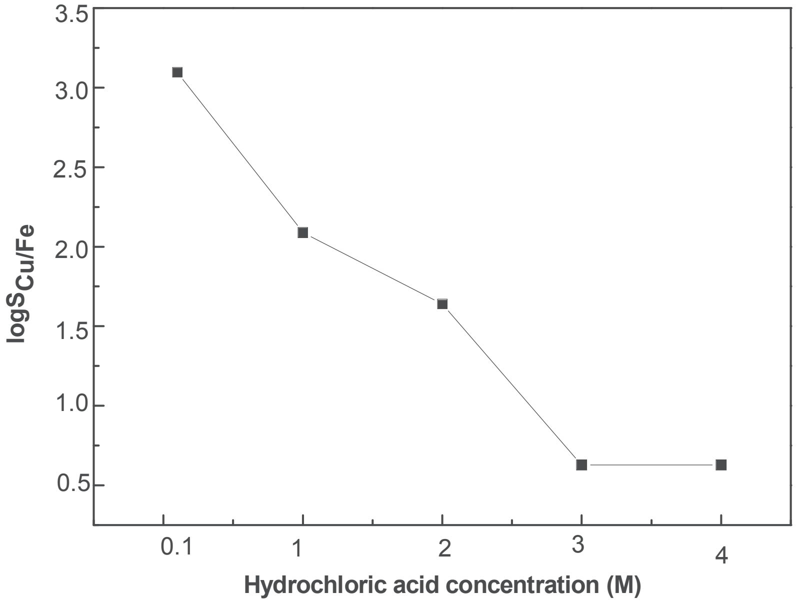

**Figure 5** Logarithm of the selectivity coefficient of Fe(III) over Cu(II) (log $S_{Fe/Cu}$) with 0.1 M $[PR_4]$[TS] in toluene vs. HCl concentration under the same experimental conditions as in Figure 3

## 4. CONCLUSION

Based on the results of the solvent extraction of Fe(III) from hydrochloric acid solutions containing Cu(II), the following conclusions may be highlighted. [A336][TS] in toluene can be recommended for the selective extraction of Fe(III) from hydrochloric acid solutions regarding both the high values of the selective coefficients of Fe(III) over Cu(III) and the extraction efficiencies of Fe(III) at high acid concentration. The use of [PR4][TS] in toluene permits to selectively extract Cu(II) over Fe(III) from 0.1 M hydrochloric acid. At higher HCl concentrations, the extraction efficiency of Cu(II) remains close to 99% but the selectivity coefficient towards Fe(III) decreases. The 0.1 M [A336][TS] is proper to extract from acid solution nearly 95% Fe(III) with very high selectivity coefficient of Fe(III) over Cu(II) (SCu/Fe= 243.3).

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