Extraction of Iron(III) from Aqueous Sulfate Solutions by Primene JMT

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The results of the extraction of iron(III) sulfates with primary amine from neutral solutions as well as from solutions containing sulfuric acid are presented. Primene JMT in benzene with octan-1-ol as a modifier of solubility was used as the extractant. The presumed stoichiometry of extraction formulated on the basis of existing literature was compared with calculations for aqueous phase equilibrium compositions and with experimental results for sulfuric acid and iron(III) sulfate extraction. The presumption of extraction of a neutral complex $\text{Fe}_2(\text{OH})_2(\text{SO}_4)_2$ from aqueous phase explains quite well the results of extraction from neutral and moderate acidic solutions. The results of extraction at higher concentrations of sulfuric acid in aqueous phase show that the complexes in organic phase could be more complicated.

Sulfuric acid is the most common reagent used for the leaching and decomposition of ores and concentrates. Iron is usually present in the leaching solution as an impurity. Efficient methods for iron removal from sulfuric acid solution are, therefore, often necessary for the recovery of a quality product. Apart from various precipitation methods solvent extraction has long been studied for removing iron from sulfate solutions. It is possible to use various types of extraction agents; the amine extraction is very suitable due to the ability of Fe(III) to form various complexes.

Primary amine Primene JMT was successfully tested for separation of iron from solution of aluminium sulfate [1, 2]. Another type of primary amine Primene 81R was used for separation of Fe(III) and Al(III) by solvent extraction treatment of sulfate leach liquors produced by the acid leaching of non-bauxitic ores [3]. A study of extraction mechanism for this process has been made [4]. The compound extracted from the organic phase with Primene 81R sulfate at 50°C has been isolated and has been shown to have the stoichiometric formula $3[(\text{RNH}_3)_2\text{SO}_4] \cdot \text{[Fe(OH)SO}_4]_2$. It has been shown that the extraction of iron(III) occurs by the adduct formation reaction between primary amine sulfate molecules and the species $\text{[Fe(OH)SO}_4]_2$. The influence of diluents of different types has been studied for iron(III) extraction by Primene 81R from aluminium sulfate solutions [5]. The best results were obtained with diluents such as toluene and benzene. It was concluded that diluent should have a low dielectric constant, weak hydrogen-bonding capacity, high aromaticity, low surface activity, permitting the surface-active amine to concentrate at the interface. These works were followed up by a similar study of Fe(III) extraction by secondary amine di(3,5,5-trimethylhexyl)amine published in [6—8]. The compound isolated from the organic phase has the formula $(\text{R}_2\text{NH}_2)_2\text{SO}_4 \cdot \text{[Fe(OH)SO}_4]_2$ and two structures for the complex have been suggested based on hydroxy and sulfate bridging which explain the association of the complex in organic phase [8]. Attempts to explain the mechanism of extraction were made by studying IR spectra [9] and the influence of the solvent [10].

The extraction of iron(III) from aqueous sulfate solutions by didecylamine has been investigated by Baes [9] who first interpreted his results by assuming extraction of partially hydrolyzed species Fe(OH)SO$_4$. Another mechanism was suggested by Good et al. [10] who explained their observations by assuming that in the extraction by Primene 81R the following ion-
exchange reaction occurred

\[
(RNH_3)_2SO_4 + 2[Fe(SO_4)_2]^{-} = 2((RNH_3)[Fe(SO_4)_2]) + SO_4^{2-}
\]

The importance of the role of water in the extraction processes was stressed for the extraction of Fe(III) by primary amine N1923 and di(2-ethylhexyl)phosphoric acid (HA) [11]. The authors proposed that the extraction of iron(III) from sulfate solutions is carried out through the formation of reverse micelle of water in oil type and that the primary amine works as a cationic surfactant. It was proposed that the mechanism of extraction and stripping involves the exchange of H\textsuperscript{+} with Fe(H\textsubscript{2}O\textsubscript{3})\textsuperscript{2-} at water/oil interface of the reverse micelle. The IR spectra showed that the sulfuric acid extracted into organic phase was in free form and did not coordinate with iron directly at its low concentration. The following extraction reactions were suggested

\[
Fe^{3+} + SO_4^{2-} + H_2O + mHA + n(RNH_3)_2SO_4 =
\]
\[
= \{[Fe(OH)SO_4][(RNH_3)_2SO_4]_n[HA]_m\} + H^+
\]

Transmission electron microscopy was used to the study of a loaded organic phase (primary amine N1923 — octane) with ferric iron and H\textsubscript{2}SO\textsubscript{4} [12]. It was confirmed that the iron—extractant complexes formed reverse micelles under conditions of practical hydrometallurgical extraction. The extraction of iron(III) by primary amine extractant is not only a simple ion-exchange process at the interface of the water/oil microemulsion droplets, but also a rearrangement of the microstructure of organic phase plays an important role.

The most difficult problem associated with the solvents that have been studied for iron removal in sulfate solution is the stripping of iron from the organic phase so that the regenerated solvent could be reused in the process. One approach to this problem is the utilization of mixed solvent systems. The common feature of these systems is that the iron can be stripped by a dilute sulfuric acid. Several works are devoted to this problem [13—16], dealing mainly with systems containing primary amines and neutral donor solvents.

**RESULTS AND DISCUSSION**

**Presumptive Stoichiometry of Extraction**

In the following text only the sulfate medium in aqueous phase will be discussed. The hydrolysis according to eqn (A) is supposed

\[
Fe_2(SO_4)_3 + 2H_2O = Fe_2(OH)_2(SO_4)_2 + H_2SO_4 \quad (A)
\]

and both products of hydrolysis can pass into organic phase. For sulfuric acid the reactions (B) and (C) can be applied

\[
2RNH_2 + H_2SO_4 = (RNH_3)_2SO_4 \quad (B)
\]
\[
RNH_2 + H_2SO_4 = RNH_3HSO_4 \quad (C)
\]

and the presence of free amine, amine sulfate, and amine hydrogensulfate is expected. Then it is supposed that only amine sulfate reacts with iron(III) species forming complexes in organic phase

\[
m(RNH_3)_2SO_4 + Fe_2(OH)_2(SO_4)_2 =
\]
\[
= (RNH_3)_{2m}Fe_2(OH)_2(SO_4)_{2+m} \quad (D)
\]

\(m = 2\) is usually supposed.

In our text these basic presumptions will be compared with calculations for aqueous phase composition and with experimental results for sulfuric acid and iron(III) complexes extraction.

**Equilibrium in Aqueous Phase**

It can be expected that the products of hydrolysis according to eqn (A) will undergo further conversions...
forming complexes of the $\text{Fe}_x(\text{OH})_{y}((\text{SO}_4)^{(3x-y-2z)+}}$ type. Even though there are some references to the existence of such complexes in the literature, the only quantitative data they give are stability constants for hydroxy and sulfato complexes \[17, 18\]

\[\text{Fe}_x(\text{OH})_{y}((\text{SO}_4)^{(3x-y-2z)+}} = \beta_{yz}[\text{Fe}^{3+}]^x[\text{OH}]^y \]  
(1)

\[\text{Fe}(\text{SO}_4)^{(3-2z)-}} = \beta_z[\text{Fe}^{3+}][\text{SO}_4]^{2-} \]  
(2)

for $yz = 11, 21, 31, 41, 22, 43$; $z = 1, 2$ together with the data for solubility of Fe(III) hydrated oxides.

The protonation constants for sulfuric acid

\[[\text{H}_s\text{SO}_4]^{-2} = K_s[\text{H}_{s-1}\text{SO}_4]^{-3}[\text{H}^+ \]  
(3)

and dissociation constant of water

\[[\text{H}^+][\text{OH}^-] = K_w[\text{H}_2\text{O}] \]  
(4)

are also available.

Solving eqns (1—4) together with mass balance equations for Fe(III) and sulfate groups and equation of electroneutrality in the range $c^0(\text{Fe}) = 0.025$—$0.125$ mol dm$^{-3}$ and $c^0(\text{H}_2\text{SO}_4) = 0.1$—$2.0$ mol dm$^{-3}$, we have found out that only the presence of two species $\text{Fe}(\text{SO}_4)^{+}$ and $\text{Fe}(\text{SO}_4)_{2}^{-}$ is significant. The concentrations of all other species were negligible (calculations were carried out with the values of constants presented in work \[18\]). The fractions of these species are shown in Fig. 1 in dependence on initial concentration of sulfuric acid. It is evident that abundance of both species does not change within the studied intervals of Fe(III) and sulfuric acid concentrations.

If a neutral molecule has to pass into organic phase, the transfer of a hydrolyzed species formed in accordance with eqn (A)

\[2\text{Fe}(\text{SO}_4)^{+} + 2\text{OH}^- = \text{Fe}_2(\text{OH})_2(\text{SO}_4)_2 \]  
(E)

or the transfer of a neutral molecule formed from both species can be expected

\[\text{Fe}(\text{SO}_4)^{+} + \text{Fe}(\text{SO}_4)_{2}^{-} = \text{Fe}_2(\text{SO}_4)_3 \]  
(F)

**Protonation of Amine**

The results of experiments with the extraction of sulfuric acid are shown in Fig. 2. It was mentioned above that according to eqns (B) and (C) free amine RNH$_2$, amine sulfate (RNH$_3$)$_2$SO$_4$, and amine hydrogen sulfate RNH$_3$.H$_2$SO$_4$ can be present in organic phase. The prevailing forms may be estimated from the proportion $c'(\text{RNH}_2)/c'(\text{SO}_4^{2-})$ ($c'$ denotes concentration in equilibrium organic phase).

**Extraction of Iron(III)**

The equilibrium concentrations (proportions of concentrations) for various initial concentration of sulfuric acid are illustrated in Figs. 3—6. The proportions of concentrations in a loaded organic phase enable us to suggest the composition of formed complex.

According to eqn (D) the limiting proportions are

\[c'(\text{RNH}_2)/c'(\text{Fe}) = m \]
EXTRACTION OF IRON(III) BY PRIMENE JMT

Fig. 3. Extraction of Fe(III) from neutral solution. 
\[ \frac{c(\text{RNH}_2)}{c(\text{Fe})}_\text{org} ; \frac{c(\text{SO}_4^2)}{c(\text{Fe})}_\text{org} \]

Fig. 4. Extraction of Fe(III) from moderate acidic solution \( (c_0(\text{H}_2\text{SO}_4) = 0.1 \text{ mol dm}^{-3}) \). 
\[ \frac{c(\text{RNH}_2)}{c(\text{Fe})}_\text{org} ; \frac{c(\text{SO}_4^2)}{c(\text{Fe})}_\text{org} \]

Fig. 5. Extraction of Fe(III) from acidic solution \( (c_0(\text{H}_2\text{SO}_4) = 0.5 \text{ mol dm}^{-3}) \). 
\[ \frac{c(\text{RNH}_2)}{c(\text{Fe})}_\text{org} ; \frac{c(\text{SO}_4^2)}{c(\text{Fe})}_\text{org} \]

then the corresponding limiting proportions are
\[ \frac{c'(\text{RNH}_2)}{c'(\text{Fe})} = n \]
\[ \frac{c'(\text{SO}_4^2)}{c'(\text{Fe})} = (3 + n)/2 \]
\[ \frac{c'(\text{RNH}_2)}{c'(\text{SO}_4^2)} = 2n/(3 + n) \] (6)

Extraction from Neutral Solutions

Acid needed for amine salt formation is released by hydrolysis according to eqn \((A)\). If all the amount of Fe(III) complex was passing into organic phase, then according to eqn \((D)\) (together with \((A)\) and \((B)\)) the only value of \(m\) could be \(m = 1\). This corresponds to the first points on the left in Fig. 3. If, considering the products of hydrolysis (eqn \((A)\)), more sulfuric acid than Fe(III) complex is passing into organic phase, then the complex in organic phase can correspond to \(m = 2\). Experimental values at higher iron concentrations in Fig. 3 are in a good agreement with this assumption. A change of colour of the organic phase was observed for Fe(III) concentration up to \(c(\text{Fe}) = 0.04 \text{ mol dm}^{-3}\). This indicated a transformation of the complex in organic phase. A precipitate in aqueous phase was observed within a narrow range of Fe(III) concentration around the above-mentioned value.

Extraction from Acidic Solutions

If we suppose the transfer of a neutral molecule according to eqn \((F)\) as well as
\[ n(\text{RNH}_3)_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3 = (\text{RNH}_3)_{2n}\text{Fe}_2(\text{SO}_4)_{3+n} \] (G)

The results in Fig. 4 (moderate acidic solution) show that the limiting proportions of concentrations approximately correspond to the complex according to...
eqn \((D)\) for \(m = 2\) and are approaching the concentrations in Fig. 3. Higher concentration of \(\text{SO}_4^{2-}\) groups could indicate partial formation of complex according to eqn \((G)\) for \(n = 2\).

The results in Fig. 5 (higher concentration of acid) show that the limiting proportions of concentrations could correspond with the complex according to eqn \((D)\) for \(m = 2\) supposing that the amine hydrogen-sulfate is present as well, or the limiting proportions correspond with the complex according to eqn \((G)\) for \(n = 3\), or of a more complicated complex than in eqns \((D),\) \((G)\) is formed. The same conclusions can be done from the results in Fig. 6 (high concentration of sulfuric acid).

CONCLUSION

The results of experiments proved that it is convenient to extract Fe(III) from the moderate acidic solution (if the free amine is used as an extraction agent) or from the neutral solutions (if the amine sulfate is used). Under such conditions the proportion of molar concentrations of amine and Fe(III) in a loaded organic phase is low and is approaching the value 2.

The presumed stoichiometry of extraction, formulated on the basis of existing literature, explains quite well the extraction from neutral and moderate acidic solutions. The complexes in organic phase, formed at higher concentration of sulfuric acid in aqueous phase, could be more complicated and need not be in agreement with our presumptions.

REFERENCES