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Novel Extraction Based Strategies for the Concentration of Ferric Chloride

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The objective of this research was to develop a novel, energy-efficient processes for concentrating ferric chloride solutions. When applying liquid-liquid extraction, the high energy for water evaporation can be avoided. Here, we report a study on the use of liquid-liquid extraction for concentration of ferric chloride solutions. First, a range of commercially available solvents (e.g. ethers, phenols, amides, thiols, amines) was screened at room temperature and under atmospheric pressure for an initial $FeCl_3$ concentration of 20 wt%, using a solvent/feed (S/F) ratio of 0.25. Hereafter, the extraction with the most interesting solvents was analyzed in more detail, and finally the recovery of $FeCl_3$ from the solvents was studied. From the screening it was concluded that diethyl ether and diisopropyl ether were the most promising, thus those two solvents were selected for a more detailed study. The $FeCl_3$-extraction was studied at equilibrium for $0.5 < S/F < 2.0$, $0 < pH < 1$, $5\ wt\% < FeCl_{3,initial} < 30\ wt\%$), and at 295.15 K and atmospheric pressure.
A complete (100% extraction yield, initial concentration 5 wt%) $FeCl_3$ extraction was coupled to a recovery by combined ether evaporation and back extraction with water to yield a final salt concentration of 45 wt%. Based on this result, we conclude that extractive concentration of $FeCl_3$ with ethers is a promising technology.

1. Introduction

Among the most energy intensive processes in the chemical industry concerns water removal from polar mixtures with high boiling components, e.g. salts. Water is usually removed by triple effect evaporation (TEE), which is highly energy demanding due to the high evaporation enthalpy of water.
Ferric chloride or anhydrous iron(III) chloride is a highly hygroscopic compound which hydrolyzes in water, resulting in a brown, acidic and corrosive solution. Ferric chloride is an important chemical, because it is used for sewage treatment and the production of drinking water (Kirk-Othmer, 2006).
The industrial manufacturing of ferric chloride is carried out by an exothermic reaction between ferric oxide and excess hydrochloric acid, resulting in an aqueous salt solution, usually ranging in concentration from 5 wt% to 30 wt% (Solvay Chem. Int. S.A., 2006). To achieve a trading concentration of at least 40%, a concentration step is required, for which typically triple effect evaporation (TEE) of water, is used, which is very energy intensive.

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Alternatively, liquid-liquid extraction (LLE) could be used to realize more energy effective concentration method. Extraction of iron (III) and other metal impurities have been reported for processing of waste chloride liquors from minerals processing streams and in the mining industry after hydrometallurgical processes of recovering a number of nonferrous metal ions such as nickel(II), cobalt(II) and copper(II) (Dodson, R. W., 1936; Nachtrieb, N. H.1948; Saji, J., 2001; Lee M.S. et al, 2005).
Here, we report a study on the use of LLE for the concentration of ferric chloride solutions. A range of commercially available and presumably acceptable solvents (e.g. ethers, phenols, amides, thiols, amines) were evaluated, after which a more detailed study was done for the most promising solvents (ethers), including optimization of the single stage equilibrium extraction conditions, and screening of recovery options.

2. Experimental

2.1 Reagents

Solid anhydrous ferric chloride (reagent grade, >97%), Nitric acid for iron(III) atomic absorption spectrometry,4-tert-butylcatechol (>97%), 2,3,6-trimethylphenol (≥97%), 1-dodecanol (≥98%), 2-ethyl-1-hexanol (≥99%), methyl tert-butyl ether (>99.8%), 2-methyl-1-propanol, (≥99%) 2-methyl-1-pentanol (99%), 2 ethyl-1-butanol(98%), phenol (≥99%), tert-butanol(≥99.7%), 2-ethyl-1-hexanol(≥99%), p-xylene(≥99%), and diisopropyl ether (≥98%) were purchased from the Sigma Aldrich, and diethyl ether was purchased from VWR. Hydrochloride acid was purchased from the Merck.

2.2 Equipment

LLE experiments were carried out in magnetically stirred (500 rpm) glass vessels of 100 and 200 mL. A separatory funnel was used to separate the phases before analysis. Recovery by solvent stripping experiments was carried out using a rotary evaporator (VWR IKA HB 10 digital in combination with an IKA RV 10 basic rotator).

2.3 Procedures

Solvent screening experiments were carried out by mixing 40 g $FeCl_3$-solutions (20 wt%) with 10 g solvent in glass vessels for 30 minutes at 500 rpm at 295.15 K and at atmospheric pressure. After stopping the stirring, the mixtures were transferred to a separatory funnel, in which the phases were allowed to settle for 1 hour. The phases were separately weighed, after which samples of 5 mL were collected from both phases for analysis of the water content (in the exract phase) and the iron content (in the raffinate phase).
For the extraction experiments to optimize the single stage extraction conditions with diethyl ether and diisopropyl ether, a similar approach was followed as above, now samples of 30 g $FeCl_3$-solutions (5 wt%) mixed with 15 g of solvent, and co-solvent HCl was added in the range of 1 – 10 mol/L
For the experiments to determine the time to equilibrium for extractions with diethyl ether and diisopropyl, the mixing time was varied from 1 minute to 90 minutes.
Recovery of diethyl ether and diisopropyl ether experiments were carried out with samples from the extraction experiments. To the extract phase of the experiments, 1 g water was added. The raffinate phase was analyzed for iron content for solvent

stripping. The same procedure was repeated for the solvent removal by the rotary evaporator. The final product was measured for the iron content.

2.4 Analytical procedures

Weight measurements were carried out using a Mettler Toledo AX205 balance (d = 0.01 mg). For salt content analysis, 2-5 mL samples were collected from the raffinate phase. The salt content was determined by atomic absorption spectrometry (AAS), using a Varian SpectrAA 110 spectrometer model (standard deviation < 2%). For water content analysis, 3-5 mL samples were collected from the extracted phase. The water content was analyzed using Karl Fischer Titration (795 KFT Titrino Metrohm, standard deviation <0.5). Total concentrations in both phases were determined from mass balances.

3. Results and Discussion

3.1 Solvent screening

The solvent screening experiments carried out as described in section 2.3, showed that two phase systems (TPS) were formed for most of solvents from the ether and alcohol groups. Furthermore, from the solvents that has created a TPS, diethyl ether and diisopropyl ether showed the highest yield of $FeCl_3$ extracted and lowest co-extraction of water (see Figure 1). For these reasons these two solvents were considered the most promising for ferric chloride extraction, and will be examined further in next section.

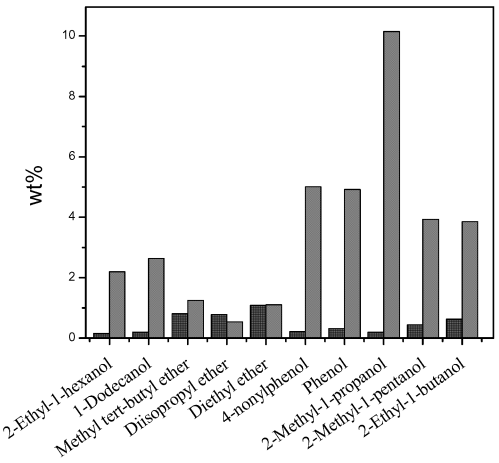

Figure 1: Ferric chloride (dark grey) and water (light grey) weight percentage concentration in extract phase after LLE

3.2 $FeCl_3$ extraction with ethers

Both diethyl ether and diisopropyl ether showed promising extraction results in the preliminary screening, and because it is known that adding HCl to the feed is beneficial for the extraction yield, we studied the effect of the HCl concentration on the extraction yield. The extraction yields are displayed in Figure 2. It can be seen that quantitative

yield was obtained in the range between 6 – 8 mol/L of HCl for both examined ethers. For concentrations of HCl between 0 – 6.5 mol/L, the extraction yield of ferric chloride is higher for diethyl ether than for diisopropyl ether. At HCl concentrations higher than 7 mol/L the extractive capacity of ethers is decreasing, because the aqueous volume is increasing due to enhanced ether solubility at higher acidity (Cambpell, D.E., 1952 et al.).

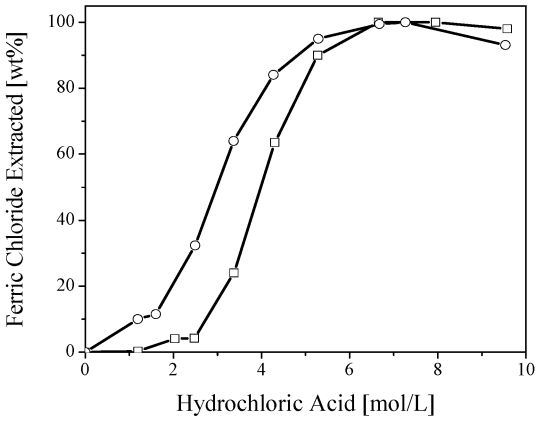

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Figure 2: Extraction capacity of diethyl ether (○), diisopropyl ether (□), as function of hydrochloric acid concentration

In Figure 3 the obtained distribution coefficients (the ratio of weight percentage of $FeCl_3$ in extract phase over the weight percentage of $FeCl_3$ in raffinate phase) are displayed as function of HCl concentration.

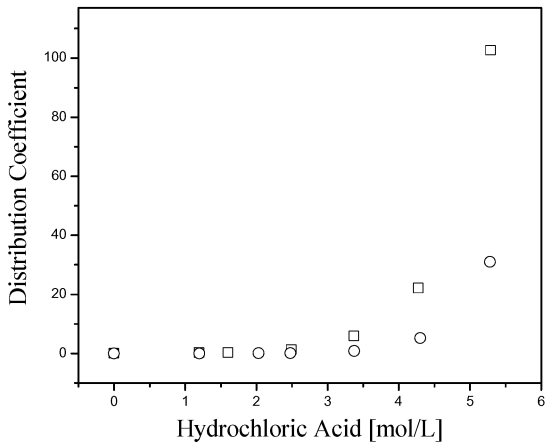

Figure 3: Distribution coefficients for ferric chloride in diethyl ether (○), diisopropyl ether (□) as function of HCl concentration

Results of time dependence experiments for extraction with ethers showed that for diethyl ether at [HCl] > 5 mol/L equilibrium is achieved within 1 minute at S/F ration of 0.5. For diisopropyl ether at [HCl] of 5.29 mol/L equilibrium is established after 20 minutes and for [HCl] of 6.65 mol/L and 7.94 mol/L equilibrium is reached within 1 minute at S/F ration of 0.5. For [HCl] of 7.20 mol/L for diethyl ether and [HCl] of 6.65 mol/L and 7.94 mol/L for diisopropyl ether quantitative yield is achieved within 1 minute at S/F ration of 0.5 (figure 4).

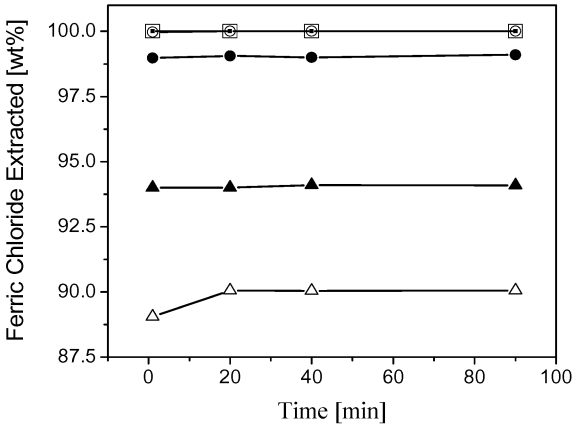

Figure 4: Extraction time for diethyl ether (▲- 5.27, ● - 6.60, ■ - 7.20 HCl mol/L) and diisopropyl ether (Δ-5.29, ○- 6.65, □ - 7.94 HCl mol/L)

3.3 Solvent recovery

Solvent stripping experiments with pure water were carried out like explained in section 2.3. It was observed that for diethyl ether the maximum concentration in the strip phase was 14wt% $FeCl_3$, and for diisopropyl ether 17.5wt% $FeCl_3$. But if in addition to adding pure water to the system, an evaporation step was applied to evaporate the ether, aqueous $FeCl_3$ concentrations up to 45 wt% were obtained. For diethyl ether, evaporation was carried at temperature of 35°C and final product of 44.97wt% $FeCl_3$ was obtained. For diisopropyl ether, evaporation was carried at temperature of 50°C and final product of 43.45wt% $FeCl_3$ was obtained.

4. Conclusions

Liquid-liquid extraction of $FeCl_3$ with ethers, followed by both stripping and back extraction used as recovery step, is a promising novel technology for concentration of ferric chloride solutions.

From starting salt solutions of 5 wt%, quantitative extraction of $FeCl_3$ could be achieved in a single equilibrium stage at HCl concentrations ranging from 5 – 8 mol/L. After recovery by combined solvent evaporation and back-extraction with pure water, a final salt concentration of 45 wt% was obtained. The extraction process is fast, equilibrium was reached within 1 minute.

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Solvay Chemical International S.A. Produc Data Sheet Ferric Chloride 40%. 2006. Ref Type: Generic